Effects of noble metal doping on hydrogen sensing performances of monolayer MoS$_2$

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Abstract

To develop a new kind of hydrogen sensor based on monolayer MoS$_2$, we investigated effects of noble metal doping on hydrogen sensing performances of the monolayer MoS$_2$ by using the first principles calculation method. The Cu, Pd, and Pt doping decrease the adsorption energy of a hydrogen molecule on the monolayer MoS$_2$, while Ag and Au doping have little effect on the adsorption energy. The adsorption energy change indicates that the Cu, Pd, and Pt doping strengthen the interaction between the hydrogen molecule and the monolayer MoS$_2$. The density of states shows that the hybridization of H-s, noble metals d, S-p, and Mo d orbitals contributes to the adsorption of the hydrogen molecule on the noble metal doped monolayer MoS$_2$. The changes in bader charge and charge density difference indicate that noble metal doping increases the charge transfer between the hydrogen molecule and the monolayer MoS$_2$. All of the results demonstrate that noble metal doping can improve the hydrogen sensing performances of the monolayer MoS$_2$, especially the Pd and Pt doping.

1. Introduction

Hydrogen is widely considered as one of the most potential clean energy sources which can replace the traditional fossil energy due to its advantages of no pollution and high caloric value [1]. However, hydrogen gas requires special caution for its combustible and high explosive properties [2]. For the safety reason, hydrogen monitoring runs through all stages of hydrogen energy utilization, including hydrogen production, hydrogen storage, and hydrogen transportation [3–5]. In nuclear energy production, the accumulation of hydrogen in the containment building can also cause a significant safety risk. During the normal operation of nuclear power plants, only a small amount of hydrogen is generated by the chemical reaction of zirconium alloy fuel cladding and water [6]. In the event of large break loss of coolant accident, the hydrogen production rate increases dramatically due to the chemical reaction between the zirconium fuel cladding and hot steam. If the hydrogen concentration in the containment building exceeds the explosion limit, the containment building might be destructed by hydrogen explosion, such as the severe nuclear accident happened in the Fukushima nuclear power plant in Japan in 2011 [7]. Therefore, the accurate monitoring of hydrogen in the containment building can help improve the safety level of nuclear power plants. As mentioned above, hydrogen monitoring is very important not only for the development and utilization of hydrogen energy [8], but also for the safety of nuclear power plants [9, 10].

To monitor hydrogen in different environments accurately, scientists have developed many kinds of hydrogen sensing materials [2], and engineers have designed different types of hydrogen sensors based on the sensing materials, including optical sensor [11], electrochemical sensor [12], semiconductor sensor [13–15], and so on. In recent years, the research of two dimensional materials has received an increasing attention from scientists because of their unique band structure, semiconductor or superconducting properties, and excellent...
mechanical performance. The two dimensional materials are widely considered for use in electronic devices, catalysis, energy storage, tools used under extreme conditions, and other fields. Previous researches have shown that graphene is a candidate material which can be used for hydrogen sensing [16–18]. Meanwhile, scientists also found that monolayer MoS2 has some adsorption capacity for toxic gas molecules [19–21]. When toxic gases adsorbed on monolayer MoS2, the electronic structure of the monolayer MoS2 is changed, so the monolayer MoS2 might be a candidate material for toxic gas sensing [22–24]. Based on the previous researches, the monolayer MoS2 might also be a candidate material which can be used for hydrogen detection. Due to the introduction of impurity is a good strategy to improve the chemical activity of the monolayer MoS2 [25–27], the adsorption of toxic gases on the monolayer MoS2 is improved by doping [21]. However, whether doping can improve the hydrogen sensing performances of the monolayer MoS2 has rarely been examined directly. More importantly, large areas and high quality MoS2 atomic layers could be prepared through the chemical vapor deposition (CVD) technology [28, 29]. Therefore, it is meaningful to develop cost-effective MoS2-based hydrogen sensing materials for monitoring the hydrogen concentration in different environments.

With the rapid progress of computer technology and computational materials science, first principles calculation method plays an increasingly important role in the research of two dimensional materials [30]. Based on our previous researches [31–33], we investigated the effects of noble metal doping on hydrogen sensing performances of the monolayer MoS2 by using the first principles calculation method in this paper. Adsorption energy determines the interaction between the hydrogen molecule and the noble metal doped monolayer MoS2, density of states is calculated to understand the adsorption mechanism, and charge transfer between the hydrogen molecule and the noble metal doped monolayer MoS2 is analyzed by bader charge and charge density difference. Through the calculations of these key parameters, we can get a further understanding of the hydrogen sensing performances of the noble metal doped monolayer MoS2.

2. Computational details

All calculations were performed by using the Vienna Ab-initio Simulation Package (VASP) [34, 35] based on the project augmented wave (PAW) formalism of density functional theory. Exchange-correlation terms were computed by using the Perdew–Burke–Ernzerhof [36] functional with generalized gradient approximation (GGA). The electron wave functions were expanded by a plane-wave basis set with a cutoff energy of 400eV. A Gaussian smearing of 0.1 eV and the Monkhorst-Pack k-point mesh of \( 3 \times 3 \times 1 \) (\( 7 \times 7 \times 1 \)) were employed for supercell geometry optimizations (total energy calculation). To study the interaction between hydrogen (H2) molecule and the noble metal doped monolayer MoS2 more accurately, the DFT-D2 method [37, 38] was adopted to account for the van der Waals interaction. In geometry optimization, the maximum Hellman–Feynman force acting on each atom was less than 0.02eV/Å, and energy convergence criterion was chosen as 1.0 × 10−6 eV. In order to avoid interlayer interactions, a vacuum layer of 16 Å was used in the c direction.

In this paper, five kinds of noble metal doped monolayer MoS2 are considered, and they are named as MoS2(Ag), MoS2(Au), MoS2(Cu), MoS2(Pd), and MoS2(Pt), respectively. According to the theoretical research [39], sorption is a good way for noble metal doping on the monolayer MoS2, and the most stable configuration of the five noble metals doped monolayer MoS2 is shown in figure 1. For a H2 molecule on the noble metal doped monolayer MoS2, there are four adsorption sites, named as \( H_{ex} \) (center of the hexagon), \( T_{Mo} \) (top of the Mo atom), \( T_{S} \) (top of the S atom), and \( T_{NM} \) (top of the noble metal atom). Due to the molecular structure of the H2 molecule, two models are considered as the initial adsorption configurations, H-model (the H2 molecule parallels to the hexagon), and V-model (the H2 molecule perpendiculars to the hexagon), and they are labeled as ‘||’ and ‘⊥’ in this paper, respectively. To estimate the difficulty of the noble metal doping, we calculated the formation energy of the noble metal doped monolayer MoS2, and the formation energy is defined as:

\[
E_f(NM) = E(\text{MoS}_2 + \text{NM}) - E(\text{MoS}_2) - E(\text{NM})
\]

(1)

where \( E(\text{MoS}_2 + \text{NM}) \) and \( E(\text{MoS}_2) \) is the energy of the noble metal doped and undoped monolayer MoS2, \( E(\text{NM}) \) is the energy of an isolated noble metal atom, respectively. The more negative the formation energy is, the easier the noble metal doping is. At the same time, the formation energy also indicates the stability of the noble metal doped monolayer MoS2, a more negative forming energy means the noble metal doped monolayer MoS2 has a higher stability. Adsorption energy determines the interaction strength between the H2 molecule and the noble metal doped monolayer MoS2, the adsorption energy of a H2 molecule on the noble metal doped monolayer MoS2 is calculated by the following equation:

\[
E_{ad}(\text{H}_2) = E(\text{MoS}_2 + \text{NM} + \text{H}_2) - E(\text{MoS}_2 + \text{NM}) - E(\text{H}_2)
\]

(2)

where \( E(\text{MoS}_2 + \text{NM} + \text{H}_2) \) and \( E(\text{MoS}_2 + \text{NM}) \) denote the total energy of the noble metal doped monolayer MoS2 with and without an adsorbed H2 molecule, and \( E(\text{H}_2) \) is the energy of a free H2 molecule, respectively.
The more negative the adsorption energy is, the stronger the adsorption of the H$_2$ molecule on the noble metal doped monolayer MoS$_2$ is.

To understand the microcosmic mechanism of the noble metal doping and the adsorption mechanism of hydrogen molecule on the noble metal doped monolayer MoS$_2$, density of states of different adsorption systems was calculated. Bader charge and charge density difference were calculated to analyze the charge transfer between the H$_2$ molecule and the noble metal doped monolayer MoS$_2$ in quantity. The charge density difference ($\nabla \rho$) was acquired to analyze the electron transfer direction by a 3D visualization program VESTA [40]. The charge density difference is defined as:

$$\nabla \rho = \rho(\text{MoS}_2 + \text{NM} + \text{H}_2) - \rho(\text{MoS}_2 + \text{NM}) - \rho(\text{H}_2)$$

where, $\rho(\text{MoS}_2 + \text{NM} + \text{H}_2)$, $\rho(\text{MoS}_2 + \text{NM})$, and $\rho(\text{H}_2)$ represent the electron density of the adsorption system, the electron density of the noble metal doped monolayer MoS$_2$, and the electron density of the H$_2$ molecule, respectively. Furthermore, the change of band structure caused by hydrogen adsorption leads to the change of the conductivity of the monolayer MoS$_2$, the hydrogen concentration can be detected through the change of the conductivity.

3. Results and discussion

To ensure the accuracy of our results in this paper, we calculated the structural parameters and electronic properties of the monolayer MoS$_2$. The lattice constant of the monolayer MoS$_2$ is 3.166 Å, and the bond length of Mo–S is 2.408 Å, and the distance between S layers in the sandwich structure is 3.137 Å, respectively. They are in good agreement with the previous theoretical results [41, 42] and experimental data [43, 44]. Figure 2(a) shows the band structure of the monolayer MoS$_2$, it indicates the band gap of the monolayer MoS$_2$ is 2.064 eV, which is in good agreement with previous experimental results [42, 43] (1.98 eV and 1.90 eV) and theoretical values [41, 44] (1.80 eV and 1.70 eV). These comparisons demonstrate that our results in this work are reliable.

3.1. Noble metal doped monolayer MoS$_2$

To explain the stability of the noble metal doped monolayer MoS$_2$, the formation energy of the five kinds of noble metal doped monolayer MoS$_2$ was calculated. The formation energy of Ag, Au, Cu, Pd, and Pt doped monolayer MoS$_2$ is $-0.996$ eV, $-1.172$ eV, $-1.931$ eV, $-2.656$ eV, and $-3.781$ eV, respectively. The formation energy of the noble metal doped monolayer MoS$_2$ in this work is in agreement with the previous theoretical results [39], which also shows that our results are reliable. The negative formation energy indicates that the five noble metal doped monolayer MoS$_2$ have high stability. According to the formation energy, the synthesizing
difficulty of the noble metal doped monolayer MoS2 is MoS2(Ag) > MoS2(Au) > MoS2(Cu) > MoS2(Pd) > MoS2(Pt), and the stability is reversed.

Band structure of the monolayer MoS2, MoS2(Ag), MoS2(Au), MoS2(Cu), MoS2(Pd), and MoS2(Pt) is shown in Figure 2, the valence band and conduction band of the noble metal doped monolayer MoS2 are moving in the direction of energy decreasing when compared with the pristine monolayer MoS2. The band gap of the monolayer MoS2(Ag), MoS2(Au), MoS2(Cu), MoS2(Pd), and MoS2(Pt) is 1.422 eV, 1.123 eV, 1.661 eV, 1.634 eV, and 1.220 eV, respectively. The noble metal doping decreases the band gap of the monolayer MoS2 due to the impurity levels appear between the original conduction band minimum and valence band maximum. The results demonstrate that the noble metal doping is a good method to regulate and control the band structure of the monolayer MoS2.

For a further understanding of the microscopic mechanism of noble metal doping on the monolayer MoS2, density of states of the noble metal atoms and their nearest S and Mo atoms on the doped monolayer MoS2 was calculated, and the results are shown in Figure 3. The electrons in the d orbital of Ag and Au atoms are mainly distributed in the higher energy region of the valence band. The d orbital of Cu atom consists of two parts, one is in the valence band and the other is in the conduction band near the Fermi energy level. The movement of the Mo atom d orbital in the conduction band to the energy decreasing direction contributes to the band gap decrease of the monolayer MoS2(Ag) and MoS2(Au). The band gap decrease of monolayer MoS2(Cu) is caused by the d orbital of the Cu atom in the conduction band. The band gap decrease of monolayer MoS2(Pd) and MoS2(Pt) is caused by the synergistic effect of Pd/Pt d and Mo d orbitals. The noble metal atoms d orbital overlaps with the nearest S atom s orbital and the nearest Mo atoms d orbital in the valence band region of −6 eV to 0 eV, it shows that the adsorption of the noble metal atoms on the monolayer MoS2 is mainly caused by the hybridization of noble metals d, S p, and Mo d orbitals.

3.2. Adsorption of H2 molecule on noble metal doped monolayer MoS2
The adsorption energy of a H2 molecule on the noble metal doped monolayer MoS2 is shown in Table 1. Our results show that if we put a H2 molecule at the adsorption site with H-model or V-model on the noble metal doped monolayer MoS2 as the initial adsorption configuration, the H2 molecule is neither parallel nor perpendicular to the noble metal doped monolayer MoS2 after relaxation. More importantly, the difference in adsorption energy between H-model and V-model is not significant. The adsorption energy of a H2 molecule on

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**Figure 2.** The band structure of the monolayer MoS2(a), MoS2(Ag)(b), MoS2(Au)(c), MoS2(Cu)(d), MoS2(Pd)(e), and MoS2(Pt)(f) without and with an adsorbed H2 molecule.

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| Material | Adsorption Energy (eV) |
|----------|-----------------------|
| MoS2(Ag) | 0.53 |
| MoS2(Au) | 0.58 |
| MoS2(Cu) | 0.59 |
| MoS2(Pd) | 0.64 |
| MoS2(Pt) | 0.67 |

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the pristine monolayer MoS$_2$ is about -0.11 eV, and this value is in good agreement with the theoretical calculations [45, 46]. Almost all the adsorption energy of a H$_2$ molecule on the undoped and noble metal doped monolayer MoS$_2$ is negative, it means that the H$_2$ molecule can be adsorbed on the monolayer MoS$_2$ stably. A more negative adsorption energy means a stronger adsorption interaction between the H$_2$ molecule and the noble metal doped monolayer MoS$_2$. The most stable configurations of the H$_2$ molecule adsorbed on the undoped and noble metal doped monolayer MoS$_2$ are shown in Figure 4. The T$_{\text{Mo}}$ site is the most energetically favorable adsorption site for a H$_2$ molecule on the pristine and Au doped monolayer MoS$_2$, while the T$_{\text{NM}}$ site is best adsorption site for the H$_2$ molecule on the others noble metal doped monolayer MoS$_2$ due to the most negative adsorption energy. The adsorption energy of a H$_2$ molecule on the monolayer MoS$_2$ is decreased by the noble metals Cu, Pd, and Pt, it means that the noble metal doping can enhance the adsorption of the H$_2$ molecule on the monolayer MoS$_2$. However, the adsorption energy of a H$_2$ molecule on monolayer MoS$_2$(Ag) and MoS$_2$(Au) changes little, it demonstrates that Ag and Au doping does not enhance the adsorption of the H$_2$ molecule on the monolayer MoS$_2$ significantly. The effect of the noble metal doping on the adsorption of the H$_2$ molecule on the monolayer MoS$_2$ is Pt > Pd > Cu > Ag > Au according to the adsorption energy change. Previous research has shown that a chemisorption exists between adsorbate and absorbent when the absolute value of adsorption energy is higher than 0.50 eV [47]. The adsorption of the H$_2$ molecule on the Pd and Pt doped monolayer MoS$_2$ belongs to chemisorption because the absolute value of the adsorption energy is greater than 0.5eV. The distance between two H atoms after adsorption was calculated, it shows that the distance is not

Table 1. Adsorption energy (in eV) of a H$_2$ molecule on the noble metal doped monolayer MoS$_2$ with different initial adsorption configurations.

| Configurations | T$_{\text{Mo}}$(∥) | T$_{\text{Mo}}$(⊥) | T$_{\text{NM}}$(∥) | T$_{\text{NM}}$(⊥) | T$_{\text{S}}$(∥) | T$_{\text{S}}$(⊥) | H$_{\text{ex}}$(∥) | H$_{\text{ex}}$(⊥) |
|----------------|-------------------|-------------------|-------------------|-------------------|-----------------|-----------------|-----------------|-----------------|
| MoS$_2$        | -0.119            | -0.112            | —                 | —                 | —               | —               | -0.109         | -0.110          |
| MoS$_2$(Ag)    | -0.127            | -0.119            | -0.155            | -0.127            | -0.128          | -0.114          | -0.123         | -0.128          |
| MoS$_2$(Au)    | -0.133            | 0.051             | 0.116             | 0.004             | -0.119          | -0.111          | -0.144         | -0.139          |
| MoS$_2$(Cu)    | -0.125            | -0.120            | -0.328            | -0.161            | -0.117          | -0.327          | -0.124         | -0.126          |
| MoS$_2$(Pd)    | -0.121            | -0.117            | -0.600            | -0.602            | -0.601          | -0.601          | -0.599         | -0.600          |
| MoS$_2$(Pt)    | -0.119            | -0.116            | -1.284            | -1.265            | -1.283          | -1.283          | -1.281         | -1.281          |
longer than the bond length (0.75 Å) in H₂ molecule, it indicates that the H₂ molecule does not dissociate on the noble metal doped monolayer MoS₂ after adsorption.

To explore the adsorption mechanism of the H₂ molecule on the noble metal doped monolayer MoS₂, the density of states of the noble metal doped monolayer MoS₂ with a H₂ molecule at the most favorable site were calculated. Figure 5 shows that the density of states of the noble metal doped monolayer MoS₂ with a H₂ molecule at the favorable adsorption site. The s orbital of the H₂ molecule adsorbed on the pristine and Ag, Au doped monolayer MoS₂ is mainly distributed in the valence band. When the H₂ molecule adsorbed on the Cu, Pd, and Pt doped monolayer MoS₂, the s orbital of the H₂ molecule splits in two parts, one is in the valence band and the other is in the conduction band. For the H₂ molecule adsorbed on the Ag, Cu, Pd, and Pt doped

Figure 4. The most stable configuration of the H₂ molecule on the monolayer MoS₂ (a), MoS₂(Ag) (b), MoS₂(Au) (c), MoS₂(Cu) (d), MoS₂(Pd) (e), and MoS₂(Pt) (f). The small pink balls represent hydrogen atoms.

Figure 5. The density of states of the monolayer MoS₂ (a), MoS₂(Ag) (b), MoS₂(Au) (c), MoS₂(Cu) (d), MoS₂(Pd) (e), and MoS₂(Pt) (f) with a H₂ molecule at the most favorable site.
monolayer MoS\textsubscript{2}, the s orbital of the H\textsubscript{2} molecule overlaps with the nearest noble metals d orbital. When the H\textsubscript{2} molecule adsorbed on the pristine and Au doped monolayer MoS\textsubscript{2}, the H\textsubscript{2} molecule s orbital overlaps with the nearest S s and Mo d orbitals. The results demonstrate that the adsorption of the H\textsubscript{2} molecule on the noble metal doped monolayer MoS\textsubscript{2} mainly caused by the hybridization of H s, noble metals d, S p, and Mo d orbitals.

### 3.3. Electronic structure change after hydrogen adsorption

Previous researches\textsuperscript{[48–50]} have shown that the more significant the change in electron structure of material after hydrogen adsorption is, the better the hydrogen sensing performance of the material is. To investigate the effect of noble metal doping on the H\textsubscript{2} sensing performances of the monolayer MoS\textsubscript{2}, we calculated the electronic structure of the noble metal doped monolayer MoS\textsubscript{2} with a H\textsubscript{2} molecule at the most favorable site. Figure 2 shows the band structure of the noble metal doped monolayer MoS\textsubscript{2} without and with the adsorbed H\textsubscript{2} molecule, and the adsorbed H\textsubscript{2} molecule is at the most favorable adsorption site as shown in the figure 4. Table 2 also shows the band gap change of the undoped and noble metal doped monolayer MoS\textsubscript{2} after the H\textsubscript{2} molecule adsorption. The band gap of the monolayer MoS\textsubscript{2} and MoS\textsubscript{2}(Au) is reduced by 0.335 eV and 0.045 eV, while the band gap of the monolayer MoS\textsubscript{2}(Ag), MoS\textsubscript{2}(Cu), MoS\textsubscript{2}(Pd), and MoS\textsubscript{2}(Pt) increased by 0.098 eV, 0.064 eV, 0.218 eV, and 0.090 eV. After the H\textsubscript{2} molecule adsorption, the band gap of the noble metal doped monolayer MoS\textsubscript{2} changed significantly, and the band gap change caused by the H\textsubscript{2} molecule adsorption is MoS\textsubscript{2} > MoS\textsubscript{2}(Pd) > MoS\textsubscript{2}(Ag) > MoS\textsubscript{2}(Pt) > MoS\textsubscript{2}(Cu) > MoS\textsubscript{2}(Au). The results demonstrate that the noble metal doped monolayer MoS\textsubscript{2} has a good hydrogen sensing property.

The bader charge of the adsorbed H\textsubscript{2} molecule at the favorable adsorption site on the noble metal doped monolayer MoS\textsubscript{2} is shown in table 3. A negative ∇Q means that electrons are transferred from the H\textsubscript{2} molecule to the noble metal doped monolayer MoS\textsubscript{2}, while a positive ∇Q indicates an opposite situation. According to the ∇Q value, there are two situations, one is electrons transfer from the H\textsubscript{2} molecule to the noble metal doped monolayer MoS\textsubscript{2} when the H\textsubscript{2} molecule is adsorbed on the monolayer MoS\textsubscript{2}(Ag), MoS\textsubscript{2}(Cu), and MoS\textsubscript{2}(Pd), and the other is electrons transfer from the noble metal doped monolayer MoS\textsubscript{2} to the H\textsubscript{2} molecule when the H\textsubscript{2} molecule is adsorbed on the monolayer MoS\textsubscript{2}, MoS\textsubscript{2}(Au), and MoS\textsubscript{2}(Pt). The ∇Q absolute value of the hydrogen molecule adsorbed on the noble metal doped monolayer MoS\textsubscript{2} is larger than that on the pristine monolayer MoS\textsubscript{2}, it means that noble metal doping increases the charge transfer between the H\textsubscript{2} molecule and the monolayer MoS\textsubscript{2}. Figure 6 shows the charge density difference of the monolayer MoS\textsubscript{2}, MoS\textsubscript{2}(Ag), MoS\textsubscript{2}(Au), MoS\textsubscript{2}(Cu), MoS\textsubscript{2}(Pd), and MoS\textsubscript{2}(Pt) with the adsorbed H\textsubscript{2} molecule at the favorable adsorption site. According to the figure 6, we can get some information about the charge transfer between the H\textsubscript{2} molecule and neighboring atoms including S, Mo, and noble metal atoms. When the H\textsubscript{2} molecule is adsorbed on the monolayer MoS\textsubscript{2}, MoS\textsubscript{2}(Au), MoS\textsubscript{2}(Cu), and MoS\textsubscript{2}(Pd), electrons are transferred from the H\textsubscript{2} molecule to the monolayer MoS\textsubscript{2}, MoS\textsubscript{2}(Cu), and MoS\textsubscript{2}(Pd). When the H\textsubscript{2} molecule is adsorbed on the monolayer MoS\textsubscript{2}, MoS\textsubscript{2}(Au), and MoS\textsubscript{2}(Pt), electrons are transferred from the monolayer MoS\textsubscript{2}, MoS\textsubscript{2}(Au), and MoS\textsubscript{2}(Pt) to the H\textsubscript{2} molecule. The results are in agreement with the bader charge analysis.

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**Table 2.** The band gap \(E_g\) (in eV) for the noble metal doped monolayer MoS\textsubscript{2} before and after hydrogen adsorption.

| Materials  | MoS\textsubscript{2} | MoS\textsubscript{2}(Ag) | MoS\textsubscript{2}(Au) | MoS\textsubscript{2}(Cu) | MoS\textsubscript{2}(Pd) | MoS\textsubscript{2}(Pt) |
|------------|----------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| \(E_g\) (Before) | 2.064 | 1.422 | 1.123 | 1.661 | 1.634 | 1.220 |
| \(E_g\) (After) | 1.729 | 1.520 | 1.078 | 1.725 | 1.416 | 1.290 |
| ∇\(E_g\) | −0.335 | 0.098 | −0.045 | 0.064 | 0.218 | 0.090 |

**Table 3.** The bader charge (in eV) of the H\textsubscript{2} molecule adsorbed on the noble metal doped monolayer MoS\textsubscript{2}.

| Materials  | MoS\textsubscript{2} | MoS\textsubscript{2}(Ag) | MoS\textsubscript{2}(Au) | MoS\textsubscript{2}(Cu) | MoS\textsubscript{2}(Pd) | MoS\textsubscript{2}(Pt) |
|------------|----------------------|--------------------------|--------------------------|--------------------------|--------------------------|--------------------------|
| \(Q_t\) | 0.998 | 0.936 | 0.984 | 0.944 | 0.987 | 1.011 |
| \(Q\) | 1.003 | 1.013 | 1.027 | 1.004 | 0.990 | 1.010 |
| ∇\(Q\) | 0.003 | −0.051 | 0.011 | −0.052 | −0.023 | 0.021 |
4. Conclusions

To develop a new kind of hydrogen sensor based on the monolayer MoS$_2$, we investigated the effects of noble metal doping on the hydrogen sensing performances of the monolayer MoS$_2$ by using the first principles calculation method. The Cu, Pd, and Pt doping decrease the adsorption energy of a H$_2$ molecule on the monolayer MoS$_2$ significantly, while the Ag and Au doping decrease the adsorption energy little. The adsorption energy change shows that the Cu, Pd, and Pt doping strengthens the interaction between the H$_2$ molecule and the monolayer MoS$_2$, the Ag and Au doping have little effects on the adsorption of the H$_2$ molecule on the monolayer MoS$_2$. The density of states show that the hybridization of H$_s$, noble metals d, S$p$, and Mo d orbitals contributes to the adsorption of the H$_2$ molecule on the monolayer MoS$_2$. The H$_2$ molecule adsorption increases the band gap of the Ag, Cu, Pd, and Pt doped monolayer MoS$_2$, while the band gap of the pristine and Au doped monolayer MoS$_2$ decreased due to the H$_2$ molecule adsorption. The changes in the bader charge and charge density difference show that the noble metal doping increases the charge transfer between the H$_2$ molecule and the monolayer MoS$_2$. All of the results demonstrate that noble metal doping can improve the hydrogen sensing performances of the monolayer MoS$_2$, especially the Pd and Pt doping.

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Figure 6. The charge density difference of the monolayer MoS$_2$ (a), MoS$_2$(Ag) (b), MoS$_2$(Au) (c), MoS$_2$(Cu) (d), MoS$_2$(Pd) (e), and MoS$_2$(Pt) (f) after the H$_2$ molecule adsorption. Yellow regions represent charge accumulation, and blue regions show charge loss. The iso-surface value is 0.01 e/Å$^3$. 

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