Enhanced Photocatalytic Activity of 2H-MoSe₂ by 3d Transition-Metal Doping

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Supporting Information

ABSTRACT: To develop MoSe₂-based photocatalysts, increasing the catalytic activity of 2H-MoSe₂ is essential. In this work, the electronic and photocatalytic properties of 3d transition metal-doped (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) 2H-MoSe₂ were investigated by first-principles calculations. The results indicate that Sc, Ti, V, Cr, Mn, Fe, and Co atoms tend to substitute the Mo atoms under a Se-rich condition, whereas Ni, Cu, and Zn atoms prefer to occupy the interstitial positions. More importantly, Sc- and Ti-doped 2H-MoSe₂ can enhance the photocatalytic activity by increasing the oxidizability of photogenerated holes, suppressing the recombination of photogenerated carriers, and increasing the number of catalytic active sites.

1. INTRODUCTION

As a member of the transition-metal dichalcogenide (TMDC) material, hexagonal MoSe₂ has three kinds of structures, such as 1T, 2H, and 3R phases, and the 2H phase is the most stable one.¹⁻³ Recently, 2H-MoSe₂ has stimulated considerable worldwide attention because of its potential catalytic applications in photocatalytic degradation of organic pollutants.⁴⁻⁶ However, its active sites only exist at the edges states and the high recombination rate limits its applications as a photocatalyst.⁷⁻⁸ Theoretical and experimental studies have shown that doping is a promising method to improve the photocatalytic activity of MoSe₂⁻⁹⁻¹⁰ because the impurity levels (ILs) generated by dopants can decrease the recombination rate of photogenerated carriers.¹¹⁻¹⁴ However, a systematic study of the effect of 3d TMs on catalytic active sites and oxygen reduction reaction (ORR) of 2H-MoSe₂ is needed.

In this work, using first-principles calculations, we have studied the electronic and photocatalytic properties of 3d TM-doped 2H-MoSe₂. It is found that Sc, Ti, V, Cr, Mn, Fe, and Co atoms tend to occupy the Mo site under the Se-rich condition, whereas Ni, Cu, and Zn atoms prefer to occupy the interstitial sites of B₁Se₂, B₁Se, and H, respectively. Moreover, Sc- and Ti-doped systems can further enhance the photocatalytic activity of 2H-MoSe₂ by separating the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LOMO), suppressing the recombination of photogenerated electrons (e⁻)/holes (h⁺), increasing the number of active sites, and enhancing the oxidizability of photogenerated h⁺.

2. COMPUTATIONAL DETAILS

A first-principles study was performed using the Vienna Ab-initio simulation package on the basis of the projected augmented wave potential approach.¹⁵⁻¹⁷ The Perdew–Burke–Ernzerhof function of the generalized gradient approximation was used as the exchange correlation function.¹⁸⁻¹⁹ To simulate the doping model of 3d TM atoms in a 3 × 3 × 1 supercell 2H-MoSe₂ with 18 Mo and 36 Se atoms, we considered the TM atoms substituting Mo atoms (TMS) (Figure 1a,b) or occupying the interstitial position (TMi); thus, the atomic doping ratio (TM/Mo) is 5.88 or 5.56%. In addition, the TMi-doped system has three doped cases: the position directly below the upper layer Mo atom (B₁Mo); the position directly below the upper layer Se atom (B₁Se); and the position above the hollow site (H) of the hexagonal rings of the lower layer (Figure 1a,c,d). In fact, B₁Mo and B₁Se describe the same position according to the symmetry of 2H-MoSe₂. Details on calculation parameters can be found elsewhere. In addition, the total energy was corrected using Grimme’s DFT-D2 method and is used to describe the VDW interactions.²¹⁻²²

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We have calculated the formation energy ($E_f$) of all doped systems to assess the stability of different TM dopants

$$E_f = E_{\text{doped}} - E_{\text{undoped}} + n\mu_{\text{Mo}} - m\mu_{\text{TM}}$$

(1)

$E_{\text{doped}}$ and $E_{\text{undoped}}$ are the total energies of 2H-MoSe$_2$ with and without a TM atom and $\mu_{\text{TM}}$ is the chemical potential of the per TM atom in bulk TM. The coefficients $m$ and $n$ represent the number of substituted Mo atoms and the number of TM atoms introduced into the supercell, respectively. $E_f$ is changing from the Mo-rich condition to the Se-rich condition. Relations between $\mu_{\text{Mo}}$ and $\mu_{\text{Se}}$ are as follows

$$\mu_{\text{Mo}} + 2\mu_{\text{Se}} = \mu(\text{MoSe}_2)$$

(2)

Under the Se-rich condition, $\mu_{\text{Se}}$ is the chemical potential of the per Se atom in bulk Se, and $\mu_{\text{Mo}}$ is obtained from eq 2. Under the Mo-rich condition, $\mu_{\text{Mo}}$ is obtained from the energy of one Mo atom in bulk Mo, and $\mu_{\text{Se}}$ is determined by eq 2. Negative $E_f$ suggests that TM atoms are very easy to enter the 2H-MoSe$_2$ lattice.

3. RESULTS AND DISCUSSION

3.1. Formation Energies and Optimized Structures.

Figure 2 lists the $E_f$ values of TM-doped 2H-MoSe$_2$. It is found that the $E_f$ of the TM$_{3}$-doped system obtained under the Se-rich condition is smaller than that under the Mo-rich condition because more Mo vacancies are present in the Se-rich condition. $E_f$ increases as the atomic number of the dopant atoms increases, except for the Cu-doped system. Second, the total energies of TM$_{1}$ (B$_{\text{Se}}$ or H)-doped systems were calculated and compared, and the results showed that Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu atoms prefer to occupy the B$_{\text{Se}}$ site. The $E_f$ of each most stable TM$_{1}$-doped system ($E_i$) is shown in Figure 2.

Moreover, by comparing the $E_i$ of TM$_{3}$- and TM$_{1}$-doped systems, we found that Sc, Ti, V, Cr, Mn, Fe, and Co atoms tend to substitute the Mo atoms, whereas Ni, Cu, and Zn atoms prefer to occupy the positions of B$_{\text{Se}}$, B$_{\text{Mo}}$, and H sites, respectively. The reason is that the atomic radius of a Ni atom is the smallest among all 3d TM atoms, so it is easy to appear at the interstitial site. For Cu and Zn atoms, because their 3d orbitals are fully occupied, the ability to lose electrons is weak, and thus they are difficult to replace Mo atoms. Further, the results of the electronic density difference suggest that Ni$_{\text{Se}}$ and Cu$_{\text{Se}}$ are chemical adsorption, whereas Zn$_{\text{H}}$ is physical adsorption (Figure S1, Supporting Information).

3.2. Electronic Properties.

2H-MoSe$_2$ is an indirect gap semiconductor with an indirect band gap of 0.89 eV, and the conduction band (CB) and the valence band (VB) are composed of Mo 4d and Se 4p states, as shown in Figure 1e,f. Figure 3 only illustrates the band structure and the average partial density of states (PDOS) of Mo, Se, and TM atoms for each most stable TM$_{1}$-doped systems. It is found that the electronic properties of Cr-doped 2H-MoSe$_2$ are similar to those of undoped one because the Cr element also belongs to

Figure 1. Three different interstitial sites and one substitute site of 2H-MoSe$_2$: top view (a) and side view (b–d). The blue, yellow, and red spheres denote Mo, Se, and TM atoms, respectively. The band structure (e) and average PDOS (f) of undoped 2H-MoSe$_2$.

Figure 2. $E_f$ of the TM-doped 2H-MoSe$_2$. The results indicate that Sc, Ti, V, Cr, Mn, Fe, and Co atoms prefer to substitute Mo atoms under the Se-rich condition, whereas Ni, Cu, and Zn atoms prefer to occupy the interstitial sites.
the VIB group as Mo. Second, substitutional doping by Sc, Ti, and V atoms creates ILs (mostly composed of TM 3d and Mo 4d states) sitting within the VB maximum (VBM) and the Fermi levels move into the VB, resulting in the p-type conductivity and metallic properties, consistent with the reported results\textsuperscript{28,29} as shown in Figure 3a,c,e. This can be attributed to the fact that the acceptor dopants can easily introduce some holes into the 2H-MoSe\textsubscript{2} lattice.

In Mn-, Fe-, and Co-doped systems, the ILs (TM 3d and Mo 4d states) are close to or overlap with the CB minimum (CBM), and the Fermi levels cross the CBM (see Figure 3i,k,m). Thus, they become n-type semiconductors and exhibit metallic properties, as the substitutional donor TM atoms introduce additional electrons into the system. Similarly, Cu- and Zn-doped systems are also n-type semiconductors, but the Ni dopant only makes the Fermi level rise a small distance. Moreover, the ILs (Zn 4s states) are within the band gap of the Zn-doped system. However, there is no ILs in the band gap of the Cu-doped system because its d orbit is the full electron state. In addition, we have found that Sc-, Cr-, Mn-, Fe-, and Co-doped systems are direct semiconductors which can improve the absorption efficiency of light. This is essential for practical applications of optoelectronic devices.

In summary, we have already found that TM dopants can change the electronic structure, such as the number and shape of the ILs (flat or curvature), the energy position of the CBM ($E_{\text{CBM}}$) and VBM ($E_{\text{VBM}}$), and the composition of the CBM and VBM. Thus, they can modulate the photocatalytic activity.

In fact, when we discuss the photocatalytic ability of common semiconductors, there are four key concerns, such as suitable band gap value, low $e^-/h^+$ recombination rate, rich catalytic active site, and suitable work function for ORR.\textsuperscript{30−32} 2H-MoSe\textsubscript{2}-based catalysts have inherently excellent optical absorption properties (absorbing all visible light). Therefore, we only need to explore the other three factors, and more details will be discussed later.

### 3.3. Effective Mass of Photogenerated Carriers

The ILs within the band gap can facilitate photoexcited $e^-/h^+$ pumping from the VB into the CB. It should be noted that curved and broad ILs can reduce the $e^-/h^+$ recombination, whereas the $e^-$ trapped in the flat ILs is easily annihilated by recombination with $h^+$.\textsuperscript{7,31} To quantify the recombination rate of ILs, the effective mass ($m^*$) has been calculated and is listed in Table 1. The smaller $m^*$ suggests higher mobility ($\mu = e\tau/m^*$) and higher chances for the photogenerated carriers to get to the

![Figure 3. Band structure and average PDOS of TM-doped 2H-MoSe\textsubscript{2}. Except for Cu-doped MoSe\textsubscript{2}, the ILs are located within the band gap. The Sc-, Cr-, Mn-, Fe-, and Co-doped systems are direct band gap semiconductors.](image)

Table 1. Summary of Calculated Results of TM-Doped MoSe\textsubscript{2}\textsuperscript{a}

<table>
<thead>
<tr>
<th>system</th>
<th>site</th>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
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<th>Mn</th>
<th>Fe</th>
<th>Co</th>
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<td>$E_{\text{CBM}}$</td>
<td>5.83</td>
<td>5.89</td>
<td>5.88</td>
<td>5.77</td>
<td>5.91</td>
<td>5.80</td>
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<td>$E_{\text{VBM}}$</td>
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<td>$E_{\text{g}}$</td>
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<td>0.93</td>
<td>0.99</td>
<td>0.78</td>
<td>0.89</td>
<td>0.91</td>
<td>0.77</td>
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<td>1.06</td>
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<td>$m^*_{ILs}$</td>
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<td>$m^*_{h}$</td>
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<td>$m^*_h$</td>
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\textsuperscript{a}Site represents the doping position of various TM atoms. $E_{\text{CBM}}$, $E_{\text{VBM}}$, and $E_{\text{g}}$ are the energy positions of CBM, VBM, and band gap in eV, respectively. $m^*_e$, $m^*_{ILs}$, and $m^*_h$ are the effective mass of electrons, ILs, and holes in $m_e$, respectively. $R = m^*_h/m^*_e$ is the relative effective mass.
It is found that all doped systems have smaller $m^*$ (0.84–1.83) of ILs ($m^*_{ILs}$); thus, they are curved and broad ILs and can reduce the recombination rate of $e^-/h^+$. Moreover, the large difference between $m^*$ of the $e^-$ ($m^*_{e^-}$) and $h^+$ ($m^*_{h^+}$) results in the large difference of diffusion length ($L_p$), $L_p = \sqrt{\frac{\hbar kT}{e} m^*_{e^-}} = \sqrt{\frac{\hbar kT}{m^*_{h^+}}}$\textsuperscript{33,34} Thus, the relative mass ($R = m^*_{h^+}/m^*_{e^-}$) has been used to evaluate the recombination rate.\textsuperscript{36} It is found that Sc- and Ti-doped 2H-MoSe\textsubscript{2} have the largest $R$, suggesting that they can greatly reduce the recombination of photogenerated carriers; see Table 1.

### 3.4. Photocatalytic Properties

Catalytic active sites were defined by the HOMO and LOMO. As shown in Figure 4a, the HOMO and LUMO of 2H-MoSe\textsubscript{2} are located at all Mo atoms simultaneously; thus, most of the photogenerated $e^-/h^+$ will be recombined on Mo atoms immediately.

![Figure 4](image-url)

**Figure 4.** HOMO and LUMO of TM-doped and undoped 2H-MoSe\textsubscript{2}. The isosurface is taken at a value of 0.03 e/bohr\textsuperscript{3}. The purple and green regions represent HOMO and LUMO, respectively. Ti-, Cr-, and Mn-doped systems are demonstrated as examples, and for other doped systems, please refer to Figure S2. The HOMO and LUMO of Sc-, Ti-, and Cr-doped 2H-MoSe\textsubscript{2} are separated in real space.

For Sc-doped 2H-MoSe\textsubscript{2}, HOMO is located only on the Mo and Sc atoms of the upper layer, whereas LUMO is similar to 2H-MoSe\textsubscript{2} (Figure 4a,b). For Ti- and V- and Ni-, Cr-, Co-, and Cu-doped 2H-MoSe\textsubscript{2}, the HOMO is similar to 2H-MoSe\textsubscript{2}. In Ti-, V-, and Ni-doped systems, the LUMO is located only on Mo atoms in the lower layer (Figure 4c is the case of a Ti-doped system. For other doped systems, please refer to Figure S2a,d). However, the LUMO in Cr-, Co-, and Cu-doped systems is located on Mo atoms in the upper layer (Figure 4d is the case of a Cr-doped system. For other doped systems, please refer to Figure S2c,e, Supporting Information). The reason is that the composition of VBM and CBM has been changed by the dopant, as shown in Figure 3. Overall, in these seven cases, the HOMO and LUMO are separated, and the number of catalytic active sites is increased dramatically. However, the HOMO and LUMO states of Mn- and Fe-doped systems are mostly located on the Mo and TM atoms of the upper layer (Figure 4e is the case of a Mn-doped system. For other doped systems, please refer to Figure S2b, Supporting Information). For Zn-doped 2H-MoSe\textsubscript{2}, the HOMO and LUMO are similar to 2H-MoSe\textsubscript{2} (Figure S2f, Supporting Information). Thus, the photogenerated $e^-/h^+$ has a good chance to recombine in those systems.

Further, Figure 5 illustrates the mechanism of photocatalytic degradation of methylene blue by using Ti-doped 2H-MoSe\textsubscript{2} as an example. Under light irradiation, $e^-$ and $h^+$ will be generated at the green and purple regions, respectively. $O_2^-$ ions (or $\cdot$OH radicals) can be reduced (or oxidized) by $e^-$ (or $h^+$). Then, methylene blue can be oxidized to $H_2O$ and $CO_2$. Thus, the amount of $e^-$ or $h^+$ that reaches the surface of the catalyst determines the photocatalytic activity of the catalyst. The Ti dopant can greatly improve the photocatalytic performance of 2H-MoSe\textsubscript{2} because it can reduce the recombination rate of carriers and increase the number of photocatalytic active sites. This effect is similar to the results of previous theoretical and experimental reports.\textsuperscript{6,12,30,37}

On the other hand, $E_{CBM}$ and $E_{VBM}$ of undoped and TM-doped 2H-MoSe\textsubscript{2} are calculated relative to the vacuum level.\textsuperscript{38} We have found that $E_{CBM}$ and $E_{VBM}$ of all doped systems move down to the low-energy region compared with those of undoped 2H-MoSe\textsubscript{2}. Therefore, the oxidizability of photogenerated $h^+$ at the HOMO is enhanced, whereas the...
reducibility of photogenerated e\textsuperscript{-} at LUMO is reduced. This suggests that a *\textsuperscript{OH} radical plays a leading role in the photocatalytic degradation process.

4. CONCLUSIONS

In this work, doping site, formation energy, and electronic and photocatalytic properties of 3d-TM-doped 2H-MoSe\textsubscript{2} were investigated by first-principles calculations. The results indicate that the Se-rich condition is energetically favorable to substitute Mo atoms by Sc, Ti, V, Cr, Mn, Fe, and Co atoms, whereas the Ni, Cu, and Zn atoms preferentially occupy the interstitial position. Moreover, Sc- and Ti-doped 2H-MoSe\textsubscript{2} have demonstrated excellent photocatalytic activity because they can suppress the recombination of photogenerated e\textsuperscript{-}/h\textsuperscript{+}, separate HOMO and LUMO, enhance oxidizability of photogenerated h\textsuperscript{+}, and increase the number of photocatalytic active sites. This work provides an important guidance for developing 2H-MoSe\textsubscript{2}-based photocatalysts.

**References**


2. Ambrosi, A.; Sofer, Z.; Pumera, M. 2H\textsuperscript{−}→1T phase transition and hydrogen evolution activity of MoSe\textsubscript{2}, MoS\textsubscript{2}, WS\textsubscript{2} and WSe\textsubscript{2}, strongly depends on the MX\textsubscript{2} composition. *Chem. Commun.* 2015, 51, 8450-8453.


8. Kibsgaard, J.; Chen, Z.; Reinecke, B. N.; Jaramillo, T. F. Engineering the surface structure of Mo\textsubscript{2}Se\textsubscript{3} to preferentially expose active edge sites for electrocatalysis. *Nat. Mater.* 2012, 11, 963-969.


12. Ma, X.; Li, J.; An, C.; Peng, J.; Chi, Y.; Liu, J.; Zhang, J.; Sun, Y. Ultrathin Co(Ni)-doped Mo\textsubscript{3}S\textsubscript{4} nanosheets as catalytic promoters enabling efficient solar hydrogen production. *Nano Res.* 2016, 9, 2284-2293.


27. Böker, T.; Severin, R.; Müller, A.; Janowits, C.; Manzke, R. Bond Structure of MoSe\textsubscript{2}, Mo\textsubscript{3}Se\textsubscript{5}, and α-MoTe\textsubscript{2}: Angle-Resolved


