



Layered MoS₂ Grown on Anatase TiO₂ {001} Promoting Interfacial Electron Transfer to Enhance Photocatalytic Evolution of H₂ From H₂S

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The treatment of hazardous hydrogen sulfide (H₂S) via photocatalysis technology has been known as one of the most promising green technologies. Photocatalytic production of hydrogen (H₂) from H₂S by two-dimensional (2D) semiconductor materials has gathered great attention owing to its large surface area and high catalytic activity. In this work, layered MoS₂ has been successfully grown on TiO₂ {001} surface to fabricate the 2D MoS₂/TiO₂ {001} composites for H₂ evolution from H₂S, which can be confirmed by the X-ray diffraction (XRD) and transmission electron microscopy (TEM) tests. Band structures and UV-Vis spectra provide important evidences that MoS₂ loading can significantly narrow the band gap and broaden the light absorbance into the visible light region. Electron transfer is obviously visualized at the interface of MoS₂/TiO₂, resulting in the built-in potential from TiO₂ to MoS₂, which is determined by the density functional theory (DFT) calculations and X-ray photoelectron spectroscopy (XPS) test. Consequently, the photo-induced electrons and holes are accumulated at the sides of TiO₂ and MoS₂ under the illumination, respectively, which largely promote the interfacial electron transfer and prolong the lifetime of photo-generated electrons that participate in the photocatalytic reactions of H₂ evolution from H₂S. This efficient separation of photo-induced carriers can be further proved by photoluminescence (PL) spectra, photocurrent responses, and electrochemical impedance spectra. As a result, the photocatalytic activity of H₂ evolution is largely increased by 9.4 times compared to the pristine TiO₂. This study could offer a new and facile way to design highly efficient 2D photocatalysts for the application of H₂S treatment.

Keywords: photo-splitting of H₂S, H₂, MoS₂/TiO₂ {001}, electron transfer, DFT

INTRODUCTION

Hydrogen sulfide (H₂S), as a highly toxic and corrosive pollutant, has been massively discharged from the natural gas extraction and oil refineries, which causes a serious threat on the air environment and human health with a fatal concentration over 700 ppm in the air. Thus, H₂S treatment has become a long-standing issue that attracts great worldwide attention. Photocatalysis

technology, directly driven by the solar energy, has been considered to be an effective new-generation green technologies (Liu et al., 2012, 2018, 2019; Wang et al., 2012; Ren et al., 2020). More importantly, clean energy H₂ can be produced during the photo-splitting of H₂S, which can alleviate the pressing global energy crisis and the environmental problems from the perspective of renewable resource utilization (Dan et al., 2017, 2019a,b; Xiang et al., 2019). Recently, anatase TiO₂ nanosheet with exposed {001} facets has been proven to be a promising candidate for photocatalytic production of H₂ because of the high reactivity and non-toxic features (Altomare et al., 2018; Chen et al., 2018; Ge et al., 2019; Yu et al., 2019), and the photocatalytic mechanism of H₂ production from H₂S on anatase TiO₂ {001} was reported in our previous work (Cai et al., 2020). However, the wide band gap and high charge recombination enormously restrict its photocatalytic activity. Surface modification via noble metal loading such as Au and Ag is usually applied to design TiO₂-based photocatalysts to pursue highly efficient production of H₂ (Zhao et al., 2018; Wang et al., 2019; Sharma et al., 2020). The high cost and limited storage of noble metals are of serious concerns. Thus, it deserves to develop economy and efficient methods to modify TiO₂ to achieve a high conversion activity of H₂. Particularly, two-dimensional (2D) layered MoS₂, as a non-noble metal catalyst, has attracted great attention because of the ability to capture electrons with the unique layered sandwich structure (Sun et al., 2018; Li Y. et al., 2019). Furthermore, various researches have reported that the layered MoS₂ can act as an excellent cocatalyst for both photocatalytic and electrocatalytic evolution of H₂ owing to the abundantly exposed edges (Li et al., 2011; Kibsgaard et al., 2012; Chang et al., 2014). It was shown that the fabrication of an MoS₂/TiO₂ heterostructure can largely promote the H₂ production from H₂O due to the much lower reaction energy barriers along the hydrogen evolution reaction paths (Tang et al., 2017). Other researchers also found that the MoS₂ nanosheets grown on TiO₂ could produce more active edges, and the efficient separation of the photo-generated carries resulted in the excellent H₂ production from H₂O (Liu Q. et al., 2013; Zhang et al., 2015). However, the promising MoS₂/TiO₂ composite has been barely applied to H₂ evolution from H₂S as yet, and the enhanced photocatalytic mechanism of H₂ production deserves in-depth study.

In the present study, a facile two-step hydrothermal method has been adopted to prepare the layered MoS₂ grown on TiO₂ {001}. The morphology, component, optical properties, and interfacial electron transfer of the fabricated MoS₂/TiO₂ {001} are investigated in-depth by experimental tests such as transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and photoluminescence (PL) spectra as well as the density functional theory (DFT) calculations.

EXPERIMENTAL METHOD AND THEORETICAL CALCULATION

TiO₂ {001} Synthesis

TiO₂ synthesis adopts a traditional hydrothermal method with the shape control agent HF (Yuan et al., 2016; Yang et al., 2018), as has been successfully prepared in our previous work (Yu

et al., 2016). First, 3.75 ml of butyl titanate and 0.6 ml of HF is placed into a 15-ml of complete dried Teflon-lined stainless-steel autoclave. Then the autoclave is sealed and placed in an electric oven held at 200°C for 24 h. Then, 0.1 M NaOH solution is applied to neutralize the F⁻ by stirring washing precipitates for 2 h after autoclave cooling to room temperature. Next, the precipitates are separated by vacuum filtration, washed with ultrapure water and alcohol several times until pH 7. Finally, the precipitates are dried overnight at 60°C in a vacuum oven.

Preparation of MoS₂/TiO₂ {001} (MoS₂/TiO₂) Composites

A two-step hydrothermal method is conducted to prepare the MoS₂/TiO₂ composites. First, 200 mg of TiO₂ powder is placed into a 50-ml Teflon-lined stainless-steel autoclave containing 25 ml of ultrapure water. Then, 7.7 mg ammonium molybdate and 72.6 mg thiourea are added into the above autoclave. After stirring for 15 min, the autoclave is heated at 180°C for 24 h. The final powder is washed several times with ultrapure water and ethanol and dried at 60°C under a vacuum environment. Finally, the prepared composite is named as MoS₂/TiO₂-0.5. Other composites with 15.4, 30.8, and 46.2 mg of ammonium molybdate and 145.2, 290.4, and 435.6 mg of thiourea are ordered as MoS₂/TiO₂-1, MoS₂/TiO₂-2, and MoS₂/TiO₂-3.

Material Characterization

The powder structure and crystal phase of the samples are determined by X^{pert} powder X-ray diffraction (XRD) radiation operated at 40 kV/40 mA. UV-Vis spectrum is recorded at room temperature by Shimadzu UV-2600 spectrophotometer equipped with a double integrating sphere, and BaSO₄ is used as the reflectance standard. XPS (Thermo ESCALAB 250XI) measurement is conducted to investigate the surface chemical environment of samples referenced to the C 1s level at 284.8 eV. TEM (JEM 2100F) tests are carried out to investigate the microstructure of samples. Energy dispersive X-ray spectroscopy (EDS) is used to obtain an elemental mapping. The photoluminescence (PL) spectra are tested with a fluorescence spectrophotometer (excitation at 340 nm). The progress of photocatalytic activity measurements is referenced to our previous work (Cai et al., 2020).

Theoretical Calculations

2D MoS₂/TiO₂ configuration is built with relaxed rectangular $5 \times \sqrt{3}$ MoS₂ monolayers and a relaxed four-layer 3×1 anatase TiO₂ {001} surface. The crystal lattice match can be quantified by $\delta = |a_{001} - a_g|/a_{001}$ (Lin et al., 2017), where a_{001} is the lattice constant of the relaxed anatase TiO₂ {001} surface, and a_g is the lattice constant of the relaxed MoS₂ monolayer. The calculated δ for the lattice parameters a and b are 2.8 and 2.1% for the MoS₂/TiO₂, respectively, which are in a reasonable and acceptable range. The bottom Ti and O atoms of MoS₂/TiO₂ composites are fixed during the calculations, while other atoms are fully relaxed to simulate the interaction between TiO₂ surface and MoS₂ sheet. A vacuum space of 20 Å is applied to construct MoS₂/TiO₂ composites in order to avoid interactions between the periodic neighboring slabs. The

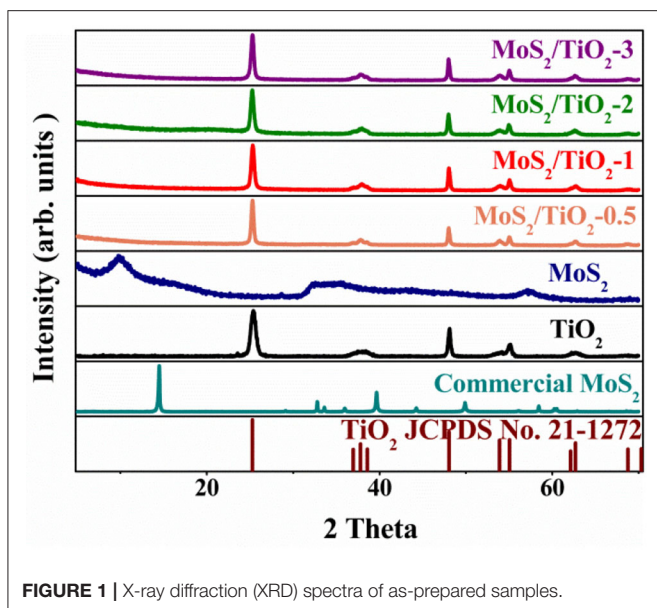


FIGURE 1 | X-ray diffraction (XRD) spectra of as-prepared samples.

Vienna *ab initio* simulation package (VASP) with the GGA-PBE exchange-correlation method is adopted in all calculation processes (Kresse and Furthmüller, 1996; Kresse and Joubert, 1999). The PAW method is used to describe the electron-ion interactions for Ti, O, Mo, and S atoms. Furthermore, to correct the strong interaction of Ti 3d and Mo 4d electron orbital, the coulombic interaction U and exchange energy J parameters are set according to the previous theoretical study (Cao et al., 2014). **Supplementary Figure 1** showed the MoS₂/TiO₂ structure after geometry optimization. To study the structural stability of the MoS₂/TiO₂ composites, the interface binding energy (E_b) is obtained in Equation (1):

$$E_b = E_{TM} - E_M - E_T \quad (1)$$

where E_{TM} , E_M , and E_T are the total energies of relaxed MoS₂/TiO₂ composites, relaxed MoS₂, and TiO₂ surface.

Interfacial electron transfer between TiO₂ and MoS₂ can be investigated by the following Equation (2):

$$\Delta\rho = \rho_{TM} - \rho_M - \rho_T \quad (2)$$

where ρ_{TM} , ρ_M , and ρ_T are the charge densities of the MoS₂/TiO₂ composites, MoS₂ structure, and TiO₂ surface, respectively. Furthermore, adsorption energy (E_{ad}) is used to describe the interaction between surface and adsorbed molecule, and the more negative E_{ad} value meant a more stable reaction progress, which can be calculated by the following Equation (3):

$$E_{ad} = E_{adsorbate/surface} - E_{adsorbate} - E_{surface} \quad (3)$$

$E_{adsorbate/surface}$ represented the energy of the surface with adsorbed molecule, $E_{adsorbate}$ is the energy of solitary adsorbed molecule, and $E_{surface}$ is the energy of surface.

Work function (Φ) is calculated by the energy difference between the electrostatic potential of the vacuum level (E_{vac}) and the Fermi energy (E_F) (Toroker et al., 2011).

$$\Phi = E_{vac} - E_F \quad (4)$$

RESULT AND DISCUSSION

Morphology Analysis

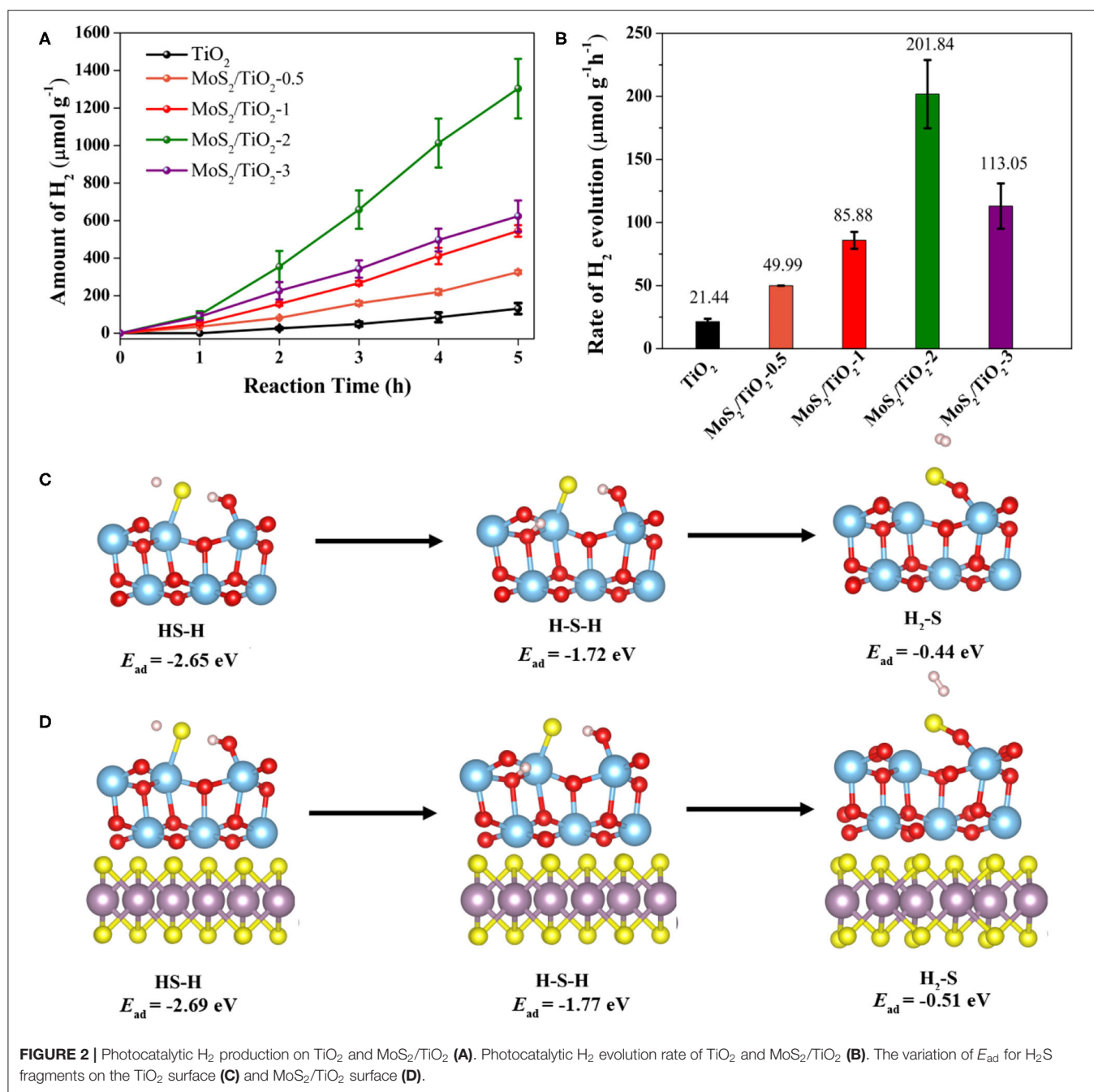
Crystallographic structures of prepared TiO₂, MoS₂, and MoS₂/TiO₂ composites are characterized by powder XRD (Figure 1). Prepared TiO₂ is indexed to the anatase phase (JCPDS No. 12-2172). It is worth noting that ammonium ions from ammonium molybdate hydrolysis can easily inlayer into MoS₂, which results in (002) peak obvious shifting to 9.65° (Liu et al., 2015; Zhang et al., 2017). Furthermore, no obvious MoS₂ peaks occur on MoS₂/TiO₂, which may be due to the small loading amount and its high dispersion on the surface of TiO₂ (Yuan et al., 2016).

Photocatalytic Activity of TiO₂ and MoS₂/TiO₂ Composites

Figure 2 shows the photocatalytic H₂ production from H₂S of pristine TiO₂ and MoS₂/TiO₂ composites. As shown in Figure 2A, TiO₂ reveals a poor photocatalytic hydrogen evolution activity. Remarkably, all the MoS₂/TiO₂ composites exhibit a higher photocatalytic performance than the pristine TiO₂. In particular, MoS₂/TiO₂-2 possesses the highest H₂ evolution rate compared to TiO₂, which is about 9.4 times higher than TiO₂ (Figure 2B). Meanwhile the H₂ evolution rate is close to the previous report (Zhang et al., 2020) using the different MoO₃/MoS₂ composites as the photocatalyst with the same reaction media (Supplementary Table 1). The stable growth trend of H₂ evolution indicated that H₂S decomposed on MoS₂/TiO₂ is steady in an H₂S environment. Meanwhile, the variation of E_{ad} also can reveal the decomposition stability of H₂S. The E_{ad} values for the decomposed fragments of H₂S including HS-H, H-S-H, and H₂-S on the TiO₂ surface are -2.65, -1.72, and -0.44 eV, while that on the MoS₂/TiO₂ surface are -2.69, -1.77, and -0.51 eV, respectively (Figures 2C,D). The more negative E_{ad} value suggests that the decomposition of H₂S fragments on the MoS₂/TiO₂ surface are more stable, which can be responsible for the high and stable photocatalytic activity. According to the activity results, the following characterizations including the crystal structure, morphology, surface chemical state, and optoelectronic properties are investigated for MoS₂/TiO₂-2 with the optimal activity as well as pristine TiO₂ for comparison.

Microstructure Analysis

To gain an intuitional understanding of the interface morphological structure between MoS₂ and TiO₂, the morphology of the TiO₂ and MoS₂/TiO₂-2 nanostructures is thoroughly investigated by the TEM test. Meanwhile, EDS mapping of MoS₂/TiO₂-2 in Supplementary Figure 2 revealed four kinds of elements including Ti, O, Mo, and S. This result suggested that Mo and S have loaded on TiO₂. The TEM image



of MoS₂/TiO₂-2 photocatalyst presented in **Figure 3c** shows that the composite exhibits a morphology similar to ultrathin pure TiO₂ nanosheet (**Figure 3a**). In addition, nanolayer materials are remarkably cladding with TiO₂ nanosheet. HRTEM is applied to explore the morphology structure of prepared photocatalysts. As displayed in **Figure 3b**, the HRTEM image recorded from a single nanosheet clearly shows that the sample is made up of anatase TiO₂ nanosheets with lattice fringes of 0.35 and 0.24 nm, which are attributed to the (101) plane and (001) plane of anatase TiO₂, respectively (Zhou et al., 2013; Yang et al., 2018). Compared to ultrathin pure TiO₂, the HRTEM image of

MoS₂/TiO₂-2 (**Figures 3c,d**) indicates the extra crystal lattice fringes of 0.63 nm, which are attributed to the (002) plane of the nanolayer MoS₂ (Liu et al., 2017).

Electronic Properties and Chemical Valence

According to the above analysis, MoS₂ loading has little effect on the morphological structure of TiO₂. To explore the reason for the high photocatalytic activity, the interfacial interaction between TiO₂ and MoS₂ are further studied. As shown in **Figure 4A**, the band gap (E_g) of TiO₂, MoS₂, and MoS₂/TiO₂

is 2.77, 1.60, and 1.54 eV, respectively. The introduction of MoS₂ largely reduced E_g by 1.23 eV compared to TiO₂, and the narrowed E_g can broaden the light absorption into the visible light region and make the electron excitation much easier. **Figure 4B** illustrates that the valence band and conduction band of MoS₂/TiO₂ are interlaced consisted by TiO₂ and MoS₂, resulting in the interfacial electron transfer from O 2p of TiO₂ to Mo 4d of MoS₂. The obvious peaks of O 2p and Mo 4d orbitals locate at the same energy level at the top of valence bands, and

this orbital hybridization features indicate the strong interface interaction between TiO₂ and MoS₂.

The chemical valence state of Ti 2p, O 1s, Mo 3d, and S 2p are analyzed by X-ray photoelectron spectroscopy (XPS), which can examine the changes in valence states. The chemical valence state of Ti 2p is shown in **Figure 5A**. The two peaks at 464.4 and 458.8 eV are ascribed to Ti 2p_{1/2} and 2p_{3/2} with +4 valence from TiO₂, which are in good agreement with the previous report (Yang, 2018). O 1s spectrum is given in **Figure 5B**; peak separation for TiO₂ shows two kinds of oxygen with binding energies of 529.7 and 530.2 eV, which are assigned to the O lattice of TiO₂ and oxygen coordination with Ti species (Gao et al., 2015; Li X. et al., 2019). In comparison, Ti 2p and O 1s of MoS₂/TiO₂-2 show an evident shift to higher energy, suggesting electron depletion or transfer at the composite interface, which is consistent with the DOS result. **Figure 5C** shows the Mo 3d valence state of MoS₂/TiO₂-2 composites. The typical peaks of 228.1 and 232.3 eV ensure the appearance Mo⁴⁺ of MoS₂ (Shuxian et al., 1986; Woo et al., 1992). Meanwhile, peaks at 231.1 and 234.9 eV are consistent with the Mo⁴⁺ of MoO₃ (Brox and Olefjord, 1988), which is due to the higher electronegativity of O (Bao et al., 2016). Furthermore, peaks at 161.2 and 162.5 eV demonstrate the existence of S²⁻ in **Figure 5D**, suggesting the formation of MoS₂ (Liu L. et al., 2013; Song et al., 2018). In addition, sulfur peak at 164.3 eV means some sulfur ions may be reduced in the reaction process (Zeng et al., 2019).

According to DOS analysis, it can be found that some electron transfer from TiO₂ to MoS₂ at the interface of MoS₂/TiO₂-2 composites, thus, causing a strong interfacial interaction. Furthermore, the electron transfer behavior at the interface is further explored by charge density difference maps as shown in **Figure 6**. A large amount of charge redistribution at MoS₂ side may be induced by the strong interaction between TiO₂ and MoS₂. Furthermore, there are 0.10 e electrons flowing from TiO₂ to MoS₂, which is larger than the previous report

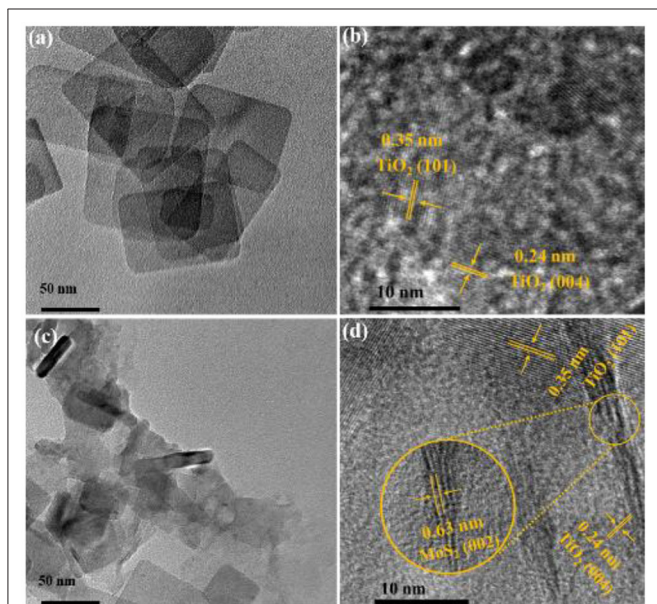


FIGURE 3 | Transmission electron microscopy (TEM) and HRTEM spectra of TiO₂ (a,b) and MoS₂/TiO₂-2 (c,d).

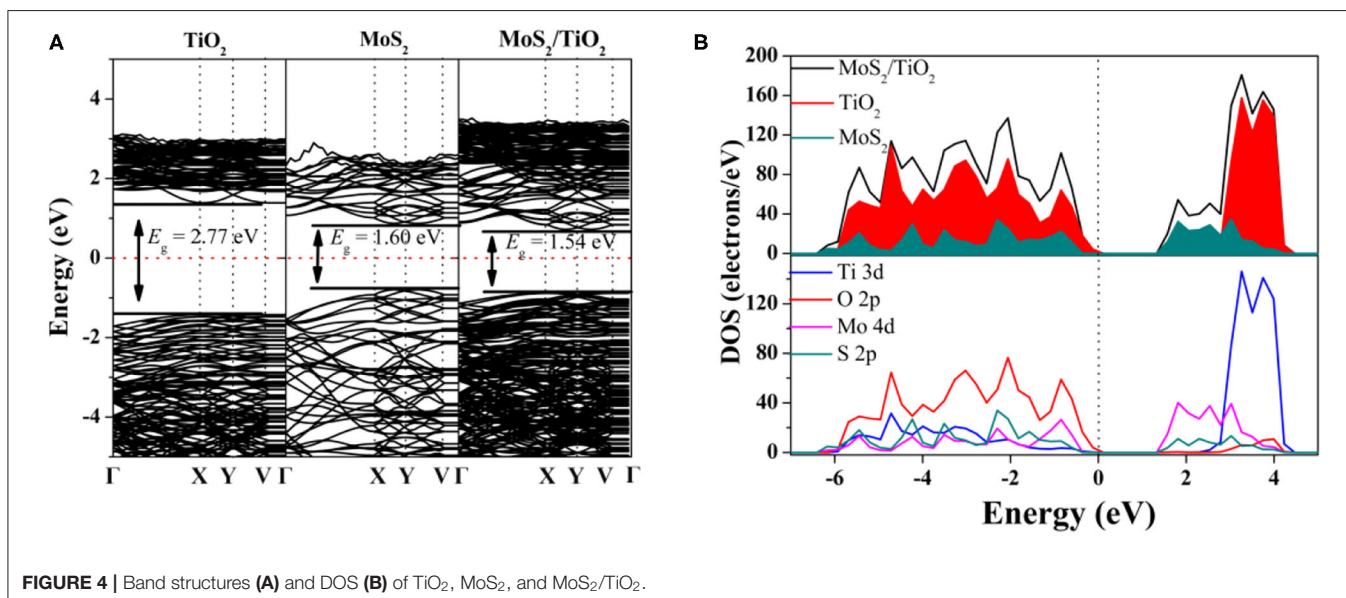
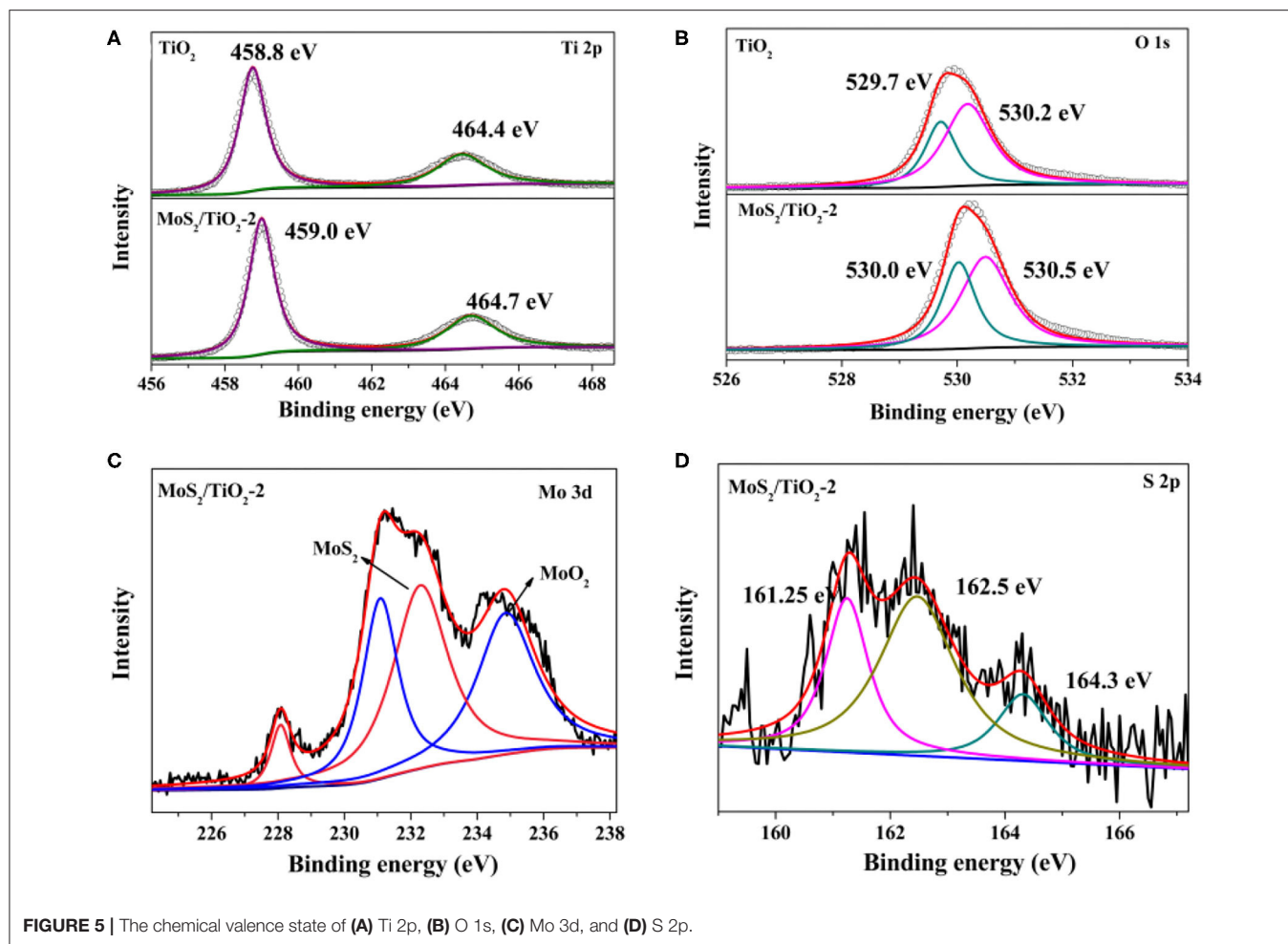


FIGURE 4 | Band structures (A) and DOS (B) of TiO₂, MoS₂, and MoS₂/TiO₂.



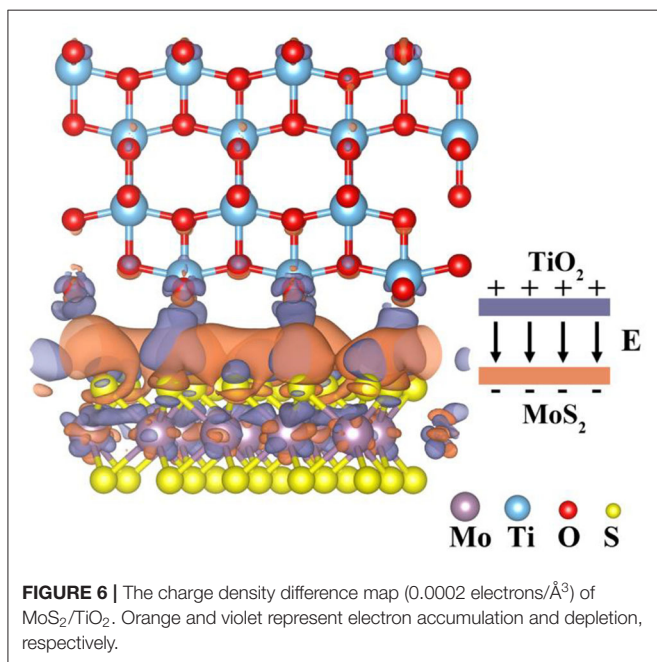
(electron transfer quantity is 0.035 e) (Cao et al., 2014). A built-in electric field with the direction from TiO₂ to MoS₂ will form at the interface after the redistribution of the electron reaches an equilibrium state. The same phenomenon also can be found in DOS and XPS, which suggests a strong interfacial interaction between TiO₂ and MoS₂. Furthermore, the binding energy (E_b) of MoS₂/TiO₂ is -0.07 eV. The more negative E_b value means the more stable constructed structure and the stronger interface bonding at the composite interface (Bhowmik et al., 2007; Rybolt et al., 2007). As a result, MoS₂/TiO₂ can provide more electrons to participate in the reaction under light irradiation, and the electron transfer quantity of H₂-S fragments on the surface (**Supplementary Figure 3**) also reveals the same result that the electron transfer quantity has increased by 0.01 e on the MoS₂/TiO₂ surface. At the same time, the interfacial photo-generated carrier transfer mechanism (**Figure 7**) illustrates the interfacial electron migration route under the illumination. According to the electrostatic potential in vacuum, the Φ value of TiO₂ and MoS₂/TiO₂ is 4.52 and 5.23 eV, respectively (**Supplementary Figure 4**). Meanwhile, due to the more negative conduction band of TiO₂ and the more positive valence band of MoS₂, electrons and holes are consumed at the TiO₂ conduction band and MoS₂ valence band to participate

in the redox reaction. Correspondingly, electrons and holes are accumulated at the MoS₂ conduction band and TiO₂ valence band, respectively. Because of the existence of the built-in electric field, the electrons at the TiO₂ conduction band cannot transfer to the MoS₂ conduction band, and holes at the MoS₂ valence band cannot transfer to the TiO₂ valence band. As a result, the translation direction of the electrons at the interface is from the MoS₂ conduction band to the TiO₂ valence band under light irradiation. Finally, the interfacial electron transfer mechanism prevents the electron from transferring from the conduction band of TiO₂ to the valence band of TiO₂ and results in a Z-scheme heterojunction. In other words, the interfacial electron transfer mechanism promotes the separation of electrons–holes and prolonged the lifetime of electrons, which facilitates the electrons accumulated at the conduction band of TiO₂ to take part in the photocatalytic reactions. This plays an important role in enhancing the H₂ production.

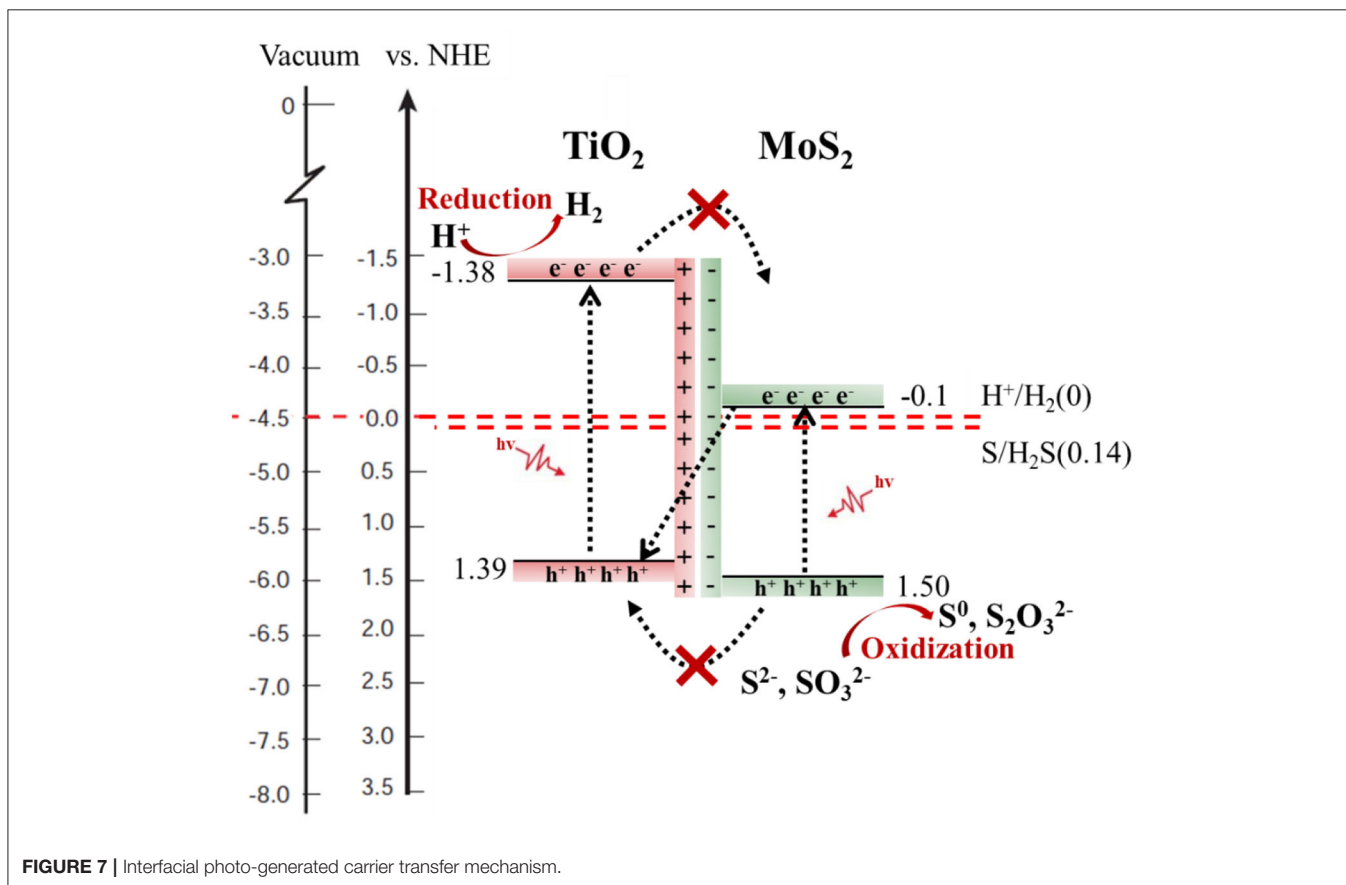
Optical and Photoelectric Properties

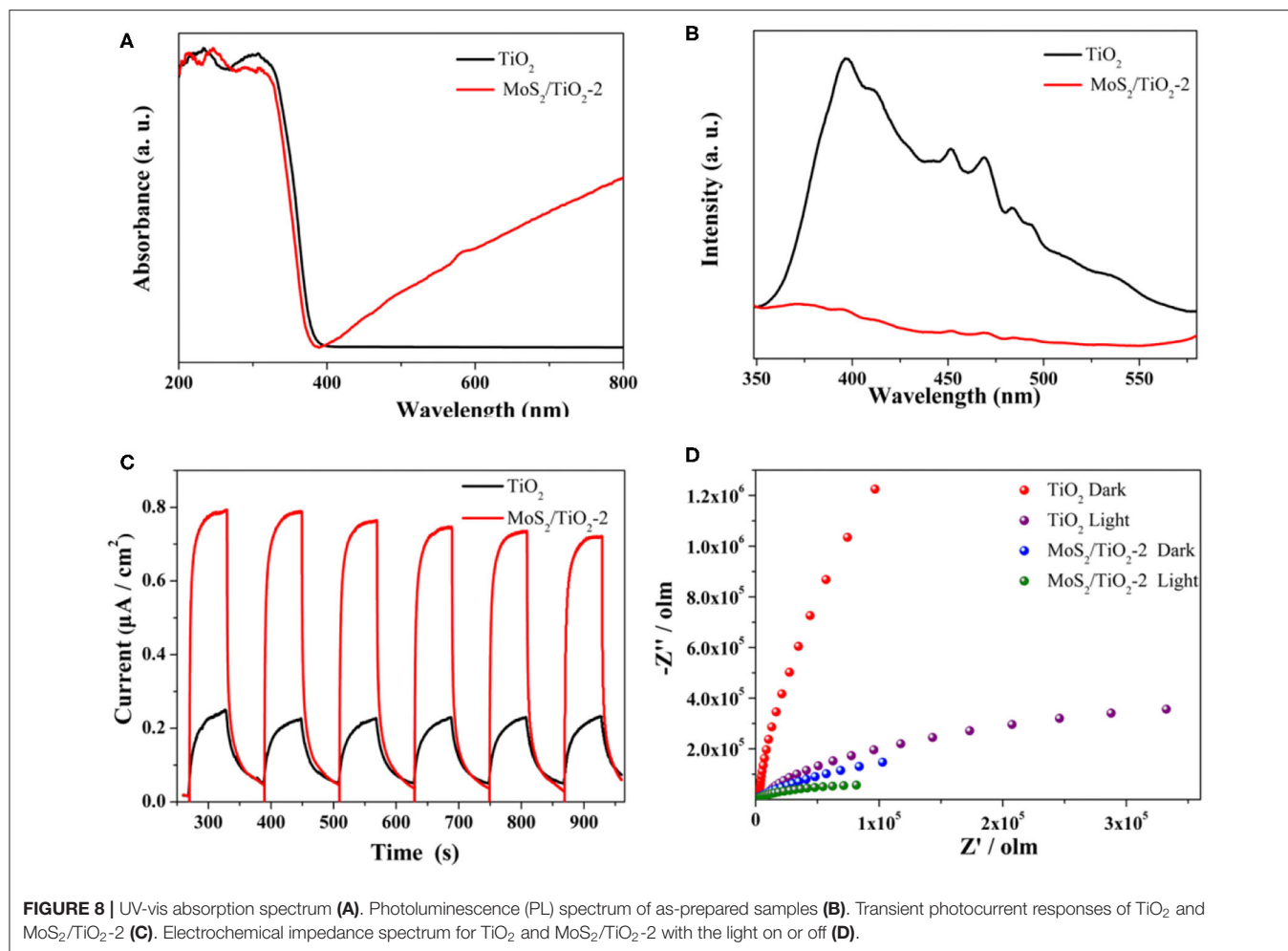
The UV-vis spectrum (**Figure 8A**) illustrates that the absorption edges of MoS₂/TiO₂ have obviously shifted to the visible light area compared with pure anatase TiO₂ nanosheets. This phenomenon suggests that the MoS₂/TiO₂ band gap is smaller

than TiO₂ and brings the light absorbance broadening to the visible-light area, which is consistent with the band structure result that MoS₂/TiO₂ with the narrower E_g should have a



better light response. Meanwhile, the broader light absorbance of MoS₂/TiO₂ can produce more photo-generated electrons and boost the photocatalytic reaction. The photoluminescence (PL) emission spectra (**Figure 8B**) are further used to investigate the behavior of photo-generated carriers. Remarkably, the lower emission peak intensity of MoS₂/TiO₂ proves a higher photo-generated carrier separation efficiency and provides more photo-generated electrons to participate in H₂ evolution reaction as possible, which has the same result with interfacial electron transfer mechanism. **Figure 8C** presents the periodic on/off photocurrent response of TiO₂ and MoS₂/TiO₂-2 under irradiation with a 300-W Xe lamp. TiO₂ generates a relatively low photocurrent density with a value of 0.25 μA cm⁻². The photocurrent density of MoS₂/TiO₂-2 significantly increases after MoS₂ loading on the surface of TiO₂ nanosheets. MoS₂/TiO₂-2 shows the highest photocurrent density of 0.79 μA cm⁻², which is about three times higher than that of TiO₂. This conclusively demonstrates that the separation efficiency of photo-generated charge carriers can be significantly enhanced by MoS₂ existing on MoS₂/TiO₂ under light irradiation, which may be caused by the interfacial electron transfer mechanism. Furthermore, MoS₂/TiO₂-2 displays the lowest electrochemical impedance under light irradiation, giving a fast carrier separation performance (**Figure 8D**). As a result, the growth of the layered MoS₂ on TiO₂ cannot only promote the photo-generated carrier separation but also stimulates photo-generated electron transfer.





According to the above analysis, the effects of the layered MoS₂ loading on TiO₂ {001} can be ascribed to the following several points. First, loading MoS₂ can enhance the photocatalytic H₂ evolution. MoS₂/TiO₂-2 shows about 9.4 times H₂ evolution rate than TiO₂. The stable growth trend of H₂ evolution indicated that H₂S decomposing on MoS₂/TiO₂ is steady in the H₂S environment. Second, the interfacial electron transfer mechanism can prolong the life-time photo-generated electrons and increased the possibility of electrons to take part in H₂ evolution reaction, which can result in high photocatalytic activity for MoS₂/TiO₂. The band structure shows that the narrower band gap of MoS₂/TiO₂ can broaden the light response into the visible light area. Meanwhile, the broader light response area means more photo-generated electron production, which is beneficial to the photocatalytic reaction. Furthermore, the lower PL intensity and higher photocurrent response of MoS₂/TiO₂ caused by the interfacial electron transfer mechanism reveals the high efficiency of photo-generated carrier separation, which can be the key factor for high H₂ evolution.

CONCLUSION

This work reports the fabrication of 2D MoS₂/TiO₂ via loading of the layered MoS₂ on TiO₂ {001} for the photocatalytic conversion of H₂ from H₂S. The introduction of MoS₂ greatly narrows the E_g and causes the admirable light absorbance in the visible light area, which is in good agreement with the UV-Vis tests. Moreover, obvious electron transfer is visualized at the interface of MoS₂/TiO₂, resulting in the built-in potential from TiO₂ to MoS₂, which is determined by DFT calculations and XPS test. Significantly, the interfacial electron transfer largely reduces the photo-generated carrier recombination and prolongs the lifetime of photo-generated electrons, which can be determined by the lower PL intensity and higher photocurrent response. Consequently, the photoactivity of H₂ evolution is significantly improved from 21.44 to 201.84 μmol g⁻¹ h⁻¹. This study can provide new insights into designing efficient 2D photocatalysts to meet high H₂ evolution from H₂S by photocatalysis technology.

DATA AVAILABILITY STATEMENT

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

AUTHOR CONTRIBUTIONS

QC wrote the original draft. FW conceptualized, wrote, reviewed, and edited the manuscript. JX made the formal analysis. MD and SY were responsible for visualization and investigation. YZ wrote, reviewed, edited, and supervised the study. All authors contributed to the article and approved the submitted version.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/fenvc.2020.591645/full#supplementary-material>

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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