

# Tungsten-doped MoS<sub>2</sub>-based nanostructure **for photocatalytic hydrogen evolution under visible light**

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### **Abstract**

In this work, we introduced a simple approach to boost the photocatalytic activity of  $MoS<sub>2</sub>$  by introducing transition metal (W) doping. The W-MoS<sub>2</sub> (10 mg) exhibited a substantial enhancement in photocatalytic activity for  $H<sub>2</sub>$  production, achieving an impressive rate of approximately 925 µmol  $g^{-1}$  after 6 h, which is 1.5-fold higher than bare MoS<sub>2</sub>. The highest H<sub>2</sub> production activity of 1740 µmol g<sup>-1</sup> after 6 h was obtained for 50 mg  $W-MoS<sub>2</sub>$  photocatalyst. The observed increase in activity can be ascribed to the formation of a Schottky barrier at the heterojunction interface, along with advantageous properties of improved active sites resulting from tungsten doping into  $MoS<sub>2</sub>$ . Furthermore, the enhanced activity of W-MoS<sub>2</sub> may be attributed to the promotion of catalytic kinetics by tungsten and molybdenum sites, exhibiting commendable activity for water dissociation and higher efficiency in  $H^+$  adsorption. These factors contribute signifcantly to the overall improved performance of the W-MoS<sub>2</sub> photocatalyst. Further, platinum (Pt) was also used as cocatalyst and enhanced photocatalytic activity of 2145 µmol  $g^{-1}$  after 6 h was observed for  $W-MoS<sub>2</sub>+5 wt%$  Pt.

**Keywords** Tungsten doped  $MoS_2 \cdot Photocatalytic system \cdot Hydrogen evolution$ 

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### **Introduction**

Currently, society is facing two pivotal challenges: the energy crisis and environmental pollution  $[1, 2]$  $[1, 2]$  $[1, 2]$  $[1, 2]$ . The predominant use of fossil fuels to fulfill the growing global energy demand not only contributes to environmental pollution but also poses the risk of irreversible anthropogenic climate change [[3,](#page-10-2) [4\]](#page-10-3). Over recent years, photocatalytic hydrogen  $(H<sub>2</sub>)$  production through the splitting of water has emerged as a viable and sustainable energy alternative to address future energy demand and manage environmental pollution [[5](#page-10-4)[–8\]](#page-10-5). Visible light-activated photocatalysts have attracted signifcant attention due to their capacity to harness the renewable and abundant energy inherent in solar radiation, presenting a clean and cost-effective solution. Consequently, the development of an efficient visible light-driven photocatalyst is deemed the "Holy Grail of material chemistry" representing a crucial element for the successful implementation of the photocatalytic process [[9\]](#page-10-6). The interaction of light with a semiconductor photocatalyst is the heart of photocatalysis [[9\]](#page-10-6). The photocatalysis process involves the generation of photo-induced charge carriers within the semiconductor photocatalyst in response to the absorption of suitable light, which then initiates the oxidation and reduction reactions [\[9](#page-10-6)]. The excited electrons in conduction from the valance band then react with  $H_2O$  or  $H^+$  species in the aqueous environment to generate the desired  $H<sub>2</sub>$  [[9\]](#page-10-6). Therefore, photocatalysis is based on three pivotal phases: light absorption, the generation and separation of charge carriers, and catalytic reactions [[5\]](#page-10-4). The equilibrium between the thermodynamics and kinetics of these three crucial reaction steps is widely recognized as the main factor determining the overall efficiency of a photocatalytic system  $[5, 9]$  $[5, 9]$  $[5, 9]$  $[5, 9]$ . Consequently, researchers have been making signifcant eforts to develop innovative photocatalysts that have better light absorption, effective separation of charge carriers, and efficient catalytic activity. From this perspective, metal chalcogenides have garnered signifcant attention, primarily due to their narrow band gap, rendering them efective photocatalysts for visible light activity [[10](#page-10-7)]. Their attractiveness is further heightened by their expansive surface area, controllable morphology, and tunable band gap [[11](#page-10-8)]. Furthermore, their optical and electric characteristics can be modifed by fne-tuning both size and morphology [[12\]](#page-10-9).

Within the realm of chalcogenides, two-dimensional (2D) molybdenum disulfide  $(MoS<sub>2</sub>)$  has emerged as a focal point for researchers in the field of material science. This is attributed to its remarkable features, including potent oxidizing activity, non-toxicity, high stability, a substantial surface area, and a notable abundance of catalytically active sites  $[13]$ . MoS<sub>2</sub> adopts a sandwiched structure with a hexagonal arrangement of Mo and S atoms (S–Mo–S), held together by van der Waals force. The exfoliation process of  $MoS<sub>2</sub>$  into a single or few layers of nanosheets shares similarities with graphene  $[13, 14]$  $[13, 14]$  $[13, 14]$  $[13, 14]$  $[13, 14]$ . MoS<sub>2</sub> possesses an indirect band gap of 1.29 eV, which can be readily converted into a direct band gap of 1.80 eV when transitioning from bulk material to thin layer  $[14]$ . This property allows  $MoS<sub>2</sub>$  to generate electron/hole pairs (e/h<sup>+</sup>) upon exposure to visible light, making it a robust candidate for visible-light-induced photocatalyst for  $H_2$ 

production through water splitting  $[14]$  $[14]$  $[14]$ . While MoS<sub>2</sub> is considered a strong candidate for visible-light-induced photocatalyst, it encounters a notable challenge. The limited ability to efectively separate and transfer photogenerated charge carriers to active sites is a common drawback [\[10\]](#page-10-7). This issue is characterized by a high rate of recombination efficiency of  $e/h^+$  pairs due to short carrier lifetimes [[15](#page-10-12)]. Additionally, the formation of Mo-S–O links during photocatalysis poses a constraint, restricting its broader application in the photocatalytic process [\[14\]](#page-10-11). To address these challenges, various strategies have been employed. These include morphological modifcations, metal doping, and coupled with other semiconductors [[15\]](#page-10-12). The introduction of metal doping, specifcally, plays a crucial role in shifting the absorption of  $MoS<sub>2</sub>$ , into the near-infrared range. [[11](#page-10-8), [15](#page-10-12)]. This process introduces defects that contribute to enhancing charge separation and interfacial charge transfer, along with a local electric feld through the formation of Schottky junctions [\[15\]](#page-10-12). Meat-doping collectively aims to overcome the limitations associated with MoS<sub>2</sub> in photocatalysis [\[10,](#page-10-7) [14](#page-10-11), [15\]](#page-10-12). The deposition of transition metals, particularly Cu, Ag, Pd, Au, and Pt has been explored as a method to create photocatalysts with enhanced visible light absorption [[11,](#page-10-8) [15](#page-10-12)]. Additionally, the introduction of metallic heteroatoms into the  $MoS<sub>2</sub>$  lattice has been shown to efectively activate the basal plane S atoms and introduce in-plane active sites for the hydrogen evolution reaction (HER) [[1\]](#page-10-0). Previous research has demonstrated that transition metals deposited on  $Mo<sub>2</sub>$  can serve as electron sinks, effectively capturing the photogenerated electron  $[15]$  $[15]$  $[15]$ . This mechanism accelerates the transfer and separation of  $e/h<sup>+</sup>$  pairs, showing the potential for improving the efficiency of the photocatalytic process. To date, various transition metal atoms, inducing Co  $[16]$ , Ni  $[17]$  and Ru  $[18]$  $[18]$  $[18]$  have been successfully doped into  $MoS<sub>2</sub>$ , demonstrating notably outstanding performance in the context of hydrogen evolution reaction. There has been a notable gap in prior research concerning the collaborative impact of defects within the  $MoS<sub>2</sub>$  lattice and the doping sites of tungsten atoms on the enhancement of  $H<sub>2</sub>$  generation. The introduction of W atoms induces lattice distortion in  $MoS<sub>2</sub>$ , as the atomic radius of W is larger than that of Mo [[19](#page-10-16)]. This distortion leads to the creation of additional defects, serving as active sites that contribute to a more effective  $H_2$  generation process [[19](#page-10-16)].

In this study, a simple and cost-efective one-step hydrothermal method was employed to synthesize the  $W@MoS<sub>2</sub>$  photocatalyst. The photocatalytic efficiency of  $H<sub>2</sub>$  generation was evaluated using various hole scavengers, revealing optimal performance in the presence of triethanolamine (TEOA). Remarkably, the  $W@MoS<sub>2</sub>$  photocatalyst demonstrated a substantial enhancement in photocatalytic activity for H<sub>2</sub> production, achieving an impressive rate of approximately 1740  $\mu$ mol  $g^{-1}$  after 6 h. The notable increase in activity can be attributed to the formation of a Schottky barrier at the heterojunction interface, coupled with advantageous properties arising from tungsten doping into  $MoS<sub>2</sub>$ . The synergistic activities of W doping and controlled  $MoS<sub>2</sub>$  surfaces effectively contribute to the separation of photo-generated charge carriers on the surface, enhancing electron transport to active regions for a more efficient photocatalytic process.

# **Experimental section**

## **Materials and chemicals**

We have purchased all the chemicals and reagents from Merck, Sigma and TCI and Fischer Scientifc and used as received. All chemicals and reagents were of analytical grade.

# Synthesis of W-MoS<sub>2</sub>

Hydrothermal is well-known promising method to synthesize the metal oxides and metal sulfdes with good reproducibility. In this work, hydrothermal method was used as synthetic technique for the synthesis of W-MoS<sub>2</sub>. 0.45 g of ammonium molybdate was completely dissolved in 20 mL of the deionized water (DI water). 5 wt% of the tungsten source (tungsten chloride) was added to this prepared solution and stirred for few min at room temperature. In fnal step, 0.85 g of thiourea was added to the above solution and stirred for 20 min at RT. This reaction solution has been further transferred to the PTEE lined stainless steel autoclave and kept under oven and temperature of the oven was maintained 200  $\degree$ C for 24 h. The W-MoS<sub>2</sub> sample was taken out from the autoclave by centrifuging the obtained solution and washed with ethanol and DI water. The W-MoS<sub>2</sub> was dried under vacuum oven at 60–70 °C for several h. The MoS<sub>2</sub> has been synthesized as discussed above except the addition of tungsten chloride.

### **Materials characterization**

The synthesized samples i.e.  $MoS<sub>2</sub>$  and W-MoS<sub>2</sub> were characterized by powder X-ray difraction (PXRD) method and PXRD patterns of the samples were analyzed on Empyrean Malvern Panalytical diffractometer with Cu K<sub>α</sub> radiation ( $\lambda$  = 1.54 Å). The micro-morphological characteristics of the samples were analyzed on Zeiss Supra-55 feld-emission electron microscope (FE-SEM) and energy dispersive X-ray spectroscopic (EDX) data has been obtained on Horiba EDX spectroscope. The photoluminescence (PL) spectrum of the samples were performed on Princeton Instruments Acton; SP2300. The X-ray photoelectron spectroscopic spectrum of the  $W-MoS<sub>2</sub>$  was obtained on Fischer-Scientific spectrometer.

### **Photocatalytic hydrogen evolution**

25 mL of the lactic acid was added to the 75 mL of the DI water in quartz tube reactor. The synthesized W-MoS<sub>2</sub> (10 mg) has been added to the above prepared solvent mixture. The quartz tube was tightly closed and nitrogen gas was purged in to the above reactor to remove the oxygen and other gases. The light source for photocatalytic studied was a xenon lamp (300 W; wavelength=420 nm). The diferent dose of the W-MoS<sub>2</sub> (10–70 mg) was used for optimization purposes. Platinum has been used as cocatalyst and diferent weight percentage of Pt (1, 2, 5 and 7%) was used. The diferent hole scavenger agents such as methanol, ethanol, triethanolamine (TEOA), glycerol was used.

### **Results and discussion**

#### **Phase purity and crystal structure analysis**

The phase purity and crystal structure of the synthesized pristine and  $W@M\omega S_2$ photocatalysts were characterized through X-ray difraction analysis, as illustrated in Fig. S1. The peaks observed at 14.1°, 34.6°, 41.3°, 51.02°, and 61.4° in the XRD spectra correspond to the hkl value of (002), (100), (103), (105) and (106). These peaks are consistently indexed to the hexagonal  $(2H-MoS<sub>2</sub>)$  crystal structure, in accordance with standard data (JCPDS fle No: 037–1492) [\[20](#page-10-17)]. It can be seen from fg s1 that there are no additional peaks associated with other phases. Due to minimal tungsten doping, no distinct peak corresponding to W is observed. However, a subtle shift towards lower angles in the characteristic peaks after tungsten doping suggests the successful incorporation of tungsten into  $MoS<sub>2</sub>$ .

#### **Surface morphology, EDX, and elemental mapping analysis**

SEM analysis was employed to investigate the surface morphology of the prepared photocatalysts. As depicted in Figs. [1a](#page-4-0) and b, the SEM images illustrate the distinct features of both pristine and  $W@MoS<sub>2</sub>$  photocatalysts. The pristine  $MOS<sub>2</sub>$  exhibits three-dimensional (3D) fower-like nanofakes, comprising multiple self-assembled thin nanosheets with remarkable uniformity (Fig. [1a](#page-4-0)). Similarly, the  $W@MoS<sub>2</sub>$  prepared with the same conditions exhibits a comparable 3D nanofower morphology, characterized by ultrathin flakes with tungsten deposited on the surface of  $MoS<sub>2</sub>$ (Fig. [1b](#page-4-0)).

EDX analysis and mapping were performed to access the deposition of tungsten on the  $MoS<sub>2</sub>$  photocatalyst. Figs, S2 and S3a-S3d present the EDX and mapping results, revealing the presence of Mo, S, and W. The outcomes from EDX and elemental mapping collectively affirm the successful deposition of tungsten on  $MoS<sub>2</sub>$ .



<span id="page-4-0"></span>**Fig. 1** SEM image of (a) the hydrothermally obtained (200 °C for 24 h) MoS<sub>2</sub> and (b) W-MoS<sub>2</sub>

# **XPS analysis**

X-ray photoelectron spectroscopy (XPS) analysis was conducted to explore the infuence of W ions in  $MoS<sub>2</sub>$ , elucidating the chemical composition, oxidation states, and bonding characterization of both pristine and  $W@MoS<sub>2</sub>$  photocatalysts. The highresolution XPS spectrum of W 4f (Fig. S4a) reveals two prominent peaks at 35.2 (4f<sub>7/2</sub>) and 37.4 eV (4f<sub>5/2</sub>), with two weaker peaks at 34.1 (4f<sub>7/2</sub>) and 36.4 eV (4f<sub>5/2</sub>), inductive of W ions existing in two different valance states within W-MoS<sub>2</sub> ( $W$ <sup>4+</sup> and  $W^{6+}$ ) [[21\]](#page-10-18). As depicted in Fig. S4b, the high-resolution XPS spectrum of Mo 3d displays three discernible peaks at 236.8, 233.2, and 229 eV, corresponding to Mo  $(IV)3d_{3/2}$ , Mo  $(IV)3d_{5/2}$  and Mo  $(IV)3d_{5/2}$  [[13\]](#page-10-10). The high-resolution XPS spectra of S 2p of W@MoS<sub>2</sub> exhibit two characteristic peaks at 161.8 and 163.1 eV, attributed to energies of S  $2p_{3/2}$  and S  $2p_{1/2}$ , respectively. These findings signify a -2 oxidation state in  $MoS<sub>2</sub>$ , as shown in Fig. S3c [[5,](#page-10-4) [8\]](#page-10-5).

### **Optical properties and bad gap analysis**

UV–vis Difuse Refectance Spectroscopy (UV-DRS) was employed to access the optical properties of both pristine and W-doped  $MoS<sub>2</sub>$ , providing insight into the light-harvesting capabilities of synthesized photocatalysts [[22\]](#page-10-19). In Fig. [2a](#page-5-0), the UV-DRS spectra of pristine and W-doped  $MoS<sub>2</sub>$  photocatalysts reveal that the visible light harvesting ability of W-doped  $MoS<sub>2</sub>$  surpasses that of the pristine  $MoS<sub>2</sub>$ . Band gap energies were determined using the formula  $(\alpha h\nu)^2 = A(h\nu-E_0)$  for direct transitions. Figure [2b](#page-5-0) illustrates the relationship between  $(αhυ)<sup>2</sup>$  and  $(hυ)$ , enabling the calculation of band energies. For pristine  $MoS<sub>2</sub>$ , the calculated band gap energy is 1.9 eV. In contrast, the band gap energy for W-doped  $MoS<sub>2</sub>$  is slightly lower at 1.8 eV. This observation suggests that the introduction of W has significantly enhanced the absorption properties of  $MoS<sub>2</sub>$ , signifying an improvement in the photo-catalyst's ability to harness light.



<span id="page-5-0"></span>**Fig. 2 a** UV–vis spectrum and **b** Tauc plots of hydrothermally obtained MoS<sub>2</sub> and W-MoS<sub>2</sub>

#### **Photoluminescence (PL) analysis**

Photoluminescence (PL) spectroscopy is a widely recognized and highly efective technique that has gained a lot of attention in the realm of photocatalysis for investigating the impact of doping/impurities [[23\]](#page-10-20). This tool is used for comprehending recombination rate, trapping phenomena, migration dynamics, and electron transfer efficiencies within semiconducting materials. The observed PL intensity corresponds to a heightened recombination rate of  $e/h^+$  pairs. In Fig. [3,](#page-6-0) the PL spectra of pristine and W-doped  $MoS<sub>2</sub>$  photocatalysts are depicted, revealing a noteworthy reduction in the PL intensity of MoS<sub>2</sub> after incorporation of W. This finding suggests that doping of W signifcantly impedes the recombination rate of photoinduced  $e/h^+$  pairs in W-doped MoS<sub>2</sub> photocatalyst. As a result, it is expected that the photocatalytic activity of W-doped  $MoS<sub>2</sub>$  will exceed that of pristine  $MoS<sub>2</sub>$  photocatalyst.

#### *Photocatalytic H2 generation activities*

<span id="page-6-0"></span>**Fig. 3** PL spectra of hydrothermally obtained MoS<sub>2</sub> and

 $W-MoS<sub>2</sub>$ 

The photocatalytic activity of both prepared pristine and W-doped  $MoS<sub>2</sub>$  was investigated through the splitting of water with lactic acid as a hole scavenger under visible light illumination (Fig. [4](#page-7-0)a). The  $H_2$  production for W-doped MoS<sub>2</sub> (10 mg catalyst) was found to be 925 µmol  $g^{-1}$ , which is higher than pristine MoS<sub>2</sub> (575 µmol  $g^{-1}$ ). These findings suggest that the introduction of W into  $MoS<sub>2</sub>$  accelerates the catalytic kinetics of the reaction, enhancing water dissociation activity and maintaining consistent hydrogen adsorption capability. Moreover, the doping of W into  $M_0S_2$ may create notable surface-active sites, leading to improved charge separation and transfer of photo-generated e<sup>−/h+</sup> pairs, thereby improving photocatalytic activity. The photocatalytic  $H_2$  production of W-doped MoS<sub>2</sub> was also evaluated in the presence of various hole scavengers under the same experimental conditions. Figure [4](#page-7-0)b presents the photocatalytic  $H_2$  production with different hole scavengers in the presence of W-doped MoS<sub>2</sub> (10 mg). Notably, the highest H<sub>2</sub> evolution (1255 µmol g<sup>-1</sup>) occurred in the presence of TEOA after 5 h, surpassing glycerol (705 µmol  $g^{-1}$ ),



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<span id="page-7-0"></span>**Fig. 4 a** H<sub>2</sub> evolution activity of MoS<sub>2</sub> (10 mg catalyst) and W-MoS<sub>2</sub> (10 mg catalyst) in lactic acid. **b** H<sub>2</sub> evolution activity of W-MoS<sub>2</sub> (10 mg catalyst) in different hole scavengers (lactic acid, glycerol, ethanol, methanol, and triethanolamine)

ethanol (605 µmol g<sup>-1</sup>), lactic acid (925 µmol g<sup>-1</sup>), and methanol (245 µmol g<sup>-1</sup>) and follows:  $TEOA >$  lactic acid  $>$  glycerol  $>$  ethanol  $>$  methanol (Fig. [4](#page-7-0)b). These results indicate the capability of the selected scavengers to trap the photo-generated holes from the valance band of the W-doped  $MoS<sub>2</sub>$  photocatalyst. This scavenging action prevents the recombination of holes with electrons, enabling the latter to actively contribute to  $H_2$ , production  $[24]$  $[24]$ . Additionally, the current doubling effect in diferent solvents may be attributed to the formation of unstable radicals, facilitating more efficient electron transfer from the hole scavenger to the conduction band of the photocatalyst [\[24](#page-10-21), [25](#page-10-22)].

To investigate the activity of W-doped  $MoS<sub>2</sub>$  photocatalysts, control studies were conducted, especially focusing on optimizing the catalyst loading. In this context, experiments were performed to determine the optimal loading of the catalyst. The enhancement in the photocatalytic activity showed a parallel trend with the increase in the doses of W-doped  $MoS<sub>2</sub>$  photocatalyst, reaching an optimum at 50 mg of photocatalyst, after which a decline was observed (Figs. S5a and S5b). It could be seen from Figs. S5a and S5 that production of  $H_2$  increases with the loading, possibly attributed to the availability of more surface-active sites  $[26]$  $[26]$ . The highest H<sub>2</sub> of 1740 µmol  $g^{-1}$  has been obtained for 50 mg catalyst (W-doped MoS<sub>2</sub>), as shown in Fig. S5a. The H<sub>2</sub> production rate of 290 µmol h<sup>-1</sup> g<sup>-1</sup> has been observed for 50 mg catalyst (W-doped  $MoS<sub>2</sub>$ ), as depicted in Fig. S5b. However, beyond the optimal loading of 50 mg, there is a reduction in the activity of W-doped  $MoS<sub>2</sub>$  for  $H<sub>2</sub>$  production. This decrease is attributed to the agglomeration of photocatalysts, leading to a reduction in available surface area, diminished light penetration, and a decrease in active sites, consequently resulting in a reduction in  $H_2$  production  $[27-29]$  $[27-29]$ .

The W-MoS<sub>2</sub> photo-catalyst (50 mg) demonstrated good catalytic activity for  $H_2$ generation but still need to be improved. The  $H_2$  production can be further improved by utilizing cocatalysts. Platinum is well-known cocatalyst for  $H<sub>2</sub>$  production under visible light. In this context, we have further analyzed the photocatalytic activity of  $W-MoS<sub>2</sub>$  photo-catalyst (50 mg) with different weight percentage (1, 2, 5, and 7%)

of the Pt in presence of TEOA hole scavenger. The obtained results have been summarized in Fig. S5a. It is observed that  $H_2$  production rate increases with increasing Pt percentage from 1 to 5% and highest H<sub>2</sub> amount of 2145 µmol  $g^{-1}$  was obtained for 5 wt% Pt (Fig. S5a). The reduced activity of H<sub>2</sub> production of 2084 µmol g<sup>-1</sup> has been observed for 7 wt% Pt. The highest H<sub>2</sub> production rate of 357.5 µmol.h<sup>-1</sup>.g<sup>-1</sup> was observed for 5 wt% Pt based photocatalytic systems (Fig. S5b).

In addition to achieving a high  $H<sub>2</sub>$  production, the long-term stability and reusability of photocatalysts are crucial considerations for their industrial application. The reusability and photostability of the W-doped  $MoS<sub>2</sub>$  were further investigated. Fig. S6a presents a slight deactivation in the photocatalyst's activity after four consecutive cycles, suggesting good stability over repeated use. The stability of the 5 wt% Pt was also checked and obtained results also demonstrated good stability for four consecutive cycles (Fig. S6b).

Finally, based on both experimental results and a comprehensive literature survey, we have established a probable reaction mechanism to elucidate the enhanced  $H<sub>2</sub>$  production observed in the W-doped MoS<sub>2</sub> photocatalyst (Fig. S6c).

In our study, TEOA serves as a hole scavenger, and visible light is employed to stimulate charge carriers for photocatalytic water-splitting experiments. A graphical representation of the charge transfer pathway for  $W-MoS<sub>2</sub>$  in the presence of Pt as co-catalysts under visible-light irradiation is shown in Fig. S4c. The positions of the conduction band (CB) and valence band (VB) of W-MoS2 were calculated using empirical Eqs. ([1\)](#page-8-0) and (2), informed by both experimental fndings and relevant literature. [\[30](#page-10-26)[–32](#page-10-27)]

$$
E_{CB} = \chi - E^0 - 0.5 E_{BG}
$$
 (1)

<span id="page-8-0"></span>
$$
E_{VB} = E_{CB} + E_{BG} \tag{2}
$$

Here  $E_{VB}$  and  $E_{CB}$  represent the VB and CB edges positions,  $\chi$  is the absolute electronegativity of the W-MoS<sub>2</sub> (5.32 eV).  $E^0$  is the free electron energy of the normal hydrogen electrode (NHE), which is 4.5 eV. Additionally,  $E_{BG}$  is represents the band gap energy of the W-MoS<sub>2</sub>, calculated from the UV-DRS measurements using Tauc plot with  $MoS<sub>2</sub>$ , s band gap estimated to be 1.8 eV. The corresponding values of E<sub>VB</sub> and E<sub>CB</sub> of W-MoS<sub>2</sub> are calculated to be – 0.08 eV and + 1.72 eV, respectively, with respect to NHE. Upon exposure to light, electrons are excited from the valance band (VB) to the conduction band (CB) of  $W\text{-MoS}_2$ , creating holes in the VB. These excited electrons are then efectively trapped by dopant (W), facilitating charge separation by mitigating the recombination rate. The Pt acted as cocatalyst and improved electron transportation. The trapped electrons will rapidly migrate to effectively reduce the captured oppositely charged  $H^+$  ions, a pivot step in the efficient production of  $H<sub>2</sub>$ . Simultaneously, the holes are scavenged by TEOA from VB of W-doped  $MoS<sub>2</sub>$  to oxide the sacrificial reagents (TEOA<sup>+</sup>). This dual process leads to an extension of the lifetime of photo-induced charge carriers, ultimately resulting in an improvement in photocatalytic  $H_2$  production.

The performance of the W-MoS<sub>2</sub> and W-MoS<sub>2</sub>+Pt (5 wt%) has been summarized in Table [1](#page-9-0) which is comparable with reported literature.

Photocatalysts	$H2$ evolution rate $(\mu$ mol. $h^{-1}$ . $g^{-1}$ )	Light source	Sacrificial agent References	
$W-MoS2$	290	$300 \text{ W}$ ; Xe lamp $(\lambda > 420 \text{ nm})$	<b>TEOA</b>	This study
$W-MoS_2 + Pt$ (5 wt%)	357.5	$300 \text{ W}$ ; Xe lamp $(\lambda > 420 \text{ nm})$	<b>TEOA</b>	This study
$ZnFe2O4/MoS2$	142.1	$300 \,\mathrm{W}$ ; Xe lamp $(\lambda > 420 \text{ nm})$	Methanol	33
Phosphorus doped MoS <sub>2</sub> 278.8		$300 \,\mathrm{W}$ ; Xe lamp $(\lambda > = 420$ nm)	$Na2SO3/Na2S$	34
$Zn_0$ 5 $Cd_0$ 5 $S$	388.2	$300 \text{ W}$ ; Xe lamp $(\lambda > = 420$ nm)		35
$g - C_3 N_4 / M_0 S_2$	84	$300 \text{ W}$ ; Xe lamp $(\lambda > 420 \text{ nm})$	<b>TEOA</b>	36
$g - C_3 N_4 / Ag/MoS_2$	208	300 W; Xe lamp $(\lambda > 420 \text{ nm})$	<b>TEOA</b>	37
$g - C_3 N_4 / M_0 S_2$	133	$300 \,\mathrm{W}$ ; Xe lamp $(\lambda > 420 \text{ nm})$	<b>TEOA</b>	38
$Bi_2O_3/MoS_2$	10	$300 \,\mathrm{W}$ ; Xe lamp $(\lambda > = 420$ nm)	Lactic acid	39

<span id="page-9-0"></span>**Table 1** Comparison of H<sub>2</sub> evolution rate of W-MoS<sub>2</sub> and W-MoS<sub>2</sub>+Pt (5 wt%) with published articles

### **Conclusions**

In summary, we successfully synthesized W-doped  $MoS<sub>2</sub>$  through a straightforward one-step hydrothermal method. Utilizing standard analytical techniques, we verifed the uniform incorporation of W without inducing any change or damage to the material. The introduction of tungsten not only enhances the absorption of visible light by widening the band gap but also facilitates improved charge separation and transfer, resulting in elevated catalytic activity. Moreover, W-doped  $MoS<sub>2</sub>$  exhibits superior stability compared to pristine  $MoS<sub>2</sub>$ , demonstrating remarkable photocatalytic  $H_2$  production. The W doping significantly enhances the  $H<sub>2</sub>$  evolution rates, achieving approximately 1.5 times the rates compared to pristine  $MoS<sub>2</sub>$ . The enhanced photocatalytic performance is attributed to extended light absorption, the creation of the Schottky barrier leading to more active sites, and suppression of charge recombination. Furthermore, the presence of a W dopant serves as an electron sink, ensuring ultrafast and efficient charge transportation for effective conversion of  $H^+$  to  $H_2$ . Additionally, the doping of W in  $MoS<sub>2</sub>$  is anticipated to improve the catalytic kinetics of the reaction, as evidenced by its robust water dissociation activity and constant  $H<sub>2</sub>$  adsorption capability. The Pt has been employed as cocatalyst which further enhanced the hydrogen production rate.

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**Data availability** Authors elect to not to share data.

#### **Declarations**

**Confict of interests** Authors declare no conficts of interests.

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