Enhanced photochemical performance of hexagonal WO₃ by metal-assisted S–O coupling for solar-driven water splitting

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ABSTRACT Hybrid density functional calculations was used to comprehensively study the electronic structure of S-, Sn- and Pb-monodoped and (Sn, S)- and (Pb, S)-codoped hexagonal WO₃ (h-WO₃) in order to improve their visible light photocatalytic activity. Results indicate that the (Sn, S)- and (Pb, S)-codoped h-WO₃ can realize a significant band gap reduction and prevent the formation of empty states in the valence band of h-WO₃, while Sn/Pb-monodoped h-WO₃ cannot, because in (Sn, S)- and (Pb, S)-codoping, the S-doping introduces the fully occupied S 3p states in the forbidden band gap of h-WO₃ and the acceptor metals (Sn and Pb) would assist the coupling of the introduced S with its nearest O. In particular, the (Sn, S)-codoped h-WO₃ has the narrowest band gap of 1.85 eV and highest reducing ability among the doped case. Moreover, the calculated optical absorption spectra show that (Sn, S)-codoping can improve the visible light absorption. In short, these results indicate that the (Sn, S)-codoped h-WO₃ is a promising material in solar-driven water splitting.

Keywords: hexagonal WO₃, hybrid density functional calculation, electronic structure, solar-driven water splitting

INTRODUCTION

In the past decades, semiconductor materials have attracted increasing interest for visible light photocatalysis [1–3]. Because of the good charge transport properties, photosensitivity and excellent chemical stability in acidic environment under solar illumination, WO₃ has been regarded as one of the most promising candidates for solar-driven water splitting [4,5]. Compared with TiO₂, a most extensively studied photocatalyst, WO₃ has a smaller band gap (2.8 eV vs. 3.2 eV for TiO₂) and a more positive

valence band edge (vs. the normal hydrogen electrode (NHE)), which expands its absorption band edge to blue region of visible light and provides a favourable alignment for the evolution of O₂ [6,7]. However, some drawbacks and limitations also exist in WO₃. Since the ideal band gap for water splitting should be 1.6–2 eV, the band gap of WO₃ is still too large to achieve high quantum yield in solar spectrum and WO₃ exhibits poor performance for hydrogen production as its bottom of the conduction band is nearly 0.3 eV below the hydrogen redox potential [8].

Tremendous efforts, such as selective doping [9,10], morphology control [11,12] and surface modification [13,14] have been devoted to overcoming these obstacles and enhancing the photocatalytic activity of WO₃ for solar-driven water splitting. Among them, selective doping is especially effective in engineering the electronic band structure of WO₃ [15,16]. A number of dopants have been explored experimentally. For example, Karpappasamy *et al.* [17] reported that vanadium doped WO₃ could significantly improve the photocatalytic efficiency, since the optical band gap of the WO₃ thin film was influenced by the defects created by V dopants. In addition, the incorporation of Mo into WO₃ lattice can also result in a decreased band gap energy and remarkably improve the photocatalytic efficiency, compared with the undoped WO₃ [18]. Also, other monodoped WO₃ such as N-, C-, Sn-WO₃ were reported to have high photocatalytic property [19–21]. On the other side, density functional theory (DFT) has been used to study the mechanism of enhanced visible light photocatalysis performance and design new WO₃-based photocatalysts. Through theoretic-

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tical calculations, Zhang [22] obtained satisfactory explanation of the pronounced improvement of solar-driven water splitting in Fe-doping of WO_3 . Wang and co-workers [23] studied the electronic properties of the doped WO_3 and found that replacing O with S could narrow the band gap and shift the conduction band minimum upwards. However, the monodoping always generates localized donor or acceptor states, which plays a detrimental role in photocatalytic activity of the materials [16,24]. Last but not the least, the majority of the research of WO_3 -based water splitting materials were focused on dealing with the most stable monoclinic WO_3 [25], whereas very few investigations were focused on relatively stable hexagonal phase of WO_3 which was generally applied to smart window or photothermal agent [8,26–29].

In recent years, codoping is found to be more efficient than monodoping in many metal oxides, such as TiO_2 [30,31]. The studies of codoped TiO_2 for the band gap narrowing are already well established [32,33], while the codoped WO_3 is seldom involved. In previous work, the donor-acceptor codoping has been considered to be an efficient approach in codoped TiO_2 [34,35]. It is found that the compensation effect of donor-acceptor pairs can not only facilitate the separation of photo-generated carriers but also improve the stability and solubility of the doping elements [36,37]. More recently, a new concept of metal-assisted nonmetal-O coupling of dopants was proposed for the band gap narrowing in TiO_2 [38,39]. This kind of coupling mechanism is much more effective than monodoping or donor-acceptor codoping for band gap reduction in TiO_2 . However, to the best of our knowledge, no studies on the dopant coupling in codoped WO_3 have been reported.

In this work, we use the first-principles calculations to comprehensively study the physical properties of hexagonal tungsten trioxide (h- WO_3) monodoped with S, Sn, and Pb and codoped with (Sn, S) and (Pb, S). First, the structural properties, formation energies and binding energies of pure and doped h- WO_3 are calculated by using standard DFT method. Then, the electronic and optical properties are investigated by using hybrid DFT calculation. Finally, the dopant coupling mechanism in these codoped systems is also analysed in details.

COMPUTATIONAL DETAILS

In this study, DFT calculations based on the projector augmented wave (PAW) method were implemented in the Vienna *ab-initio* simulation package (VASP) [40,41]. The generalized gradient approximation (GGA) of Perdew-Burke-Ennzerhof (PBE) was adopted to study the

Figure 1 Perspective view of the $2 \times 2 \times 1$ supercell of h- WO_3 . The red and light blue spheres represent O and W atom, respectively. O1 is replaced by S atom and W1 is substituted by Sn (Pb) atom in S-containing and Sn (Pb)-containing systems, respectively.

energies and structures of the undoped and doped models [42]. The valence electron configurations for O, S, Sn, W, and Pb are $2s^2 2p^4$, $3s^2 3p^4$, $5s^2 5p^2$, $6s^2 5d^4$ and $6s^2 6p^2$, respectively. The kinetic cutoff energy for basis functions was set to 500 eV. In the geometry optimization, the k -point meshes for Brillouin zone sampling were generated with a $3 \times 3 \times 11$ grid based on Monkhorst and Pack [43] scheme to relax the $2 \times 2 \times 1$ hexagonal supercell containing 36 atoms of O and 12 atoms of W (Fig. 1). In the case of all the S-containing systems, one O atom is replaced by one S atom, while for the Sn (Pb)-containing systems one W1 atom is substituted by one Sn (Pb) atom. The energy convergence criteria for self-consistent iteration were set to 10^{-4} eV/atom along with the residual atomic forces that were smaller than $0.01 \text{ eV } \text{\AA}^{-1}$.

Although the standard DFT functions (localized density approximation (LDA) and GGA) present good results for the materials, there is still big difference between the LDA/GGA band gap and experimental band gap, affecting the accuracy of prediction on the electronic and optical properties [39]. In this work, Heyd-Scuseria-Ernzerhof (HSE06) hybrid function [44,45] was applied to the calculations of electronic structure (i.e. band structure and density of states) and dielectric constants (i.e. optical absorption spectra). In the HSE06 function, the exchange-correlation function uses short-ranged and long-ranged parts of exchange. The exchange-correlation in HSE06 was expressed as follows:

$$E_{\text{XC}}^{\text{HSE}} = \frac{1}{4} E_{\text{X}}^{\text{HF,SR}}(\mu) + \frac{3}{4} E_{\text{X}}^{\text{PBE,SR}}(\mu) + E_{\text{X}}^{\text{PBE,LR}}(\mu) + E_{\text{C}}^{\text{PBE}}, \quad (1)$$

where SR and LR denote the short- and long-ranged parts of the exchange interaction, respectively. μ represents the range-separation parameter and was set to $0.2 \text{ \AA}^{-1}$. The hybrid functional was defined as the mixing of 45% PBE function and 55% exact Hartree-Fock (HF). A reduced k -points mesh of $3 \times 3 \times 3$ was used for the calculation of

Table 1 The calculated lattice parameters (a , b , and c), formation energy (E_f) of pure and S-, Sn-, Pb-monodoped, and (Sn, S)- and (Pb, S)-codoped h-WO₃

	a (Å)	b (Å)	c (Å)	$E_f^{\text{O-rich}}$ (eV)	$E_f^{\text{W-rich}}$ (eV)
Pure h-WO ₃ (experimental [44])	7.298	7.298	3.899	-	-
Pure h-WO ₃ (theoretical [45])	7.438	7.438	3.827	-	-
Pure h-WO ₃ (this work)	7.453	7.453	3.833	0	0
S-monodoped	7.579	7.579	3.806	2.736	-0.541
Sn-monodoped	7.507	7.474	3.847	-2.943	6.888
Pb-monodoped	7.539	7.499	3.861	-0.871	5.683
(Sn, S)-codoped	7.521	7.646	3.793	-3.756	2.798
(Pb, S)-codoped	7.584	7.645	3.797	-1.565	4.988

band structure. For the density of states (DOS) and optical absorption spectra calculations, more accurate k -mesh containing at least 125 k -points was adopted.

RESULTS AND DISCUSSION

To investigate the relative difficulty of doping, the formation energies of the S-, Sn-, and Pb-monodoped and (Sn, S)- and (Pb, S)-codoped h-WO₃ were calculated by the following formula:

$$E_f = E(\text{doped}) - E(\text{pure}) - \mu_{\text{dopant}} + \mu', \quad (2)$$

where $E(\text{doped})$ and $E(\text{pure})$ represent the total energies of the h-WO₃ with and without the dopants, respectively; μ_{dopant} is the chemical potential of the dopants, where the μ_{S} of S is obtained from the rhombic sulfur ($\mu_{\text{S}} = \mu(\text{rhombic sulfur})/258$), and the chemical potentials of tin and lead are determined by their bulk materials; μ' is the chemical potential of O or W (μ_{O} or μ_{W}). It should be noted that under different growth condition (W-rich or O-rich) the formation energy is varied. Under the O-rich condition, μ_{O} is assumed as the ground state energy of O₂ molecule ($\mu_{\text{O}} = \mu(\text{O}_2)/2$) and the μ_{W} can be obtained from the thermodynamic equilibrium relation:

$$\mu_{\text{W}} + 3\mu_{\text{O}} = \mu(\text{WO}_3), \quad (3)$$

where μ_{W} is obtained from the tungsten atom under the W-rich condition, and the chemical potential is calculated by Equation 3. The calculated formation energies of all the doped systems are listed in Table 1. It can be seen that aside from the S-monodoped h-WO₃, lower formation energies are obtained for Sn-, Pb-, (Sn, S)- and (Pb, S)-doped h-WO₃ under O-rich growth condition, which means that these doped system can be prepared more easily by controlling O₂ pressure. This observation has already been proven to be feasible and efficient in other WO₃ systems [46–48].

To determine the relative stability of the dopant combination in codoped systems, the binding energies have also been calculated by using the following equation:

$$E_b = E(\text{S-monodoped}) + E(\text{M-monodoped}) - E(\text{codoped}) - E(\text{pure}), \quad (4)$$

where $E(\text{pure})$, $E(\text{S-monodoped})$, $E(\text{M-monodoped})$, and $E(\text{doped})$ are the total energies of the pure, and the S-, M- (M = Sn and Pb) monodoped and the (M, S)-codoped h-WO₃, respectively. A positive value of E_b reflects a stable condition when dopants exist in h-WO₃ [49]. As a result, the calculated binding energies for the (Sn, S)- and (Pb, S)-codoped h-WO₃ are 3.68 eV and 3.81 eV, respectively, indicating that the strong bonding between the dopants and the codoped systems are of more stability compared with their respective monodoped systems.

The results of geometry optimization for pure h-WO₃, monodoped and codoped systems are summarized in Table 1, where the calculated lattice parameters for the pure h-WO₃ are very close to the previous experimental and theoretical results [50,51]. For the doped systems, various degrees of lattice distortions are found and the incorporation of Pb leads to distinct lattice expansions due to the large ionic radius of Pb⁴⁺ (Pb⁴⁺, 0.77 Å; W⁶⁺, 0.6 Å).

The optimized inner parts of the structure for pure and doped h-WO₃ are displayed in Fig. 2, where the equivalent oxygen atoms of WO₆ octahedra form a hexagonal cavity in h-WO₃. It can be seen that although the structures of monodoped systems are distorted in some extent, and the basic structure of primitive h-WO₃ is retained. The positions of Sn and Pb are of inconsiderable change while the S atom shifts from the initial position to the hexagonal cavity and its adjacent W atoms slightly move outward (Fig. 2b). This trend was also observed in the calculation of S-monodoped monoclinic WO₃ [23]. On the contrary, it is found that the S atom in the codoped system has an obvious movement and the distance between S and the nearest O atom is 1.67 Å in (Sn, S) and 1.68 Å in (Pb, S), suggesting the possible formation of S–O bond. However, it should be noticed that the locations

Figure 2 Inner part of the optimized structures of (a) pure h-WO₃, (b) S-, (c) Sn- and (d) Pb-monodoped and (e) (Sn, S)- and (f) (Pb, S)-codoped h-WO₃. The red, yellow, gray, deep green and light blue spheres represent O, S, Sn, Pb and W atoms, respectively.

of the dopant atoms are almost the same as the counterparts of their monodoping cases when the dopants are separated (Fig. S1 in Supplementary information).

The calculated band structure for pure h-WO₃ is shown in Fig. 3a. It can be seen that the h-WO₃ is an indirect band gap semiconductor with the valence band maximum (VBM) positioning at A point and the conduction band minimum (CBM) at Γ point. The calculated band gap is 2.90 eV, which is close to the experimental value (2.8 eV) [52]. Apparently, the HSE06 function overcomes the shortcomings of the standard DFT calculations and guarantees the accurate prediction on the electronic structure of the WO₃ system. For S-monodoped h-WO₃, the fully occupied impurity levels appear above the host VBM (Fig. 3b). This is because the incorporation of S (isovalent to O) does not cause charge mismatch problems and the energy of S 3p states is higher than that of O 2p states. Thus, an effective band gap reduction is realized. Upon Sn and Pb monodoping (Fig. 3c, d), the band structures and band gaps rarely are affected. Nevertheless, since both Sn and Pb have two less valence electrons than W, adding two holes to the system, the Fermi levels enter into the VB. Contrarily, the p-type behaviours are vanished and the occupied midgap states still exist in the forbidden band of h-WO₃ when S and Sn (Pb) are incorporated. Significantly reduced band gap and upshift of VBM and CBM are found in codoped systems, but the nature of indirect band gap semiconductor still remains. In the present calculations, the band gaps for S-, Sn-, Pb-, (Sn, S)- and (Pb, S)-doped h-WO₃ are 2.12, 2.84, 2.94, 1.85, and 1.97 eV, respectively. Obviously, the S-

monodoping and the codoping can effectively narrow the band gap of h-WO₃, which results in the improvement of the photochemical efficiency under visible light. Furthermore, the electron-hole recombination rate might be accelerated in Sn- and Pb-monodoping because of the existence of the unoccupied states.

Due to the presences of the acceptor states, which are not beneficial for water splitting, the Sn- and Pb-monodoping can be ignored. Thus, our study is mainly focused on the S-containing systems. Total density of states (TDOS) and the partial density of states (PDOS) of the S-containing h-WO₃ were calculated to obtain detailed information of the doping influence on the electronic structure of h-WO₃. For comparison, the TDOS and PDOS of h-WO₃ are also displayed in Fig. 4a. It is seen that in h-WO₃, the VB mainly consists of O 2p states while the CB is largely dominated by W 5d states [53]. The most distinct feature from the TDOS of the S-monodoped h-WO₃ is that the hybridized states have arisen from S 3p and O 2p, located in the band gap, which enables electron to be excited to the conduction band under low-frequency visible light irradiation. For the codoped systems (Fig. 4c, d), besides the narrower band gap, small hump in the vicinity of the Fermi level can also be found. These states possess not only the O 2p and S 3p characteristic but also an increasing contribution from W 5d states. However, it is found that in the separated codoping case only partially occupied S 3p states in the band gap (Fig. S2) is observed, which also reduces the band gap but may become the recombination centre. The formation energy shows that under the O-rich condition the neighboring codoping is more stable than the separated codoping ($E_f^{\text{O-rich}} = -1.29$ eV). Thus it can be known that the neighboring codoping states can be obtained by tuning the oxygen pressure during the preparation of the materials.

In order to further understand the charge transfer and the chemical bonding in S-containing h-WO₃, the charge density of S-, (Sn, S)- and (Pb, S)-doped h-WO₃ were explored. The W–O bonds in pure h-WO₃ can be regarded as ionic bonds because only a few overlaps are found in the charge density around W and O atoms. Resulting from the fact that the electronegativity of S is less than that of O, it can be seen that there is a charge accumulation close to S in the bonding region between S and the neighboring W atoms (Fig. 5b). What is to be noted is that the (Sn, S)- and (Pb, S)-codoping induce remarkable changes in the charge density profile of the S atom. As displayed in Fig. 5c, d, relatively high density of electrons are found in the volume between S and the

Figure 3 The calculated band structures of (a) pure h-WO₃, (b) S-, (c) Sn- and (d) Pb-monodoped and (e) (Sn, S)- and (f) (Pb, S)-codoped h-WO₃. The red dashed horizontal lines represent the Fermi levels.

nearest neighboring O atom, suggesting a stable S–O covalent bond is formed, which is consistent with the previous suggestions obtained from the binding energies results. Furthermore, the interaction between S and W atom can also strongly corroborate the DOS analyses of the impurity energy levels as discussed above.

The mechanism of the acceptor metals assisted S–O coupling is illustrated in Fig. 6. The introduction of the acceptor metal (Sn or Pb) creates two holes in the first place and then these holes are compensated by the two electrons of S atom owing to its weaker electronegativity than O atom. After the charge compensation, the 2p_z orbital of S become empty, which promotes the S–O bond formation. During the process of S–O bonding, their p_z orbitals start to form bonding state σ and antibonding states σ^* , where the former lying below the VB and the later distributing in the CB, respectively. Meanwhile, their p_x and p_y orbitals form π bonding and π^* antibonding

states. After the bonding, an effective band gap reduction is realized due to the appearance of fully occupied impurity levels in the band gap of WO₃. It is worth noting that the π^* antibonding states are also contributed by the W 5d orbitals.

Since both of the band gap and the positions of the CBM and VBM are the key factors in determining the photocatalytic activity of a semiconductor [54], the band position alignment of the pure and doped h-WO₃ systems are summarized and the results are shown in Fig. 7. The pure h-WO₃, our reference system, has the CBM 0.3 eV lower than the H⁺/H₂ potential, and its VBM is more positive (about 1.9 eV) than O₂/H₂O potential [8]. The VBM of S, (Sn, S) and (Pb, S) has been lifted up a lot where the CBM also shifts upwards in some degree, which endows the h-WO₃ with the enhanced reducing ability. Among them, the codoping-caused band gap narrowing is larger than that caused by S-monodoping,

Figure 4 The calculated TDOS and PDOS of (a) pure h-WO₃, (b) S-monodoped, and (c) (Sn, S)- and (d) (Pb, S)-codoped h-WO₃. Only the O 2p and W 5d states of the nearest O and W atoms are presented downward for clarification in (Sn, S)- and (Pb, S)-codoped WO₃. The black dashed vertical lines represent the Fermi levels.

and the CBM in codoped systems lies higher than that in S-monodoped case. In addition, the intrinsic oxidizing capability of WO₃ is retained after codoping although the VBM shifts upwards. Therefore, it is suggested that these doped WO₃ materials, especially (Sn, S)-codoped WO₃, are promising candidate materials for water splitting.

To verify the enhanced solar energy conversion of the S-containing system, we calculated the optical absorption spectrum of pure, S-monodoped, and (Sn, S)-codoped h-WO₃ by using the following formula [55]:

$$\alpha(\omega) = \sqrt{2} \omega \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]^{1/2}, \quad (5)$$

where $\alpha(\omega)$ is the absorption coefficient, $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary parts of the frequency de-

pendent complex dielectric function $\varepsilon(\omega)$, respectively. Considering the tensor nature of the dielectric function, the $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ were averaged over three polarization vectors (x , y and z). As shown in Fig. 8, the absorption of pure h-WO₃ only covers high frequency of visible light and whole ultraviolet area. On the contrary, because of the effective band gap reduction, the S-monodoping and (Sn, S)-codoping h-WO₃ show significant red-shift of the absorption band edge, extending their abilities to make use of more visible light.

CONCLUSIONS

In summary, we used hybrid density functional calculations to comprehensively study the electronic structures

Figure 5 Part of charge density profile of the (a) pure h-WO₃, (b) S-monodoped, and (c) (Sn, S)- and (d) (Pb, S)-codoped h-WO₃ plotted at (001) plane.

Figure 7 Band alignment of undoped, S-monodoped and (Sn, S)- and (Pb, S)-codoped h-WO₃. The horizontal dashed lines and plus sign (+) represent the water redox potential levels and upshift of VBM or CBM, respectively.

of S-, Sn-, Pb-monodoped and (Sn, S)- and (Pb, S)-codoped h-WO₃. The formation energies reveal that the doped h-WO₃ is easier to be prepared under O-rich environment except the S-monodoped case. The binding energies indicate that the codoped systems are more stable than the monodoped systems. In the monodoped system, the S creates fully occupied states into the forbidden band gap of h-WO₃, reducing the band gap significantly, while the Sn- or Pb-monodoping brings unfavored p-type characteristic to the electronic structure of the host with little changed band gap and positions. However, these acceptor states vanish and the impurity energy levels between the VBM and the Fermi levels are kept in the (Sn, S) and (Pb, S) codoped h-WO₃, which are

Figure 6 Schematic plot of the bonding mechanism for the S atom and its neighboring O atom in (Sn, S)- and (Pb, S)-codoped h-WO₃.

Figure 8 The calculated optical absorption spectra for pure, S-monodoped and (Sn, S)-codoped h-WO₃.

ascribed to the S–O coupling in codoped systems. Moreover, the band-edge alignment shows that the (Sn, S) and (Pb, S) codoped systems retain the main advantages of WO₃ and also have narrowed band gap and enhanced ability for reduction. Among these systems, the (Sn, S)-codoped h-WO₃ has the narrowest band gap of 1.85 eV, and high reducing ability. The calculated optical properties also further reveal that the (Sn, S) could harvest the broader spectrum of the solar visible light. In addition, since monoclinic WO₃ (m-WO₃) tends to have less oxygen vacancies and is more stable and active than h-WO₃ [56], it is expected that this kind of codoping can endow the m-WO₃ with similar or even higher photocatalytic properties. Moreover, it is also necessary to in-

investigate the influence of the dopant concentration since it plays an important part in determining the photoelectric properties of semiconductors. Our theoretical calculations provide instructive insights for the pursuit of the new WO_3 -based materials for photocatalytic water splitting and further experimental work is expected to evaluate our theoretical predictions.

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Author contributions Chen JF proposed and guided the project. Yang C performed the first principle calculations and wrote the paper. Zeng X and Cheng D supervised the project and revised the paper. The final version of the manuscript was approved by all authors.

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Supplementary information Supporting data are available in the online version of the paper.

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金属受体辅助S–O耦合作用改善六方相三氧化钨光解水性能的研究

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摘要 本文采用杂化密度泛函理论计算研究了S、Sn、Pb单掺杂和(Sn, S)、(Pb, S)共掺杂六方相三氧化钨(h - WO_3)材料的电子结构及其在可见光范围内的光催化特性. 结果表明: (Sn, S)和(Pb, S)共掺杂体系可有效减小 h - WO_3 的带隙, 且能够避免由于Sn、Pb单掺杂形成 h - WO_3 价带中空穴的现象. 这主要是因为(Sn, S)和(Pb, S)共掺杂体系中, 金属受体(Sn、Pb)杂质的掺入会导致杂质S原子与邻近的O原子耦合, 形成S–O键, 该S–O键的反键轨道在 h - WO_3 的禁带中引入两条完全占据的杂质能级. 值得注意的是, (Sn, S)共掺杂可使 h - WO_3 的带隙减小至1.85 eV, 同时赋予其最高的还原能力. 此外, (Sn, S)共掺杂也提高了 h - WO_3 对可见光的吸收能力. 这些结果表明, (Sn, S)共掺杂 h - WO_3 是一种在太阳光分解水领域有潜在应用前景的材料.