



The Advanced Progress of MoS₂ and WS₂ for Multi-Catalytic Hydrogen Evolution Reaction Systems

Haoxuan Yu, Mengyang Zhang, Yuntao Cai, Yanling Zhuang and Longlu Wang *

College of Electronic and Optical Engineering & College of Flexible Electronics (Future Technology), Nanjing University of Posts & Telecommunications (NUPT), 9 Wenyuan Road, Nanjing 210023, China; 1221025308@njupt.edu.cn (H.Y.); b22020220@njupt.edu.cn (M.Z.); b21020428@njupt.edu.cn (Y.C.); zhuangyanling@njupt.edu.cn (Y.Z.)

* Correspondence: wanglonglu@njupt.edu.cn

Abstract: Two-dimensional transition-metal dichalcogenides (TMDs) are considered as the next generation of hydrogen evolution electrocatalysts due to their adjustable band gap, near-zero Gibbs free energy, and lower cost compared to noble metal catalysts. However, the electrochemical catalytic hydrogen evolution performance of TMDs with two-dimensional properties is limited by innate sparse catalytic active sites, poor electrical conductivity, and weak electrical contact with the substrate. It remains challenging for the intrinsic activity of TMDs for electrocatalytic and photocatalytic hydrogen evolution reactions (HERs) to compete with the noble metal platinum. In recent years, significant development of transition metal chalcogenides, especially MoS₂ and WS₂, as catalysts for electrocatalytic and photocatalytic HERs has proceeded drastically. It is indispensable to summarize the research progress in this area. This review summarizes recent research results of electrocatalysts and photocatalysts for hydrogen evolution reactions based on two-dimensional materials, mainly including MoS₂, WS₂, and their compounds. The challenges and future development directions of two-dimensional hydrogen evolution reaction electrocatalysts and photocatalysts are summarized and prospected as well.

Keywords: two-dimensional transition-metal dichalcogenides; structural engineering; co-catalyst; EY/TEOA system; hydrogen evolution reaction

1. Introduction

For a long time, researchers have been dedicated to exploiting renewable and clean energy sources to pursue sustainable development and avoid catastrophic climate change. Hydrogen has the highest energy density and can be converted to enormous energy without producing harmful by-products. The near-perfect production and recycling path from solar energy to hydrogen energy has always been a great prospect and expectation. It will not only address human daily needs but also enhance the energy security of all countries and reduce international conflicts caused by the fossil energy crisis, thereby promoting harmonious global development, enhancing sustainability and reducing pollution [1–3]. Ultrathin MoS₂ nanosheet is a typical material in transition metal sulfide systems attracting extensive attention in recent years, possessing superior structural and photocatalytic properties, and becoming a substitute for platinum in highly active hydrogen production reactions [4,5].

Among TMD materials, MoS₂ has attracted attention due to its excellent physical, chemical, and mechanical properties [6,7], and has been widely used in electrocatalytic hydrogen evolution (HER). Early studies concluded that the catalytic HER activity of MoS₂ was deficient. In 2005, Nørskov et al. calculated Δ GH at the Mo (1010) edge of MoS₂ by using DFT, and the results showed 0.08 eV Δ G_H value at 50% hydrogen coverage, approaching the optimal (0 eV). This value is comparable to platinum, theoretically indicating that MoS₂ has great application potential in HER catalysis [8]. Subsequently, Jaramillo et al. confirmed that the catalytic performance of MoS₂ layers is positively correlated with the length from



Citation: Yu, H.; Zhang, M.; Cai, Y.; Zhuang, Y.; Wang, L. The Advanced Progress of MoS₂ and WS₂ for Multi-Catalytic Hydrogen Evolution Reaction Systems. *Catalysts* **2023**, *13*, 1148. https://doi.org/10.3390/ catal13081148

Academic Editors: Chantal Guillard and Didier Robert

Received: 19 June 2023 Revised: 7 July 2023 Accepted: 21 July 2023 Published: 25 July 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). the active edge and that the inert substrate limits its potential HER performance [9]. To this end, researchers are committed to activating the inert MoS_2 substrate using strategies such as defect engineering, phase engineering [10–19], strain engineering [20–24], and doping engineering to improve HER catalytic performance [25–32].

In addition to being used in electrocatalytic hydrogen evolution, MoS₂ and WS₂ are also used as cocatalysts to promote photocatalysts. Due to the clean, low-cost and environment-friendly characteristics of solar energy, solar photocatalytic hydrogen production has become an effective strategy to solve the energy problem. It is challenging for a single semiconductor photocatalyst to meet all the requirements of photocatalysis due to its low utilization rate of light, easy recombination of electrons and holes, and lack of sufficient active sites [33–37]. Supported cocatalysts can promote charge separation and improve photocatalytic efficiency [38–40]. This review mainly introduces the role of MoS₂ and WS₂ as cocatalysts in photocatalytic hydrogen production, such as enhancing light absorption, promoting charge separation, increasing the active sites, etc. At the same time, the loading method of MoS₂ and WS₂ on semiconductors such as TiO₂, CdS, and ZnIn₂S₄ also are introduced [41–46].

Recent research results of electrocatalysts for hydrogen evolution reactions based on two-dimensional materials, mainly including MoS_2 and WS_2 , are recapitulated. Subsequently, the research progress of MoS_2 and WS_2 as cocatalysts to promote photocatalysts for HERs are collated and summarized. The challenges and future development tendencies of two-dimensional hydrogen evolution reaction electrocatalysts and photocatalysts are summarized and prospected.

2. Structural Engineering for Electrocatalytic Systems and the EY/TEOA System

One promising approach to improve electrocatalysis and photocatalysis is to increase the density of active sites, activate the intrinsic activity of the original inert site, and adjust the electronic structure of the catalyst by structural engineering. To achieve highly efficient and economical electrocatalysis and photocatalysis, research has been dedicated to fine-tuning the structure of catalysts by defect engineering, doping engineering, phase engineering, and strain engineering.

2.1. Defect Engineering

Defect engineering shows tremendous significance in modulating the electronic properties of catalysts, bringing about surprising optimizations of physical and chemical properties to improve the intrinsic bottleneck, thereby boosting HER performance. Presently, considerable efforts have been made to induce point defects (0-dimensional defects), line defects (1-dimensional defects), surface defects (2-dimensional defects), and body defects (3-dimensional defects) into the inert plane and bulk to increase intrinsic potential activity [47–54]. To achieve efficiency and a low-cost approach to forming defects that boost HER performance, methods including chemical and physical etch, ball milling, interlayer regulation, and finely tuned synthesis steps were applied [47–51].

A method using a ball mill to cut MoS_2 nanosheets vertically and horizontally to form S-vacancy point defects was presented by Luo et al. [55], resulting in a significant change in the surface tension of the original MoS_2 , followed by an ultrasonic irradiation process to shear the defective MoS_2 to form a single-layer MoS_2 nanomesh, as shown in Figure 1A. Approximately seven layers of the intact MoS_2 nanosheets pile up, forming a wavy edge, as shown in Figure 1B. As can be observed in Figure 1C,D, the ball-milled and ultrasonically treated multilayer MoS_2 nanosheets turn into many small pieces with holes. As shown in Figure 1E, the MoS_2 nanomesh exhibits the best catalytic activity with a low overpotential of 160 mV (V vs. RHE), compared to the overpotential of 230 mV for MoS_2 nanosheets and 208 mV for defective MoS_2 nanosheets at 10 mA cm⁻². It indicates that the defective atomic-sized pores in the basal planes of MoS_2 nanomesh can significantly increase the electrochemical HER activity. The corresponding Tafel slopes derived from the polarization curves are shown in Figure 1F. A lower Tafel slope means more efficient kinesis of H₂ evolution at a constant increase in overpotential. The MoS₂ nanomesh displays a Tafel slope of 46 mV·dec⁻¹, which is smaller than those of other catalysts except for the state-of-the-art Pt/C catalyst. Figure 1G shows that in visible light, using eosin Y (EY) as photosensitizer and triethanolamine (TEOA) as the sacrificial reagent, MoS₂ nanomesh exhibits the highest hydrogen production efficiency and considerable stability in the hydrogen evolution time process.



Figure 1. (A) Schematic illustration of the fabrication of monolayer MoS₂ nanomesh with defective atomic-sized pores in the basal plane for amplifying HER catalysis. TEM images of (**B**) pristine MoS₂ nanosheets and (**C**) MoS₂ nanomesh. (**D**) HRTEM image of the MoS₂ nanomesh. Polarization curves (**E**) and Tafel slope (**F**) of Pt, MoS₂ nanosheets, defective MoS₂ nanosheets, and MoS₂ nanomesh in 0.5 M H₂SO₄ at a scan rate of 5 mV. (**G**) H₂ evolution rates on the EY-sensitized photocatalysts in 80 mL of 15% (v/v) TEOA aqueous solution under visible light irradiation (\geq 420 nm). Catalysts: 20 mg and EY: 20 mg. Reproduced with permission from [56] © 2018 Elsevier B.V.

By adjusting and improving the nanostructure of the material, the performance of the material in catalysis can be significantly optimized [52–54]. Through theoretical and experimental calculations, it was found that the preparation of an unsaturated and coordinated 1D metal Mo chain on the structure of MoS₂ leads to a significant improvement of HER activity [57–59]. Figure 2A shows the formation of 1D Mo chains by removing S atoms from the MoS₂ atomic layer. Such 1D Mo chains act as HER catalytic active sites on the surface. In the wake of the first formed S-vacancy, the adjacent S atoms present an unstable state, and thus tend to fall out of the lattice to form more S-vacancies. As a result, a line defect can be induced with the accumulation of the S-vacancies. Also, the longer the line defect, the higher the stability. S atoms are disengaged from MoS₂ to form a quasi-one-dimensional Mo chain by inserting electrochemical sodium. The Mo chain can be observed in Figure 2B after phase correction and monochromatic processing of the Mo channel in the HRTEM



image of MoS_2 . It can be observed that a single Mo chain, two parallel Mo chains, and three parallel Mo chains emerged after S-vacancies formed.

Figure 2. (**A**) A schematic depicting 1D Mo chains created by successive removal of S atoms along a row. The Mo is shown in cyan, and S atoms are shown in yellow, respectively. (**B**) HRTEM images of 1D Mo channels in a MoS₂ monolayer. (**C**) Free energy diagram of 1D Mo atomic chains for the HER following the Volmer–Heyrovsky pathway. (**D**) Comparison of the polarization curves obtained after 100 cycles for Mo/MoS₂ and MoS₂ catalysts on reduced graphene oxide (RGO) relative to that of Pt nanoparticles on a glassy carbon electrode. (**E**) Tafel plots obtained from the polarization curves. (**F**) The effect of increasing number of rows of 1D Mo atomic chain on the band structure. Reproduced with permission from [60], © 2019 Elsevier Ltd.

The HER free energy diagram through Volmer–Heyrovsky pathways was constructed to unravel its reaction mechanism. To gain a deeper understanding of the Tafel mechanism and kinetics of H atom recombination and release of H_2 , the quasi-1D Mo atomic chains were used as a representative to locate the minimum energy paths and the transition states via the nudged elastic band (NEB) method. The corresponding initial, intermediate or transition, and final states are displayed in Figure 2C. As the NEB method predicted, in Figure 2D, the quasi-one-dimensional Mo chain shows a low overpotential of 45 mV to achieve a current density of 10 mA cm⁻², outperforming commercial Pt/C near the practically meaningful high-current region. The corresponding Tafel plots in Figure 2E showed that 1D unsaturated Mo chains in Mo/MoS₂ reduce the Tafel slope from 90 mV dec⁻¹ to $40 \text{ mV} \text{ dec}^{-1}$. The influence of Mo chains on HER can be inferred from the band structure of 2H-MoS₂ with an increasing number of quasi-1D Mo atomic chains in Figure 2F. In the presence of Mo chains, new bands appear in the gap near the Fermi level, responsible for hydrogen adsorption on unsaturated Mo atomic chains. The corresponding Kohn-Sham orbitals for the band directly below the Fermi level indicate that these states are localized around the Mo chains.

The structure of MoS_2 with the quasi-one-dimensional Mo chain is more conducive to the Tafel reaction's rapid progression, making the H adsorption and release process more accessible. As a result, the hydrogen production rate has been dramatically improved.

A method is introduced to improve the catalytic hydrogen evolution performance of MoS_2 nanosheets by using dislocation as a line defect [61]. The synthesis diagram of a high-density misaligned flexible MoS₂ nanosheet is shown in Figure 3A; with ammonium molybdate tetrahydrate and high-concentration thiourea as precursors, MoS₂ nanowire with high dislocation density can be prepared by hydrothermal reaction at low temperature for ten days. The formation mechanism of D-S-MoS₂ is shown in Figure 3B, where $[Mo_7O_{24}]^{2-}$ decomposed by $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ produces two different sulfides under the action of a high concentration source of sulfur. After ten days of hydrothermal reaction without splicing, the two kinds of sulfide clusters gradually form MoS₂ nanosheets with a weak crystalline structure, which show short-range order and relatively low crystallinity. It has a porous structure and abundant dislocations (in-plane and out-of-plane). The (100) crystal phase image with a large number of dislocations obtained by FFT processing is shown in Figure 3C due to the presence of plentiful dislocations (these dislocations are represented by "T"); in-plane strain appears at the corresponding position. In addition, dislocations in one crystal phase may lead to strain effects in another crystal phase, and dislocations are not included in the same region and are marked with white squares. The synthesized D-S-MoS₂ not only has an in-plane dislocation structure but also shows an out-of-plane dislocation structure. The formation mechanism of out-of-plane dislocations is shown in Figure 3D. The strain induced by the dislocations can cause the surface of MoS₂ nanosheets to be raised or sunken, resulting in interlayer lattice distortion and a more significant Burger vector. The sharp edge dislocations indicate that they are caused by atomic slippage.



Figure 3. (A) Schematic diagram of synthetic high-density dislocation intrinsic flexible MoS_2 nanosheets. (B) Schematic diagram of low temperature hydrothermal processing. (C) The (100) crystal phase images containing numerous dislocations obtained by IFFT processing, in which the dislocations are represented by "T". (D) Schematic illustration of edge dislocations. (E) Time courses of photocatalytic H₂ evolution over D-S-MoS₂. (F) Gibbs free energies of D-S-MoS₂ at different lattice compressibility. Reproduced with permission from [62], © Tsinghua University Press 2022.

The time course of photocatalytic hydrogen evolution on D-S-MoS₂ is shown in Figure 3E, and hydrogen production linearly increases with irradiation time. The results show that it has not only good hydrogen evolution performance but also has specific stability. The Gibbs free energy of D-S-MoS₂ at different lattice compressibility is shown in Figure 3F. Dislocations usually consist of different structural motifs, of which 5/7 nuclei are more accessible to obtain due to their lower formation energy. This article uses a 5/7 dislocation core as a model. From a thermodynamic point of view, the ideal Gibbs free energy value for hydrogen adsorption is 0 eV [63]. The strain effect caused by dislocations causes the lattice to stretch or contract. In contrast, the presence of high-density dislocations causes the lattice to compress by 0.1~4%, as can be seen from the diagram when the lattice compression ratio is 0.1%, the ΔG_H of D-S-MoS₂ is about 0.42 eV and can be optimized to -0.18 eV when the lattice compression ratio is 4%. The results show that the dislocation-strain interaction is a crucial factor in improving the activity of the catalyst.

The discovery of moiré superlattices (MSLs), caused by the twisting of van der Waals force-stacked two-dimensional layered materials, [64,65]. Research on the relationship between this unique structure and electrical properties has become a hot topic in electrocatalysis [66–68]. Zhao et al. proposed a new method to synthesize two-dimensional MSLs [69]. A one-step solvothermal method was used to prepare helical WS_2 nanobelts with local torsion deformation, and moiré stripes were formed due to the torsion angle between the layers. A single conical tube curled from one end of the WS_2 nanobelt can be observed through a scanning transmission electron microscope, as shown in Figure 4A. WS₂ nanobelts are easily twisted by force imbalances during synthesis [55,70], forming a nano-cone at one end. The relative stress distribution can be known through finite element analysis, as shown in Figure 4B. Strain generation may activate the substrate of the nanobelts [62,71], primarily by altering the electronic structure of the active catalytic site and facilitating mass transfer. The strain generated by the distortion weakens the van der Waals forces between the corresponding multilayer WS₂ nanobelts, causing a high probability of layer slip formation. As shown in Figure 4C, honeycomb moiré patterns due to layer slip are observed through HRTEM. Further analysis of the production of moiré patterns in Figure 4D shows a simulation diagram of the atomic structure of WS_2 MSLs. Twisting can be observed between nanofilm layers at an angle of 14° . Twisting and folding can easily cause S atoms to slide in the WS_2 MSLs to produce $1T'-WS_2$, for which the ΔG_H of 14° twisted bilayer 1T'-WS₂ NSs is calculated using density functional theory (DFT). The experimental data showed that the ΔG_{H} of 1T'-WS₂ MSLs' basal plane site (-0.24 eV) was close to zero, indicating high activity of the HER. As an HER catalyst, WS₂ MSLs have a unique structure due to strain and phase engineering, which promotes the generation of active sites on the basal plane and dramatically reduces the ΔG_H of sites. At the same time, it also allows other TMDs to be used for MSL engineering. This research on MSLs dramatically expands the research direction of topophysical engineering based on mechanical flexibility. It provides a broad idea for designing catalysts for more diversified structures in the future.



Figure 4. (**A**) STEM image of single screwed WS₂ nanobelt. Scale bar, 300 nm. (**B**) Finite-element calculations of strain in a nano-cone. The color bar shows the relative scale of the strain distribution. (**C**) High-resolution transmission electron microscopy (HRTEM) characterization of as-prepared WS₂ nano-cone. Scale bar, 2 nm. (**D**) Schematic diagram of the WS₂ MSLs. A twist angle of 14° is set in the bilayer regions and distinctive moiré patterns are clearly shown. Yellow and cyan balls represent S and W atoms. Reproduced with permission from [69], © The Author(s), 2021.

2.2. Doping Engineering

Heteroatom doping is considered to be an effective method to enhance catalytic activity. Ni atoms are doped to replace Mo, and the induced S_V formation and phase transition will transform into a stable distorted 1T' phase [72,73]. 1T'-MoS₂ S_V is a catalyst with a high electrical conductivity that integrates all multifunctional active sites, which is expected to enhance HER activity. Ni atomic doping can introduce S_V and trigger phase transition to control the electronic structure of MoS₂ [74–76], as shown in Figure 5A, including three aspects of defect engineering, phase transition, and electronic features. This method of doping low-valent metal atoms ensures more exposure to active sites at the edge of MoS₂ nanosheets. It is another important way to improve the catalytic performance of HERs.

The atomic structure of Ni-doped 1T'-MoS₂ is shown in Figure 5B. In general, a regular octahedron with Ni doping as the center and S as vertices is formed, in which S₀–S₅ represents the S atoms connected to the doping atoms. Compared with the undoped 1T'-MoS₂ structure, DFT can calculate the respective S_V formation energies. The analysis shows that the S_V formation energies around Ni atoms in Ni-doped 1T'-MoS₂ are much lower, indicating a high concentration of S_Vs is generated in the structure after doping with Ni atoms and that the conversion of semiconducting MoS₂ to metallic MoS₂ can be accelerated due to the existence of S_Vs. The primary process for the preparation of Ni-doped 1T'-MoS₂ is illustrated in Figure 5C. The preparation mainly used three crystalline substances, (NH₄)₆Mo₇O₂₄·4H₂O, NiSO₄·6H₂O, and CH₄N₂S. Firstly, a certain amount of (NH4)₆Mo₇O₂₄·4H₂O as a reducing agent and an excess amount of CH₄N₂S as a source of S are completely dissolved in a solution of NiSO₄·6H₂O as a source of Ni. Moreover, the two crystals are evenly distributed in the solution, and the desired solution can be obtained when thoroughly combined. Then the solution was dried in a vacuum oven at 200 °C for 24h, and the final drying was completed to obtain Ni-doped 1T'-MoS₂.

8 of 26



Figure 5. (**A**) Electronic structure regulation to improve MoS₂ catalytic performance, including defect engineering, phase transition, and electronic features. (**B**) Structural modules of Ni-doped 1T'-MoS₂. (**C**) Process schematic of the composite of synthesis of Ni-doped 1T'-MoS₂. (**D**) TEM image of the synthesis of Ni-doped 1T'-MoS₂, scale bar: 200 nm. (**E**) Simulated image of 1T' phase for MoS₂. (**F**) HAADF-STEM characterization of Ni-1T'-MoS₂. (**G**) Corresponding cumulative hydrogen yield. (**H**,**I**) Structural models for the DFT calculations of 1T'-MoS₂ SV and Ni-1T'-MoS₂ S_V. Reproduced with permission from [77], © Tsinghua University Press 2022.

Transmission electron microscopy (TEM) scanning was carried out in the experiment. The Ni-doped 1T'-MoS₂ has a sheet-like structure in the nanoscale, as illustrated in Figure 5D. In order to further understand the electronic structure of Ni-doped 1T'-MoS₂, a high-precision observation instrument is used in Figure 5E. Two parallel rows of bright spots (Mo atoms) were close to each other to form a one-dimensional zigzag Mo atom chain, which also illustrates the asymmetric feature of the distorted 1T' structure. The two red dashed lines b and c in the figure can also show in further experiments that there is a sizeable Mo-Mo gap in the structure of 1T'-MoS₂. As shown in Figure 5F, the experimental characterization of Ni-1T'-MoS₂ by high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) shows that the structural phase matches well with 1T'-MoS₂. The effect of Ni-doped 1T'-MoS₂ catalysts on the hydrogen production index under different catalyst dosages is shown in Figure 5G. The black curve in the figure represents the cumulative hydrogen yield under the influence of only solution eosin Y (EY) (without Ni-doped 1T'-MoS₂). It can be seen that the cumulative hydrogen yield is almost unchanged after 90 min, which indicates that water splitting has stopped after this. Furthermore, compared with other samples with linear function curves of Ni-doped 1T'-MoS2 catalysts, this also means that their hydrogen production almost maintains the original growth rate throughout the experimental time. It can also be seen from the figure that the optimal sample value is 10 mg, and the hydrogen evolution value is 91.625 μ mol·h⁻¹.

DFT calculations are further performed to explore the effect of Ni-1T'-MoS₂ S_V on the catalytic activity. The Gibbs free energy (ΔG_H) of hydrogen adsorption for 1T'-MoS₂ S_V and Ni-doped 1T'-MoS₂ S_V at three different active sites H₀-H₂ is shown in Figures 5H and 5I,

respectively. By comparing the two figures, it can be seen that the ΔG_H of the corresponding active sites decreases sharply after Ni doping. This clearly shows that Ni-doped 1T'-MoS₂ has an optimized ΔG_H and confirms that Ni-doping enhances the H adsorption capacity and thus activates the S_V. This synthetic method of doping low-valent metal atoms opens a new route to synthesize diverse active sites and enables the study of doping-dependent properties and applications.

The catalytic activity of MoS₂-based catalysts would be affected by the existing oxygen in the photocatalytic hydrogen evolution reaction [78–81]. The mechanism of the atomic oxygen doped in intrinsic flexible MoS₂ is further explored through theoretical analysis and experiments [82–85]. A Bader analysis based on the experimental data is performed at the start, as shown in Figure 6A. The oxygen substitution site has excellent electron affinity, which is beneficial for proton attraction and thus improves HER efficiency. In addition, strain engineering basis on O-doping is implemented. The synergistic effect of oxygen doping and strain engineering adjusts the catalytic activity of MoS₂-based catalysts. Figure 6B shows the influence of O-doping and strain engineering on the band gap of MoS₂. Single-layer MoS₂ is a direct band gap semiconductor, and after oxygen doping, it becomes an indirect band gap semiconductor. It can be found that oxygen doping and strain can reduce the band gap of MoS₂, and the strain could evidently change the band gap.

In order to explore the effect of oxygen doping on the catalytic hydrogen evolution activity of MoS_2 in the actual process, the change of hydrogen production rate per hour in the hydrogen evolution process is elaborately recorded through experiments, as shown in Figure 6C. The maximum hydrogen production rate of oxygen-doped MoS_2 can reach 1.6 mmol h⁻¹ g⁻¹. The catalytic activity of the catalyst tends to be stable with the increase in catalytic time, which confirms that oxygen doping improves the actual catalytic effect of MoS_2 .

The internal structure and properties of MoS_2 doped with oxygen were analyzed by XPS, as shown in Figure 6D. It can be found that the formation of Mo-O bonds and O with more electron contribution ability to reduce the electron density around the substitution site, resulting in the decrease in binding energy.

Figure 6E is the formation mechanism of $MoS_{2-x}O_x$ in actual photo-catalytic reactions. The sensitizer EY is irradiated by sunlight to produce excited state EY^{1*} , which can easily become triplet EY^{3*} under the action of ISC. Through the reduction quenching of TEOA, electrons and free radicals EY⁻ are produced, and electrons are easily transferred from EY⁻ to O₂ to produce highly active O₂⁻, which reacts with MoS₂ to produce MoS_{2-x}O_x. The top schematic of MoS_2 doped with O on the base surface is shown in Figure 6F. It is easy to observe the oxygen substitution site as the active site of the hydrogen evolution reaction. Figure 6G shows HAADF-STEM images of the lattice distortion of MoS₂ with O-doping. The formation of O-Mo bonds may be the reason for the strain in the internal structure [86–88]. ΔG_H is an important indicator for the hydrogen evolution reaction activity of the catalyst. In order to study the synergistic effect of oxygen doping and strain on HER performance, the DFT calculation method was used. The calculation results clearly show in Figure 6H that the ΔG_H of oxygen-doped strain MoS₂ is the lowest, only 0.3 eV. Overall, the synergistic effect of oxygen doping and strain on MoS₂ could greatly improve its catalytic hydrogen evolution rate, which provides new insights and new ideas for preparing efficient photocatalysts in the future.



Figure 6. (**A**) Bader charge analysis of the $Mo_{16}S_{31}O$ surface reveals the electron acceptor ability of O-doping site characterized by -1.22 eV negative charge compared to -0.85 eV on the S atoms. (**B**) Marked band structure changes for MoS_2 with O-doping as a function of strain. As the strain increases (0~10%), the bands move downward and upward close to the Fermi level, causing bandwidth to be reduced. (**C**) Photo-catalytic properties of MoS_2 with 1.2 mL O_2 amount treatment at each hour in the PHER process. The gas content was monitored every 15 min via an online gas chromatograph. (**D**) High-resolution XPS spectrums of O1s for original MoS_2 and S-O- MoS_2 . (**E**) The formation mechanism of $MoS_{2-x}O_x$ in actual photo-catalytic reactions. (**F**) Schematic of the top (upper panel) views of strained MoS_2 with O-doping on the basal plane, where O atom sites serve as the active sites for hydrogen evolution. (**G**) HAADF-STEM images of strained MoS_2 (S- MoS_2 , 6% strain), MoS_2 with O-doping (O- MoS_2 , 25 atoms% O), and strained MoS_2 with O-doping (S-O- MoS_2 , 6% strain, 25 atoms% O). Reproduced with permission from [82], © 2020 Elsevier B.V.

2.3. Phase Engineering

As shown in Figure 7A, vertical 1T-WS₂ nanosheets were prepared on a flat Ti substrate to improve HER catalytic efficiency. The nanosheets are cross-linked, facilitating the exposure of WS₂ edge sites and the rapid transport of protons throughout the catalyst, thus enhancing H₂ evolution. Figure 7B shows that the 1T-WS₂ nanosheets are very transparent, implying that the nanosheets are ultrathin [89]. One of the white luminescent lines represents its good conductivity, which is crucial for H₂ evolution. X-ray photoelectron spectroscopy (XPS) can confirm the chemical state and composition of 1T-WS₂ and distinguish the different metallic phases of WS₂. Figure 7C indicates that the WS₂ nanosheets are a mixture of 1T and 2H phases [90,91]. The Tafel plots in Figure 7D were measured in a 0.5 M H₂SO₄ solution using a typical three-electrode cell setup. The Tafel slope is an important parameter to describe the HER activity of the catalyst. The black linear part of the figure is the Tafel plot of a vertical 1T-WS₂ nanosheet at a small overpotential, which has a Tafel slope of 43 mV dec⁻¹. The Tafel slopes of Pt/C and WS₂ nanosheets are 52 mV dec⁻¹ and 30 mV dec⁻¹, respectively. As shown in Figure 7E, the polarization curves of the 1T-WS₂ nanosheets after 5000 cycles almost overlapped with those of the initial cycles. This demonstrates that the vertical 1T-WS₂ nanosheets are very stable in the acidic environment and remain intact during repeated cycles. Figure 7F examines the ability associated with the continuous catalytic generation of H₂ from vertical 1T-WS₂ nanosheets using time measurements (j–t). This quasi-electrolytic process was carried out in 0.5 M H₂SO₄ at a constant voltage of 160 mV. Apparently, the current density curve presents almost a horizontal line in the 30 h test at a continuous current density, which indicates the ultra-high stability of the vertical 1T-WS₂ nanosheets.



Figure 7. (**A**) Top-view SEM image of a vertical 1T-WS₂ nanosheet prepared on a Ti substrate. (**B**) HAADF-STEM images of 1T-WS₂ nanosheets. (**C**) XPS spectra of W 4f binding energy of vertical 1T-WS₂ nanosheets. (**D**) Tafel plots of Pt/C, WS₂ nanosheets, and vertical 1T-WS₂ nanosheets in 0.5 M H₂SO₄ at a scan rate of 5 mV/s. (**E**) Durability test showing negligible current loss even after 5000 CV cycles. (**F**) time dependence of the current density curve at an overpotential of 160 mV versus RHE for vertical 1T-WS₂ nanosheets. Reproduced with permission from [46], © The Author(s). 2018.

2.4. Strain Engineering

Strain is one of the most common means of changing the structure of a catalyst to improve its HER performance. The electronic, magnetic, and catalytic properties of materials can be enhanced by topology [92]. The aqueous solution electrochemical activation method can promote the topological transformation of WS₂ from the 2H phase to the 1T phase [93]. The phase transition caused by this strain greatly improves the catalytic performance of the spiral-shaped 1T phase of WS₂ [94]. Figure 8A shows the relationship between the number of potential cycles and the cathode current density. It can be seen that the early current density increases significantly with the increase in the number of cycles and the cathode even after 20,000 cycles. It can be seen that WS₂ nanosheets are the ideal catalysts for long-term electrochemical processes. To explore the main reason for the above outstanding performance of WS₂, in situ Raman spectroscopy of WS₂ nanosheets was implemented, as shown in Figure 8B. It can be seen that the peaks of the Raman activity pattern corresponding to the 1T phase become sharper and more prominent. By calculating the area under the peak, it is found that the proportion of 1T is 70% and the proportion of 2H is 30% due to

the strain that causes the WS_2 nanosheets to transition from the 2H phase to the 1T phase. The electrochemical activity of the WS_2 nanosheets is improved because the transition phase reduces the charge transfer resistance. As shown in Figure 8C, the morphology of the WS_2 nanosheets also evolves during the cycle. As the number of cycles increases, the WS_2 nanosheets gradually twist and rotate from the original straight to helical.



Figure 8. (A) Change in the HER cathodic current density (at -0.20 V vs. RHE) with the number of potential cycles. (B) In situ Raman spectroscopy as a function of CV cycles (phase transformation process). (C) Morphological evolution of WS₂ nanobelts with an increasing number of cycles. (D) Comparison of the influence of different sites and strains for the 1T- and 2H-WS₂ phases on the HER performance. ΔG_H diagram of the different H adsorption sites. The inset is a TEM image (with false color) of WS₂ nanohelices. Reproduced with permission from [83], © 2019 Elsevier B.V.

The driving force of the process from straight to helical is the strain in the WS_2 nanohelices caused by the H_2 bubbles. In Figure 8D, we introduced Gibbs free energy for comparison to understand further the effect of different strains and phases on the catalytic performance of WS_2 nanohelices. The closer the value of Gibbs free energy is to 0, the better the balance between the absorption and removal of hydrogen atoms at the active site is. The 1T phase WS_2 nanohelices at 3% strain have the best catalytic performance because the Gibbs free energy is closest to 0. For comparison, the Gibbs free energy of strain on WS_2 nanobelts in the 2H phase was also calculated, and it was found that the strain had no effect on its catalytic performance. From these data, we can draw a conclusion that the strain has caused the transformation of WS_2 nanosheets from the 2H phase to the 1T phase. The synergy of strain and phase transition leads to decreasing charge transfer resistance, increases in activity at each active site, and increases in the number of spiral-shaped active sites of WS_2 nanosheets. All these changes have a positive effect on the HER of WS_2 nanosheets.

Structural engineering offers a promising strategy to artificially regulate and control catalysts' inherent activity in electrocatalysis and photocatalysis, thus achieving catalytic targets for specific scenarios. Table 1 summarizes the performance of different catalyst modified by structural engineering in recent advances.

Catalyst	Engineering Strategy	Electrolyte	η@10 mA cm ⁻² (mV)	Tafel Slope (mV dec ⁻¹)	Ref.
Monolayer MoS ₂	Defect/strain	0.5 M H ₂ SO ₄	170	60	[95]
Monolayer MoS ₂	Defect	$0.5 \text{ M} \text{H}_2\text{SO}_4$	362.4	135	[96]
MoS ₂ thin-film	Defect	$0.5 \text{ M} \text{H}_2\text{SO}_4$	350 (η10.97)	105	[97]
MSOR _x	Doping	1 M KOH	63	43	[98]
MoS_2/NiS_2	Doping	1M KOH	62	50	[99]
Ru/np-MoS ₂	Strain/doping	1M KOH	30	31	[100]
F-MoS ₂	Strain	$0.5 \text{ M} \text{H}_2\text{SO}_4$	-	59	[101]
$1T'-MoS_2$	Phase	$0.5 \text{ M} \text{H}_2\text{SO}_4$	65	100	[102]
Ni-1T-MoS ₂	Phase/doping	1M KOH	199	103	[103]

Table 1. Comparison of HER performance on different catalysts modified by structural engineering.

3. As Co-Catalyst to Compound with Various Semiconductors

The number of exposed active edges of MoS₂ nanosheets is the key to the catalytic activity of MoS_2 for HER [104–106]. Making single- or few-layer MoS_2 nanosheets vertically stand on a substrate with maximally exposed edge sites is a reasonable way to enhance HER catalytic activity [107]. Porous TiO_2 nanofibers with abundant defects are appropriate for MoS₂ nanosheets to grow as nucleation centers. Single- or few-layer MoS₂ nanosheets standing vertically on porous TiO_2 nanofibers ($TiO_2@MoS_2$) were successfully prepared by a simple hydrothermal method, as illustrated in Figure 9A. Firstly, the Na₂MoO₄ and C_2H_5NS were dissolved in deionized water to form a transparent solution. Then TiO₂ nanofibers were immersed into the above solution and stirred to obtain a suspension. The extremely tough and porous TiO₂ nanofibers with vast numbers of defects can easily interact with metallic precursors and then act as nucleation for the growth of MoS_2 nanosheets. MoS_2 embryos grew from inside to outside of the pores of TiO_2 nanofibers. The dark field FESEM-STEM images of the TiO₂@MoS₂ heterostructures are shown in Figure 9B. It can be seen that the transparent, flexible, and curly MoS_2 sheets with a lateral size of about 100 nm vertically stand on the surface of TiO₂ nanofibers. The shapes of MoS₂ nanosheets that grow vertically in the dioxide pores of TiO₂ nanofibers are similar to tender shoots growing on the surface of bamboo. The photocatalytic HER mechanism of the TiO2@MoS2 heterostructure in Figure 9C indicated that the growing method ensures the 2D MoS₂ nanosheets are firmly attached to the TiO_2 nanofibers. The mechanism of $TiO_2@MoS_2$ heterostructure can not only strengthen the contacts between TiO₂ and MoS₂ but also accelerate electron transfer in the TiO₂@MoS₂ heterostructures. To further improve the HER catalytic activity of the $TiO_2@MoS_2$ heterostructure, the MoS_2 nanosheets in the $TiO_2@MoS_2$ heterostructure were exfoliated by Li intercalation. Then, the 1T phase of MoS_2 could be obtained, as shown in Figure 9D. Figure 9E indicated that the excited S vacancies and strain were the main reason for the stability of the 1T phase by reducing the surface energy.

As shown in Figure 9F, the amount of H_2 evolution of $TiO_2@MoS_2$ heterostructure after exfoliation showed a nonlinear increase compared with the $TiO_2@MoS_2$ before exfoliation. The phenomena indicate that the active sites of the $TiO_2@MoS_2$ after exfoliation had been optimized during the process of PHER. To uncover the self-optimization mechanism, an enlarged HRTEM image of MoS_2 in exfoliated $TiO_2@MoS_2$ after seven hours of HER was obtained as shown in Figure 9G. The distorted 1T' phase with the super-lattice structure from Mo atom clustering into zigzag chains can be clearly observed. Figure 9H shows eight S sites with different H adsorption coverages. The relationship between Gibbs free energy and strain of 1T' phase was conducted in Figure 9I. It is easy to find that 1T' phase is highly active for the HER and the strain has huge influences on the catalytic activity of the MoS_2 basal plane.



Figure 9. (A) Schematic illustration for the nucleation and growth of MoS₂ nanosheets. (B) Dark field FESEM-STEM image of $TiO_2@MoS_2$ heterostructures. (C) Schematic illustration of the energy band structure of the $TiO_2@MoS_2$ heterostructure and the proposed charge transfer mechanism. (D) HRTEM images of the MoS₂ in $TiO_2@MoS_2$ exfoliation by Li-ion intercalation. (E) Difference between the surface energies of the 1T and 1H phase MoS₂ phases as a function of strain with various concentrations of S vacancies. (F) H₂ accumulation over exfoliated $TiO_2@MoS_2$ (G) HRTEM image of the MoS₂ in the exfoliated $TiO_2@MoS_2$ after seven hours HER. (H) Supercells for H adsorption on the surface of single-layered 1T'-MoS₂ (I) Calculated Gibbs free energies for H adsorption under strain from 0% to 3.0% for 1T'-MoS₂. Reproduced with permission from [84], © 2017 Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

To achieve idealized photocatalytic H₂ evolution performance under visible light irradiation, the TiO₂ nanofibers of TiO₂@MoS₂ could be replaced by narrow bandgap semiconductor CdS nanowires to design a CdS/MoS₂ heterojunction. The CdS/MoS₂ heterojunction was produced by a simple hydrothermal reaction with or without adding glucose. With the help of glucose, the MoS₂ nanosheets grow nearly vertically on the CdS nanowires, which allows a high exposure of the active edge sites and improves the charge separation and transfer rates. In addition, glucose can make MoS₂ thinner and can act as a binder to help MoS₂ nanosheets grow along the longitudinal axis, simultaneously forming 1D/2D nearly vertical CdS/MoS₂ heterojunctions for efficient photocatalytic hydrogen evolution. Figure 10A shows the synthesis process of CdS/MoS₂(G) and CdS/MoS₂(W) heterojunctions by a two-step solvothermal approach. As shown in Figure 10B,C, the MoS₂ nanosheets are grown nearly perpendicularly to the CdS nanowires with an acid of glucose, while MoS₂ nanosheets are discrete connected to the CdS nanowires without glucose. The TEM image of CdS/MoS_2 heterojunctions in Figure 10D further indicates that MoS₂ nanosheets grow almost vertically on the outer surface of CdS nanowires. Figure 10E shows that the layer number of MoS₂ nanosheets is almost 1–2 layers, indicating a reduced tendency of MoS₂ nanosheet agglomeration.



Figure 10. (**A**) Schematic illustration of the growth processes of CdS/MoS₂ heterostructures under different conditions (a) without glucose and (b) with glucose. (**B**) CdS/MoS₂(W) composites prepared without adding glucose. (**C**) CdS/MoS₂(G) composites prepared with the addition of glucose. (**D**) TEM images show the nearly vertical structure of CdS/MoS₂(G) composites. (**E**) HRTEM images of CdS/MoS₂(G) composites. (**F**) UV–vis spectra of MoS₂, CdS, CdS/MoS₂(W) and CdS/MoS₂(G) samples. (**G**) Average photocatalytic H₂ evolution rate over CdS/MoS₂(G) loaded with different amounts of MoS₂. (**H**) comparison of H₂ evolution rate on CdS, CdS/MoS₂(G) 10 wt%, and CdS/MoS₂(W) 10 wt%, MoS₂ nanosheets, and the physical mixture of 10 wt% MoS₂ and 90 wt% CdS. (**I**) Cycling test of photocatalytic H₂ evolution for CdS/MoS₂(G) samples. Reproduced with permission from [43], © 2017 Elsevier B.V.

Figure 10F shows the UV diffuse reflectance spectra (DRS) of CdS, MoS_2 , CdS/ MoS_2 (W) and CdS/ MoS_2 (G) samples. The light-harvesting ability of the CdS/ MoS_2 (G) sample is higher than that of the CdS/ MoS_2 (W) sample in both the UV and visible regions, which indicates that the MoS_2 nanosheets have better adhesion on the CdS nanowires and the open near-vertical structure of the CdS/ MoS_2 (G) sample has almost no effect on the light

absorption of the CdS core. Figure 10G shows the photocatalytic hydrogen production activity of CdS/MoS₂(G) catalysts with different MoS₂ loadings under visible light irradiation. With the increasing MoS_2 content in the heterojunction, the H₂ evolution rate of $CdS/MoS_2(G)$ increases. Even if the loading of MoS_2 on the $CdS/MoS_2(G)$ heterojunction is 1 wt%, the hydrogen production rate is higher than that of pure CdS. The hydrogen production performance achieves the best maximum value of 9.73 mmol h^{-1} g⁻¹ when the MoS_2 loading contents reaches 10 wt%., It is 36.04 times higher than that of pure CdS nanowires. However, the degradation of photocatalytic performance appeared when the MoS₂ content exceeded 10 wt%, the decline being due to the excessive MoS₂ hindering the absorption of visible light by CdS. In addition, the high overlap of MoS₂ also reduces the exposure of active sites, thus weakening photocatalytic H_2 evolution. Figure 10H shows that the H_2 evolution rate of CdS/MoS₂(G) is the highest and much higher than that of $CdS/MoS_2(W)$. This indicates that the almost vertical MoS_2 nanosheets on $CdS/MoS_2(G)$ maximally expose the HER active edge, thus enhancing H_2 evolution. In contrast, the MoS₂ nanosheets on $CdS/MoS_2(W)$ with random orientation and severe aggregation inhibit H₂ evolution. In addition, the physical mixture of CdS nanowires and MoS₂ nanosheets showed poor HER activity, indicating that the close contact between MoS_2 and CdS is an important factor for H_2 evolution. The CdS/MoS₂(G) catalyst exhibits the best hydrogen production rate due to the near-vertical nanostructure and the tight heterogeneous interface. Figure 10I show that the $CdS/MoS_2(G)$ heterojunction was tested for five reaction cycles under visible light irradiation. The test data indicate that the introduction of MoS_2 has the function of inhibiting the photocorrosion of CdS, which leads to the good stability of $CdS/MoS_2(G)$. The nearly vertical and open structure can provide an optimal electron transport pathway and a high density of active sites; thus, the electron-hole pair separation and photocatalytic performance are improved.

To further enhance the photocatalytic hydrogen production activity of $TiO_2@MoS_2$ heterostructure, zero-dimensional CdS nanocrystals acting as the light-harvesting centers could be loaded onto the MoS₂ nanosheets in $TiO_2@MoS_2$ heterostructure to broaden the light absorption range of the catalyst. The fabrication process of the $TiO_2@MoS_2@CdS$ heterostructure with a "cauline-leaf" structure is shown in Figure 11A. This delicate structural design helps to increase the specific surface area and enhance light capture. The TEM image of $TiO_2@MoS_2@CdS$ is shown in Figure 11B. The MoS₂ nanosheets grow vertically on TiO_2 nanofibers, and the CdS nanoparticles are uniformly distributed on the surface of the MoS₂ nanosheets. The presence of a single or few layers of MoS₂ nanosheets in Figure 11C indicates that the MoS₂ nanosheet is ultrathin. The good crystallinity of MoS₂ and CdS could be confirmed by clear lattice stripes in Figure 11D. The apparent lattice distortion at the interface can indicate that the perfect heterostructure is formed between MoS₂ and CdS.

The photocatalytic hydrogen production activity of TiO₂@MoS₂@CdS with different CdS content under simulated sunlight (320–780 nm) or visible light (>420 nm) irradiation is shown in Figure 11E. When the content of CdS reached 60 wt%, the highest H₂ yield was 12.3 or 6.2 mmol h⁻¹ g⁻¹. In the simulated sunlight irradiation, the photocatalytic HER mechanism of TiO₂@MoS₂@CdS is shown in Figure 11F. The multistage biomimetic cauline-leaf structure facilitates light capture and absorption by photon scattering and multiple absorption effects. The gradient of energy levels between different semiconductors promotes the transfer of photogenerated carriers. The photogenerated electrons are eventually transferred to the enriched edge-exposed MoS₂ to produce hydrogen. This delicate structure design is crucial for the development of photocatalysis. This perfect "cauline-leaf" design is essential for developing photocatalytic materials.



Figure 11. (**A**) Schematic illustration of the processing steps to prepare $TiO_2@MoS_2@CdS$ "caulineleaf"-like structure. (**B**) TEM image, (**C**) HRTEM image with (**d**) 0.61 nm lattice spacing, and (**D**) HRTEM image of $TiO_2@MoS_2@CdS$ with (f) lattice distortion. (**E**) The photocatalytic hydrogen production activities of $TiO_2@MoS_2@CdS$ (50, 60, and 70 wt%) CdS and CdS@MoS_2 with the optimum amount of 95 wt% CdS under simulated solar light (320–780) nm or visible light (>420 nm) irradiation at zero potential. The reaction was conducted with 20 mg of photocatalysts in an 80 mL mixed aqueous solution (pH 13.2, 0.35 M Na₂S, 0.25 M Na₂SO₃). $TiO_2@CdS$, $TiO_2@MoS_2$, CdS, MoS_2 nanosheets and the physical mixture of 40 wt% $TiO_2@MoS_2$ and 60 wt% CdS. (**F**) Illustration of the HER mechanism over $TiO_2@MoS_2@CdS$ under simulated solar light irradiation. Reproduced with permission from [85], © 2016 Elsevier B.V.

The key to photocatalytic efficiency for hydrogen evolution reactions lies in the development and utilization of catalytic materials [108–111]. Among many semiconductor photocatalysts, ZnIn₂S₄ has attracted the attention of researchers due to its stable chemical properties, narrowband gap, and excellent photoelectric properties [112–114]. However, ZnIn₂S₄ has a high recombination rate of photogenerated carriers in the hydrogen evolution reaction, which could be solved by loading MoS₂ as cocatalysts [115,116]. The main active sites of MoS₂ are located at the edge, while this sandwich-layered structure formed by van der Waals force leads to its very inert basal plane. Ni atoms doped in MoS₂ would activate its inert basal plane. Firstly, ZnIn₂S₄ and Ni-Mo-S were synthesized by a simple solvothermal and hydrothermal method, and the preparation process is shown in Figure 12A. The



prepared ZnIn₂S₄ and Ni-Mo-S powders were uniformly mixed by grinding in a specific proportion in a mortar. Finally, ZnIn₂S₄/Ni-Mo-S composite materials were formed.

Figure 12. (**A**) Schematic illustration of the synthesis of Ni-doped $MoS_2/ZnIn_2S_4$ composite. (**B**) Diagram of the carrier migration process of Ni-Mo-S in EY/TEOA aqueous solution (pH 7) under visible light irradiation. (**C**) Schematic of the charge carrier migration process of $ZnIn_2S_4/Ni-Mo-S$ composite materials in Na_2S/Na_2SO_3 aqueous solution (pH 13.2) under visible light irradiation. (**D**) Schematic of the charge carrier migration process of $ZnIn_2S_4/Ni-Mo-S$ composite materials in lactic acid aqueous solution (pH 2.5) under visible light irradiation. (**E**) Comparison of photocatalytic H₂ evolution activities over EY, MoS_2/EY , Ni-Mo-S/EY (Ni:Mo = 1:2), and Ni-Mo-S/EY (Ni:Mo = 1:1) in EY/TEOA aqueous solution (pH 7). (**F**) Comparison of photocatalytic H₂ evolution activities over $ZnIn_2S_4/NoS_2/ZnIn_2S_4/Ni-Mo-S$ (Ni:Mo = 1:2), and $ZnIn_2S_4/Ni-Mo-S$ (Ni:Mo = 1:1) in Na_2S/Na_2SO_3 aqueous solution (pH 13.2). (**G**) Comparison of photocatalytic H₂ evolution activities over $ZnIn_2S_4$, $MoS_2/ZnIn_2S_4$, $ZnIn_2S_4/Ni-Mo-S$ (Ni:Mo = 1:2), and $ZnIn_2S_4/Ni-Mo-S$ (Ni:Mo = 1:1) in lactic acid aqueous solution (pH 2.5). Reproduced with permission from [42], © 2021 Published by Elsevier B.V. on behalf of Chinese Chemical Society and Institute of Materia Medica, Chinese Academy of Medical Sciences.

In order to meet the needs of photocatalytic hydrogen production under different media environments, three hydrogen evolution experimental systems were designed under neutral, alkaline and acidic conditions. To evaluate the HER catalytic activity of Ni-Mo-S nanosheets in the neutral medium environment, the prepared Ni-Mo-S nanosheets were used as the photocatalyst, EY was used as the sensitizer, and TEOA was used as the hole scavenger. Figure 12B shows the photocatalytic hydrogen evolution process of EY/Ni-Mo-S in TEOA aqueous solution under visible light irradiation. As a sensitizer with excellent photocatalytic hydrogen production performance, EY can absorb visible light from the ground state to single-line excited state EY^{1*} after being excited by light with energy greater than the band gap. The single-line excited state EY^{1*} has a short lifetime, which is easy to compound and causes fluorescence quenching. However, the single-line excited state

electrons are easy to transform into triple excited state EY^{3^*} with a long lifetime through inter-system crossing (ISC) through gap hopping. Subsequently, electrons were extracted from TEOA by reductive quenching, resulting in free radicals EY^- and $TEOA^+$. It is easy to transfer electrons from highly reducible EY^- to the conduction band of Ni-Mo-S nanosheets, resulting in the spatial separation of photogenerated charges and inducing H⁺ reduction from H₂O decomposition to generate excited state H^{*}. Two excited states H^{*} react with each other to produce H₂. At the same time, the holes generated on the valence band of Ni-Mo-S nanosheets will be consumed by TEOA to generate the oxidation donor (TEOA⁺).

In terms of acidic and alkaline media environments, we studied the hydrogen evolution reaction mechanism under the conditions of Na_2S/Na_2SO_3 and lactic acid as hole sacrificial agents by using visible light irradiation on $ZnIn_2S_4/Ni$ -Mo-S composites. We can observe the carrier migration in different media environments in the photocatalytic process in Figure 12C,D, respectively. Under visible light irradiation, $ZnIn_2S_4$ generates photogenerated carriers from the valence band (VB) to the conduction band (CB). However, because the conduction band of Ni-Mo-S is higher than that of $ZnIn_2S_4$, the photogenerated electrons of $ZnIn_2S_4$ transfer easily to Ni-Mo-S. In $ZnIn_2S_4/Ni$ -Mo-S composites, which are closely bound, the photogenerated carriers can be effectively separated, and the recombination and other consumption of photogenerated carriers can be avoided. The H⁺ decomposed by H₂O is reduced to the excited state H^{*} under the action of electrons, and then the H^{*} of the two excited states are combined to produce H₂.

For the photocatalytic properties of Ni-Mo-S/EY with different Ni doping amounts, the experimental results can be obtained from Figure 12E. Without any semiconductor as a catalyst, photogenerated carrier recombination rate is high, and pure EY dye shows low photocatalytic hydrogen evolution activity. When pure MoS₂ (Ni:Mo = 0) was used as a catalyst, the hydrogen evolution rate of EY/MoS₂ under visible light was 1.25 mmol h⁻¹ g⁻¹. When the ratio of Ni:Mo in Ni-Mo-S was increased, the amount of hydrogen evolution increased. Through experiments, it was found that the catalytic performance was better when the ratio of Ni:Mo in Ni-Mo-S was 1:1. The maximum production rate of H₂ reached 2.26 mmol h⁻¹ g⁻¹, 2.72 times that of pure EY dye photocatalytic hydrogen evolution, indicating the superiority of EY-sensitized Ni-Mo-S in photocatalytic hydrogen evolution.

The research results of the hydrogen evolution reaction of ZnIn₂S₄/Ni-Mo-S composites in different media environments can be obtained from Figure 12F,G. Pure $ZnIn_2S_4$ has the lowest hydrogen production performance, which is attributed to its high photogenerated carrier recombination on the surface. When MoS_2 is added as a cocatalyst, the hydrogen production performance is only slightly improved [117–119]. The reason is that the inert basal plane of MoS₂ exists, and the active sites still need to be more numerous, so the experimental hydrogen evolution performance is still limited. When Ni atoms doped in MoS_2 were used as cocatalysts, the hydrogen production performance was significantly improved. Through experimental comparison, it is found that when the value of Ni:Mo in Ni-Mo-S nanosheets is 1:2, the hydrogen evolution performance is the best, and the maximum hydrogen evolution rate reaches 3.63 mmol $h^{-1} g^{-1}$, which is 2.33 times that of pure ZnIn₂S₄. Compared with the lactic acid system, the hydrogen production rate of pure ZnIn₂S₄ in the Na₂S/Na₂SO₃ system was higher (1.56 mmol h^{-1} g⁻¹), indicating that Na_2S/Na_2SO_3 was more suitable to be used as hole scavenger under the $ZnIn_2S_4$ system. The maximum hydrogen evolution rate of $ZnIn_2S_4/Ni$ -Mo-S is 6.07 mmol h⁻¹ g⁻¹, which is 5.28 times the hydrogen production rate of pure ZnIn₂S₄. It is proved that the precise design of ZnIn₂S₄/Ni–Mo–S composite system in an acidic medium can significantly improve the performance of photocatalytic hydrogen evolution. $ZnIn_2S_4$ and MoS₂ with two-dimensional properties have great potential in the field of photocatalysis due to their large surface area and many active sites. In general, the ZnIn₂S₄/Ni-Mo-S composite materials prepared through experiments showed excellent performance in different media environments, which provided new ideas for the further development of new photocatalytic materials based on ZnIn₂S₄ and MoS₂.

Various strategies of photocatalysis using transition metal sulfide as a cocatalyst have achieved profound development and great progress. MoS₂ as co-catalyst to compound with various semiconductors had been widely applied in boosting photocatalytic hydrogen evolution performance, by exposing the reactive facets or edge sites, designing heterophase/heterofacet junctions and engineering the interfacial coupling and confinement effect. MoS₂ compounds with different semiconductors to strengthen photocatalytic performance are summarized in Table 2.

Combine with Semiconductor	Light Source	Reaction Condition	Photocatalytic Performance	Ref.
MoS_2 with $ZbIn_2S_4$	300 W xenon lamp (>420 nm)	0.25 M Na ₂ SO ₃ and 0.35 M Na ₂ S solution	~117 μ mol h ⁻¹ g ⁻¹	[120]
MoS_2 with Fe_3O_4	100 W halogen lamp	15% <i>v/v</i> triethanolamine solution	2480 μ mol h ⁻¹ g ⁻¹	[121]
MoS ₂ with CdS	300 W xenon lamp (>400 nm)	30 vol% lactic acid solution	29 mmol $h^{-1} g^{-1}$	[122]
MoS ₂ with CdS	300 W xenon lamp (>400 nm)	30 vol% lactic acid solution	$31 \text{ mmol } h^{-1} \text{ g}^{-1}$	[123]
MoS ₂ with CdS	300 W xenon lamp (>300 nm)	20 vol% lactic acid solution	$1.695 \text{ mmol } h^{-1} \text{ g}^{-1}$	[124]
MoS_2 with CdSe	300 W xenon lamp (>400 nm)	$0.1~M~Na_2SO_3$ and $0.1~M~Na_2S$ solution	890 μ mol h ⁻¹ g ⁻¹	[125]
MoS ₂ with AgInZnS	300 W xenon lamp (>420 nm)	10 vol% lactic acid solution	944 mmol $h^{-1} g^{-1}$	[126]
MoS_2 with TiO_2	300 W xenon lamp	20% methanol solution	4300 μ mol h ⁻¹ g ⁻¹	[127]
MoS ₂ with CdS	300 W xenon lamp (350–800 nm)	20% methanol solution	$580 \text{ mmol } h^{-1} \text{ g}^{-1}$	[128]

Table 2. Comparison of photocatalytic performance on MoS₂ compound with semiconductors.

4. Conclusions and Outlook

So far, the application of photocatalysis technology is still only in laboratory-scale research, and the application of the actual industrial equipment is faced with significant technical barriers, which limits the application of photocatalysis technology [129–132]. Therefore, in the following research, it is urgent to carry out research continuously strengthening the understanding of the theories related to photocatalysis, such as the development of more advanced material preparation methods and characterization technology [133–135]; to strengthen interdisciplinary ideas and further explore photocatalytic technology in the process of integrating with different disciplines; develop new catalysts that are efficient, stable, safe, economical, and green, and suitable for industrial hydrogen production [136,137].

In the follow-up work, the photocatalysis mechanism under multi-field coupling of light, heat, electricity, and force, such as the principle of carrier separation, will be further studied. The dynamic mechanism of energy capture, efficient conversion, and storage under multi-field coupling should be revealed. The traditional mode of single matching of thermal kinetic energy and energy potential of heat flux, independent use of energy carriers, and the simple thermal cycle will be transformed into the new mode of overall matching of multiple physical and chemical energy and energy potential of energy-carrying substances (such as the overall matching and step utilization of light, heat, and chemical energy potential), the complementarity of multiple energy-carrying forms of photoacoustic-thermal coupling, and the synchronous exploitation of a material cycle and thermal cycle. **Author Contributions:** Writing—review and editing, H.Y., M.Z., Y.C. and Y.Z.; project administration, L.W. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the Natural Science Foundation of China (51902101), the Natural Science Foundation of Jiangsu Province (BK20201381), and the Science Foundation of Nanjing University of Posts and Telecommunications (NY219144).

Data Availability Statement: All of the data analyzed in this review came from articles that mentioned studies.

Conflicts of Interest: The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

References

- 1. Lei, T.; Gu, M.Y.; Fu, H.W.; Wang, J.; Wang, L.L.; Zhou, J.; Liu, H.; Lu, B.A. Bond modulation of MoSe_{2+x} driving combined intercalation and conversion reactions for high-performance K cathodes. *Chem. Sci.* **2023**, *14*, 2528–2536. [CrossRef] [PubMed]
- Chu, K.; Liu, Y.P.; Li, Y.B.; Guo, Y.L.; Tian, Y. Two-dimensional (2D)/2D Interface Engineering of a MoS₂/C₃N₄ Heterostructure for Promoted Electrocatalytic Nitrogen Fixation. ACS Appl. Mater. Interfaces 2020, 12, 7081–7090. [CrossRef] [PubMed]
- Fu, Q.; Han, J.; Wang, X.; Xu, P.; Yao, T.; Zhong, J.; Zhong, W.; Liu, S.; Gao, T.; Zhang, Z.; et al. 2D Transition Metal Dichalcogenides: Design, Modulation, and Challenges in Electrocatalysis. *Adv. Mater.* 2021, 33, 1907818. [CrossRef]
- Wei, Z.; Tang, J.; Li, X.; Chi, Z.; Wang, Y.; Wang, Q.; Han, B.; Li, N.; Huang, B.; Li, J.; et al. Wafer-Scale Oxygen-Doped MoS₂ Monolayer. *Small Methods* 2021, 5, 2100091. [CrossRef] [PubMed]
- Peng, Q.; Qi, X.; Gong, X.; Chen, Y. 1T-MoS₂ Coordinated Bimetal Atoms as Active Centers to Facilitate Hydrogen Generation. *Materials* 2021, 14, 4073. [CrossRef]
- 6. Zhai, W.; Xiong, T.; He, Z.; Lu, S.; Lai, Z.; He, Q.; Tan, C.; Zhang, H. Nanodots Derived from Layered Materials: Synthesis and Applications. *Adv. Mater.* **2021**, *33*, 2006661. [CrossRef]
- 7. Yang, W.; Chen, S. Recent progress in electrode fabrication for electrocatalytic hydrogen evolution reaction: A mini review. *Chem. Eng. J.* **2020**, *393*, 124726. [CrossRef]
- Noerskov, J.K.; Bligaard, T.; Logadottir, A.; Kitchin, J.R.; Chen, J.G.; Pandelov, S.; Stimming, U. Trends in the Exchange Current for Hydrogen Evolution. *ChemInform* 2005, 36, 152. [CrossRef]
- 9. Jaramillo, T.F.; Jørgensen, K.P.; Bonde, J.; Nielsen, J.H.; Horch, S.; Chorkendorff, I. Identification of active edge sites for electrochemical H₂ evolution from MoS₂ nanocatalysts. *Science* **2007**, *317*, 100–102. [CrossRef]
- 10. Seok, J.; Lee, J.; Cho, S.; Ji, B.; Kim, H.; Kwon, M.; Kim, D.; Kim, Y.; Oh, S.; Kim, S.; et al. Active hydrogen evolution through lattice distortion in metallic MoTe₂. 2D Mater. **2017**, *4*, 025061. [CrossRef]
- 11. Zhao, X.; Ning, S.; Fu, W.; Pennycook, S.J.; Loh, K. Differentiating Polymorphs in Molybdenum Disulfide via Electron Microscopy. *Adv. Mater.* **2018**, *30*, 1802397. [CrossRef]
- 12. Vedhanarayanan, B.; Shi, J.; Lin, J.; Yun, S.; Lin, T. Enhanced activity and stability of MoS₂ through enriching 1T-phase by covalent functionalization for energy conversion applications. *Chem. Eng. J.* **2021**, *403*, 126318. [CrossRef]
- Strachan, J.; Masters, A.F.; Maschmeyer, T. Chevrel Phase Nanoparticles as Electrocatalysts for Hydrogen Evolution. ACS Appl. Nano. Mater. 2021, 4, 2030–2036. [CrossRef]
- 14. Lai, Z.; He, Q.; Tran, T.H.; Repaka, D.V.M.; Zhou, D.D.; Sun, Y.; Xi, S.; Li, Y.; Chaturvedi, A.; Tan, C.; et al. MetasTable 1T'-phase group VIB transition metal dichalcogenide crystals. *Nat. Mater.* **2021**, *20*, 1113–1120. [CrossRef] [PubMed]
- 15. Shi, Y.; Zheng, D.; Zhang, X.; Lv, K.; Wang, F.; Dong, B.; Wang, S.; Yang, C.; Li, J.; Yang, F.; et al. Self-Supported Ceramic Electrode of 1T-2H MoS₂ Grown on the TiC Membrane for Hydrogen Production. *Chem. Mater.* **2021**, *33*, 6217–6226. [CrossRef]
- 16. Mathankumar, M.; Karthick, K.; Nanda Kumar, A.K.; Kundu, S.; Balasubramanian, S. Aiding Time-Dependent Laser Ablation to Direct 1T-MoS₂ for an Improved Hydrogen Evolution Reaction. *ACS Sustain. Chem. Eng.* **2021**, *9*, 14744–14755. [CrossRef]
- Nie, K.; Qu, X.; Gao, D.; Li, B.; Yuan, Y.; Liu, Q.; Li, X.; Chong, S.; Liu, Z. Engineering Phase Stability of Semimetallic MoS₂ Monolayers for Sustainable Electrocatalytic Hydrogen Production. ACS Appl. Mater. Interfaces 2022, 14, 19847–19856. [CrossRef]
- Guo, Z.; Wang, L.; Han, M.; Zhao, E.; Zhu, L.; Guo, W.; Tan, J.; Liu, B.; Chen, X.; Lin, J. One-Step Growth of Bilayer 2H–1T' MoTe₂ van der Waals Heterostructures with Interlayer-Coupled Resonant Phonon Vibration. ACS Nano 2022, 16, 11268–11277. [CrossRef]
- 19. Okada, M.; Pu, J.; Lin, Y.; Endo, T.; Okada, N.; Chang, W.; Lu, A.; Nakanishi, T.; Shimizu, T.; Kubo, T.; et al. Large-Scale 1T'-Phase Tungsten Disulfide Atomic Layers Grown by Gas-Source Chemical Vapor Deposition. ACS Nano 2022, 16, 13069–13081. [CrossRef]
- 20. Saha, D.; Patel, V.; Selvaganapathy, P.R.; Kruse, P. Facile fabrication of conductive MoS₂ thin films by sonication in hot water and evaluation of their electrocatalytic performance in the hydrogen evolution reaction. *Nanoscale Adv.* **2022**, *4*, 125–137. [CrossRef]
- Nguyen, D.; Tran, D.; Doan, T.; Kim, D.; Kim, N.; Lee, J. Rational Design of Core@shell Structured CoS_x@Cu₂MoS₄ Hybridized MoS₂/N,S-Codoped Graphene as Advanced Electrocatalyst for Water Splitting and Zn-Air Battery. *Adv. Energy Mater.* 2020, 10, 1903289. [CrossRef]
- 22. Wang, X.; Zheng, Y.; Sheng, W.; Xu, Z.J.; Jaroniec, M.; Qiao, S.-Z. Strategies for design of electrocatalysts for hydrogen evolution under alkaline conditions. *Mater. Today* 2020, *36*, 125–138. [CrossRef]

- 23. Sebastian, A.; Pendurthi, R.; Choudhury, T.H.; Redwing, J.M.; Das, S. Benchmarking monolayer MoS₂ and WS₂ field-effect transistors. *Nat. Commun.* **2021**, *12*, 693. [CrossRef]
- 24. Shi, Y.; Ma, Z.; Xiao, Y.; Yin, Y.; Huang, W.; Huang, Z.; Zheng, Y.; Mu, F.; Huang, R.; Shi, G.; et al. Electronic metal-support interaction modulates single-atom platinum catalysis for hydrogen evolution reaction. *Nat. Commun.* **2021**, *12*, 3021. [CrossRef]
- Wang, H.; Tsai, C.; Kong, D.; Chan, K.; Abild-Pedersen, F.; Nørskov, J.K.; Cui, Y. Transition-metal doped edge sites in vertically aligned MoS₂ catalysts for enhanced hydrogen evolution. *Nano Res.* 2015, *8*, 566–575. [CrossRef]
- 26. Fu, Y.; Shan, Y.; Zhou, G.; Long, L.; Wang, L.; Yin, K.; Guo, J.; Shen, J.; Liu, L.; Wu, X. Electric Strain in Dual Metal Janus Nanosheets Induces Structural Phase Transition for Efficient Hydrogen Evolution. *Joule* **2019**, *3*, 2955–2967. [CrossRef]
- 27. Pan, J.; Zhang, W.; Xu, X.; Hu, J. The mechanism of enhanced photocatalytic activity for water-splitting of ReS₂ by strain and electric field engineering. *RSC Adv.* **2021**, *11*, 23055–23063. [CrossRef]
- Trainer, D.J.; Nieminen, J.; Bobba, F.; Wang, B.; Xi, X.; Bansil, A.; Iavarone, M. Visualization of defect induced in-gap states in monolayer MoS₂. NPJ 2D Mater. Appl. 2022, 6, 13. [CrossRef]
- 29. Wu, X.; Gu, Y.; Ge, R.; Serna, M.I.; Huang, Y.; Lee, J.C.; Akinwande, D. Electron irradiation-induced defects for reliability improvement in monolayer MoS₂-based conductive-point memory devices. *NPJ 2D Mater. Appl.* **2022**, *6*, 31. [CrossRef]
- 30. Jia, L.; Liu, B.; Zhao, Y.; Chen, W.; Mou, D.; Fu, J.; Wang, Y.; Xin, W.; Zhao, L. Structure design of MoS₂@Mo₂C on nitrogen-doped carbon for enhanced alkaline hydrogen evolution reaction. *J. Mater. Sci.* **2020**, *55*, 16197–16210. [CrossRef]
- 31. Zhang, L.; Zheng, Y.; Wang, J.; Geng, Y.; Zhang, B.; He, J.; Xue, J.; Frauenheim, T.; Li, M. Ni/Mo Bimetallic-Oxide-Derived Heterointerface-Rich Sulfide Nanosheets with Co-Doping for Efficient Alkaline Hydrogen Evolution by Boosting Volmer Reaction. *Small* **2021**, *17*, 2006730. [CrossRef] [PubMed]
- 32. Kang, S.; Koo, J.J.; Seo, H.; Truong, Q.T.; Park, J.B.; Park, S.C.; Jung, Y.; Cho, S.; Nam, K.T.; Kim, Z.H.; et al. Defect-engineered MoS₂ with extended photoluminescence lifetime for high-performance hydrogen evolution. *J. Mater. Chem. C Mater.* **2019**, *7*, 10173–10178. [CrossRef]
- Zhang, S.; Wang, L.; Liu, C.; Luo, J.; Crittenden, J.; Liu, X.; Cai, T.; Yuan, J.; Pei, Y.; Liu, Y. Photocatalytic wastewater purification with simultaneous hydrogen production using MoS₂ QD-decorated hierarchical assembly of ZnIn₂S₄ on reduced graphene oxide photocatalyst. *Water Res.* 2017, 121, 11–19. [CrossRef]
- Feng, C.; Wu, Z.P.; Huang, K.W.; Ye, J.; Zhang, H. Surface Modification of 2D Photocatalysts for Solar Energy Conversion. *Adv. Mater.* 2022, 34, 2200180. [CrossRef]
- Kumar, R.; Das, D.; Singh, A.K. C₂N/WS₂ van der Waals type-II heterostructure as a promising water splitting photocatalyst. *J. Catal.* 2018, 359, 143–150. [CrossRef]
- 36. Li, Y.; Ding, L.; Yin, S.; Liang, Z.; Xue, Y.; Wang, X.; Cui, H.; Tian, J. Photocatalytic H⁻² Evolution on TiO₂ Assembled with Ti₃C₂ MXene and Metallic 1T-WS₂ as Co-catalysts. *Nano-Micro Lett.* **2020**, *12*, *6*. [CrossRef]
- Qorbani, M.; Sabbah, A.; Lai, Y.; Kholimatussadiah, S.; Quadir, S.; Huang, C.; Shown, I.; Huang, Y.; Hayashi, M.; Chen, K.; et al. Atomistic insights into highly active reconstructed edges of monolayer 2H-WSe₂ photocatalyst. *Nat. Commun.* 2022, 13, 1256. [CrossRef]
- Li, S.; Sun, J.; Guan, J. Strategies to improve electrocatalytic and photocatalytic performance of two-dimensional materials for hydrogen evolution reaction. *Chin. J. Catal.* 2021, 42, 511–556. [CrossRef]
- Cheng, X.; Wang, L.; Xie, L.; Sun, C.; Zhao, W.; Liu, X.; Zhuang, Z.; Liu, S.; Zhao, Q. Defect-driven selective oxidation of MoS₂ nanosheets with photothermal effect for Photo-Catalytic hydrogen evolution reaction. *Chem. Eng. J.* 2022, 439, 135757. [CrossRef]
- 40. Liang, Z.; Xue, Y.; Wang, X.; Zhou, Y.; Zhang, X.; Cui, H.; Cheng, G.; Tian, J. Co doped MoS₂ as cocatalyst considerably improved photocatalytic hydrogen evolution of g-C₃N₄ in an alkalescent environment. *Chem. Eng. J.* **2021**, 421, 130016. [CrossRef]
- 41. Zhou, J.; Guo, M.; Wang, L.; Ding, Y.; Zhang, Z.; Tang, Y.; Liu, C.; Luo, S. 1T-MoS₂ nanosheets confined among TiO₂ nanotube arrays for high performance supercapacitor. *Chem. Eng. J.* **2019**, *366*, 163–171. [CrossRef]
- Chen, J.; Tang, Y.; Wang, S.; Xie, L.; Chang, C.; Cheng, X.; Liu, M.; Wang, L.; Wang, L. Ingeniously designed Ni-Mo-S/ZnIn₂S₄ composite for multi-photocatalytic reaction systems. *Chin. Chem. Lett.* 2022, *33*, 1468–1474. [CrossRef]
- Li, Y.; Wang, L.; Cai, T.; Zhang, S.; Liu, Y.; Song, Y.; Dong, X.; Hu, L. Glucose-assisted synthesize 1D/2D nearly vertical CdS/MoS₂ heterostructures for efficient photocatalytic hydrogen evolution. *Chem. Eng. J.* 2017, 321, 366–374. [CrossRef]
- 44. Liu, C.; Wang, L.; Tang, Y.; Luo, S.; Liu, Y.; Zhang, S.; Zeng, Y.; Xu, Y. Vertical single or few-layer MoS₂ nanosheets rooting into TiO₂ nanofibers for highly efficient photocatalytic hydrogen evolution. *Appl. Catal. B* **2015**, *164*, 1–9. [CrossRef]
- Nguyen, D.; Luyen Doan, T.; Prabhakaran, S.; Tran, D.; Kim, D.; Lee, J.; Kim, N. Hierarchical Co and Nb dual-doped MoS₂ nanosheets shelled micro-TiO₂ hollow spheres as effective multifunctional electrocatalysts for HER, OER, and ORR. *Nano Energy* **2021**, *82*, 105750. [CrossRef]
- He, Q.; Wang, L.; Yin, K.; Luo, S. Vertically Aligned Ultrathin 1T-WS₂ Nanosheets Enhanced the Electrocatalytic Hydrogen Evolution. *Nanoscale Res. Lett.* 2018, 13, 167. [CrossRef] [PubMed]
- 47. Sun, K.; Liu, Y.; Liu, C. Rare-Earth Elements Modified 1T Phase Mos₂ Synergy with Defects for Enhanced Hydrogen Evolution. *IOP Conf. Ser. Earth Environ. Sci.* **2019**, 252, 022136. [CrossRef]
- 48. Murthy, A.A.; Stanev, T.K.; dos Reis, R.; Hao, S.; Wolverton, C.; Stern, N.P.; Dravid, V.P. Direct Visualization of Electric-Field-Induced Structural Dynamics in Monolayer Transition Metal Dichalcogenides. *ACS Nano* 2020, *14*, 1569–1576. [CrossRef]
- Robinson, J.A.; Schuler, B. Engineering and probing atomic quantum defects in 2D semiconductors: A perspective. *Appl. Phys.* Lett. 2021, 119, 140501. [CrossRef]

- Sukanya, R.; da Silva Alves, D.C.; Breslin, C.B. Review—Recent Developments in the Applications of 2D Transition Metal Dichalcogenides as Electrocatalysts in the Generation of Hydrogen for Renewable Energy Conversion. *J. Electrochem. Soc.* 2022, 169, 064504. [CrossRef]
- 51. Zakerian, F.; Fathipour, M.; Faez, R.; Darvish, G. The effect of structural defects on the electron transport of MoS₂ nanoribbons based on density functional theory. *J. Theor. Appl. Phys.* **2019**, *13*, 55–62. [CrossRef]
- Ji, Q.; Kan, M.; Zhang, Y.; Guo, Y.; Ma, D.; Shi, J.; Sun, Q.; Chen, Q.; Zhang, Y.; Liu, Z. Unravelling Orientation Distribution and Merging Behavior of Monolayer MoS₂ Domains on Sapphire. *Nano Lett.* **2014**, *15*, 198–205. [CrossRef]
- 53. Man, P.; Srolovitz, D.; Zhao, J.; Ly, T. Functional Grain Boundaries in Two-Dimensional Transition-Metal Dichalcogenides. *Acc. Chem. Res.* 2021, 54, 4191–4202. [CrossRef]
- 54. Su, H.; Ma, X.; Sun, K. Single-atom metal tuned sulfur vacancy for efficient H₂ activation and hydrogen evolution reaction on MoS₂ basal plane. *Appl. Surf. Sci.* 2022, 597, 153614. [CrossRef]
- Bose, R.; Balasingam, S.K.; Shin, S.; Jin, Z.; Kwon, D.H.; Jun, Y.; Min, Y.S. Importance of hydrophilic pretreatment in the hydrothermal growth of amorphous molybdenum sulfide for hydrogen evolution catalysis. *Langmuir* 2015, *31*, 5220–5227. [CrossRef] [PubMed]
- Li, Y.; Yin, K.; Wang, L.; Lu, X.; Zhang, Y.; Liu, Y.; Yan, D.; Song, Y.; Luo, S. Engineering MoS₂ nanomesh with holes and lattice defects for highly active hydrogen evolution reaction. *Appl. Catal. B* 2018, 239, 537–544. [CrossRef]
- Li, Y.; Yu, B.; Li, H.M.; Liu, B.; Yu, X.; Zhang, K.W.; Qin, G.; Lu, J.H.; Zhang, L.H.; Wang, L.L. Activation of hydrogen peroxide by molybdenum disulfide as Fenton-like catalyst and cocatalyst: Phase-dependent catalytic performance and degradation mechanism. *Chin. Chem. Lett.* 2023, *34*, 107874. [CrossRef]
- 58. Li, J.W.; Yin, W.N.; Pan, J.A.; Zhang, Y.B.; Wang, F.S.; Wang, L.L.; Zhao, Q. External field assisted hydrogen evolution reaction. *Nano Res.* **2023**. [CrossRef]
- Sun, C.; Wang, L.; Zhao, W.; Xie, L.; Wang, J.; Li, J.; Li, B.; Liu, S.; Zhuang, Z.; Zhao, Q. Atomic-Level Design of Active Site on Two-Dimensional MoS₂ toward Efficient Hydrogen Evolution: Experiment, Theory, and Artificial Intelligence Modelling. *Adv. Funct. Mater.* 2022, 32, 2206163. [CrossRef]
- Wang, L.; Liu, X.; Zhang, Q.; Zhou, G.; Pei, Y.; Chen, S.; Wang, J.; Rao, A.; Yang, H.; Lu, B. Quasi-one-dimensional Mo chains for efficient hydrogen evolution reaction. *Nano Energy* 2019, *61*, 194–200. [CrossRef]
- 61. Wang, S.; Wang, L.; Xie, L.; Zhao, W.; Liu, X.; Zhuang, Z.; Zhuang, Y.; Chen, J.; Liu, S.; Zhao, Q. Dislocation-strained MoS₂ nanosheets for high-efficiency hydrogen evolution reaction. *Nano Res.* **2022**, *15*, 4996–5003. [CrossRef]
- Lin, W.; Zhang, B.; Jiang, J.; Liu, E.; Sha, J.; Ma, L. Anionic and Cationic Co-Substitutions of S into Vertically Aligned WTe2 Nanosheets as Catalysis for Hydrogen Evolution under Alkaline Conditions. ACS Appl. Nano. Mater. 2022, 5, 7123–7131. [CrossRef]
- 63. Geng, S.; Tian, F.; Li, M.; Liu, Y.; Sheng, J.; Yang, W.; Yu, Y.; Hou, Y. Activating interfacial S sites of MoS₂ boosts hydrogen evolution electrocatalysis. *Nano Res.* 2022, *15*, 1809–1816. [CrossRef]
- Mao, M.; Lin, Z.; Tong, Y.; Yue, J.; Zhao, C.; Lu, J.; Zhang, Q.; Gu, L.; Suo, L.; Hu, Y.-S.; et al. Iodine Vapor Transport-Triggered Preferential Growth of Chevrel Mo₆S₈ Nanosheets for Advanced Multivalent Batteries. ACS Nano 2020, 14, 1102–1110. [CrossRef]
- 65. Huang, X.; Wang, T.; Miao, S.; Wang, C.; Li, Z.; Lian, Z.; Taniguchi, T.; Watanabe, K.; Okamoto, S.; Xiao, D.; et al. Correlated insulating states at fractional fillings of the WS₂/WSe₂ moire lattice. *Nat. Phys.* **2021**, *17*, 715–719. [CrossRef]
- Cheng, Z.; Xiao, Y.; Wu, W.; Zhang, X.; Fu, Q.; Zhao, Y.; Qu, L. All-pH-Tolerant In-Plane Heterostructures for Efficient Hydrogen Evolution Reaction. ACS Nano 2021, 15, 11417–11427. [CrossRef]
- Han, Q.; Cao, H.; Sun, Y.; Wang, G.; Poon, S.; Wang, M.; Liu, B.; Wang, Y.; Wang, Z.; Mi, B. Tuning phase compositions of MoS₂ nanomaterials for enhanced heavy metal removal: Performance and mechanism. *Phys. Chem. Chem. Phys.* 2022, 24, 13305–13316. [CrossRef] [PubMed]
- 68. Li, Y.; Wang, L.; Zhang, S.; Dong, X.; Song, Y.; Cai, T.; Liu, Y. Cracked monolayer 1T MoS₂ with abundant active sites for enhanced electrocatalytic hydrogen evolution. *Catal. Sci. Technol.* **2017**, *7*, 718–724. [CrossRef]
- Xie, L.; Wang, L.; Zhao, W.; Liu, S.; Huang, W.; Zhao, Q. WS₂ moire superlattices derived from mechanical flexibility for hydrogen evolution reaction. *Nat. Commun.* 2021, 12, 5070. [CrossRef] [PubMed]
- Jiao, S.; Kong, M.; Hu, Z.; Zhou, S.; Xu, X.; Liu, L. Pt Atom on the Wall of Atomic Layer Deposition (ALD)-Made MoS₂ Nanotubes for Efficient Hydrogen Evolution. *Small* 2022, 18, 2105129. [CrossRef] [PubMed]
- Liu, X.; Li, B.; Soto, F.A.; Li, X.; Unocic, R.R.; Balbuena, P.B.; Harutyunyan, A.R.; Hone, J.; Esposito, D.V. Enhancing Hydrogen Evolution Activity of Monolayer Molybdenum Disulfide via a Molecular Proton Mediator. ACS Catal. 2021, 11, 12159–12169. [CrossRef]
- Pan, J.; Wang, R.; Xu, X.; Hu, J.; Ma, L. Transition Metal Doping Activated Basal-Plane Catalytic Activity of Two-Dimensional 1T'-ReS₂ for Hydrogen Evolution Reaction: A First-Principles Calculation Study. *Nanoscale* 2019, *11*, 10402–10409. [CrossRef] [PubMed]
- Wang, S.; Zhang, D.; Li, B.; Zhang, C.; Du, Z.; Yin, H.; Bi, X.; Yang, S. Ultrastable In-Plane 1T–2H MoS₂ Heterostructures for Enhanced Hydrogen Evolution Reaction. *Adv. Energy Mater.* 2018, *8*, 1801345. [CrossRef]
- Wang, Z.; Wang, S.; Ma, L.; Guo, Y.; Sun, J.; Zhang, N.; Jiang, R. Water-Induced Formation of Ni₂P-Ni₁₂P₅ Interfaces with Superior Electrocatalytic Activity toward Hydrogen Evolution Reaction. *Small* 2021, *17*, 2006770. [CrossRef] [PubMed]

- Kim, S.H.; Lim, J.; Sahu, R.; Kasian, O.; Stephenson, L.T.; Scheu, C.; Gault, B. Direct Imaging of Dopant and Impurity Distributions in 2D MoS₂. Adv. Mater. 2020, 32, 1907235. [CrossRef] [PubMed]
- Li, M.; Cai, B.; Tian, R.; Yu, X.; Breese, M.B.H.; Chu, X.; Han, Z.; Li, S.; Joshi, R.; Vinu, A.; et al. Vanadium doped 1T MoS₂ nanosheets for highly efficient electrocatalytic hydrogen evolution in both acidic and alkaline solutions. *Chem. Eng. J.* 2021, 409, 128158. [CrossRef]
- Liu, M.; Li, H.; Liu, S.; Wang, L.; Xie, L.; Zhuang, Z.; Sun, C.; Wang, J.; Tang, M.; Sun, S.; et al. Tailoring activation sites of metastable distorted 1T'-phase MoS₂ by Ni doping for enhanced hydrogen evolution. *Nano Res.* 2022, 15, 5946–5952. [CrossRef]
- 78. Wang, L.; Zhang, Q.; Zhu, J.; Duan, X.; Xu, Z.; Liu, Y.; Yang, H.; Lu, B. Nature of extra capacity in MoS₂ electrodes: Molybdenum atoms accommodate with lithium. *Energy. Storage. Mater.* **2019**, *16*, 37–45. [CrossRef]
- 79. Xia, F.; Li, B.; Liu, Y.; Liu, Y.; Gao, S.; Lu, K.; Kaelin, J.; Wang, R.; Marks, T.J.; Cheng, Y. Carbon Free and Noble Metal Free Ni₂Mo₆S₈ Electrocatalyst for Selective Electrosynthesis of H₂O₂. *Adv. Funct. Mater.* **2021**, *31*, 2104716. [CrossRef]
- Zeng, J.; Zhang, L.; Zhou, Q.; Liao, L.; Qi, Y.; Zhou, H.; Li, D.; Cai, F.; Wang, H.; Tang, D.; et al. Boosting Alkaline Hydrogen and Oxygen Evolution Kinetic Process of Tungsten Disulfide-Based Heterostructures by Multi-Site Engineering. *Small* 2022, 18, 2104624. [CrossRef]
- Zhang, X.; Jia, F.; Song, S. Recent advances in structural engineering of molybdenum disulfide for electrocatalytic hydrogen evolution reaction. *Chem. Eng. J.* 2021, 405, 127013. [CrossRef]
- Wang, L.; Xie, L.; Zhao, W.; Liu, S.; Zhao, Q. Oxygen-facilitated dynamic active-site generation on strained MoS₂ during photo-catalytic hydrogen evolution. *Chem. Eng. J.* 2021, 405, 127028. [CrossRef]
- Wang, L.; Zhou, G.; Luo, H.; Zhang, Q.; Wang, J.; Zhao, C.; Rao, A.; Xu, B.; Lu, B. Enhancing catalytic activity of tungsten disulfide through topology. *Appl. Catal. B* 2019, 256, 117802. [CrossRef]
- Wang, L.; Liu, X.; Luo, J.; Duan, X.; Crittenden, J.; Liu, C.; Zhang, S.; Pei, Y.; Zeng, Y.; Duan, X. Self-Optimization of the Active Site of Molybdenum Disulfide by an Irreversible Phase Transition during Photocatalytic Hydrogen Evolution. *Angew. Chem. Int. Ed. Engl.* 2017, 56, 7610–7614. [CrossRef]
- Wang, L.; Duan, X.; Wang, G.; Liu, C.; Luo, S.; Zhang, S.; Zeng, Y.; Xu, Y.; Liu, Y.; Duan, X. Omnidirectional enhancement of photocatalytic hydrogen evolution over hierarchical "cauline leaf" nanoarchitectures. *Appl. Catal. B* 2016, 186, 88–96. [CrossRef]
- Liu, Y.; Chen, Y.; Tian, Y.; Sakthivel, T.; Liu, H.; Guo, S.; Zeng, H.; Dai, Z. Synergizing Hydrogen Spillover and Deprotonation by the Internal Polarization Field in a MoS₂/NiPS3 Vertical Heterostructure for Boosted Water Electrolysis. *Adv. Mater.* 2022, 34, 2203615. [CrossRef] [PubMed]
- Zhang, W.; Cui, L.; Liu, J. Recent advances in cobalt-based electrocatalysts for hydrogen and oxygen evolution reactions. J. Alloys. Compd. 2020, 821, 153542. [CrossRef]
- 88. Zheng, Z.; Yu, L.; Gao, M.; Chen, X.; Zhou, W.; Ma, C.; Wu, L.; Zhu, J.; Meng, X.; Hu, J.; et al. Boosting hydrogen evolution on MoS₂ via co-confining selenium in surface and cobalt in inner layer. *Nat. Commun.* **2020**, *11*, 3315. [CrossRef]
- Chen, X.; Lei, B.; Zhu, Y.; Zhou, J.; Liu, Z.; Ji, W.; Zhou, W. Pristine edge structures of T^{''}-phase transition metal dichalcogenides (ReSe₂, ReS₂) atomic layers. *Nanoscale* 2020, *12*, 17005–17012. [CrossRef]
- 90. Li, M.Z.; Wang, L.L.; Zhang, X.Y.; Yin, W.A.; Zhang, Y.B.; Li, J.W.; Yin, Z.Y.; Cai, Y.T.; Liu, S.J.; Zhao, Q. Recent status and future perspectives of ZnIn₂S₄ for energy conversion and environmental remediation. *Chin. Chem. Lett.* **2023**, *34*, 107775. [CrossRef]
- Li, Y.; Hua, Y.Q.; Sun, N.; Liu, S.J.; Li, H.X.; Wang, C.; Yang, X.Y.; Zhuang, Z.C.; Wang, L.L. Moire superlattice engineering of two-dimensional materials for electrocatalytic hydrogen evolution reaction. *Nano Res.* 2023. [CrossRef]
- Zhou, B.; Gao, R.; Zou, J.; Yang, H. Surface Design Strategy of Catalysts for Water Electrolysis. *Small* 2022, *18*, 2202336. [CrossRef]
 Chen, S.; Pan, Y. Influence of Group III and IV Elements on the Hydrogen Evolution Reaction of MoS₂ Disulfide. *J. Phys. Chem. C*
- 2021, 125, 11848–11856. [CrossRef]
 94. Lin, L.; Sherrell, P.; Liu, Y.; Lei, W.; Zhang, S.; Zhang, H.; Wallace, G.G.; Chen, J. Engineered 2D Transition Metal Dichalcogenides-A
- 94. Lin, L.; Sherrell, F.; Liu, T.; Lei, W.; Zhang, S.; Zhang, H.; Wallace, G.G.; Chen, J. Engineered 2D Transition Metal Dichalcogenides-A Vision of Viable Hydrogen Evolution Reaction Catalysis. *Adv. Energy Mater.* **2020**, *10*, 1903870. [CrossRef]
- 95. Li, H.; Xu, L.; Sitinamaluwa, H.; Wasalathilake, K.; Yan, C. Coating Fe2O3 with graphene oxide for high-performance sodium-ion battery anode. *Compos. Commun.* **2016**, *1*, 48–53. [CrossRef]
- Sanchez, J.; Hellstern, T.R.; King, L.A.; Jaramillo, T.F. Surface Engineering of 3D Gas Diffusion Electrodes for High-Performance H2 Production with Nonprecious Metal Catalysts. *Adv. Energy Mater.* 2019, *9*, 1901824. [CrossRef]
- Tao, L.; Duan, X.; Wang, C.; Duan, X.; Wang, S. Plasma-engineered MoS₂ thin-film as an efficient electrocatalyst for hydrogen evolution reaction. *Chem. Commun.* 2015, *51*, 7470–7473. [CrossRef]
- Zhang, Y.; Yang, T.; Li, J.; Zhang, Q.; Li, B.; Gao, M. Construction of Ru, O Co-Doping MoS₂ for Hydrogen Evolution Reaction Electrocatalyst and Surface-Enhanced Raman Scattering Substrate: High-Performance, Recyclable, and Durability Improvement. *Adv. Funct. Mater.* 2023, *33*, 2210939. [CrossRef]
- Lin, J.; Wang, P.; Wang, H.; Li, C.; Si, X.; Qi, J.; Cao, J.; Zhong, Z.; Fei, W.; Feng, J. Defect-Rich Heterogeneous MoS₂/NiS₂ Nanosheets Electrocatalysts for Efficient Overall Water Splitting. *Adv. Sci.* 2019, *6*, 1900246. [CrossRef] [PubMed]
- 100. Jiang, K.; Luo, M.; Liu, Z.; Peng, M.; Chen, D.; Lu, Y.-R.; Chan, T.-S.; de Groot, F.M.F.; Tan, Y. Rational strain engineering of single-atom ruthenium on nanoporous MoS₂ for highly efficient hydrogen evolution. *Nat. Commun.* **2021**, *12*, 1687. [CrossRef]
- Wang, S.; Li, J.; Hu, S.; Kang, H.; Zhao, S.; Xiao, R.; Sui, Y.; Chen, Z.; Peng, S.; Jin, Z.; et al. Morphology Regulation of MoS₂ Nanosheet-Based Domain Boundaries for the Hydrogen Evolution Reaction. ACS Appl. Nano. Mater. 2022, 5, 2273–2279. [CrossRef]

- 102. Yu, Y.; Nam, G.-H.; He, Q.; Wu, X.-J.; Zhang, K.; Yang, Z.; Chen, J.; Ma, Q.; Zhao, M.; Liu, Z.; et al. High phase-purity 1T'-MoS₂-and 1T'-MoSe2-layered crystals. *Nat. Chem.* **2018**, *10*, 638–643. [CrossRef] [PubMed]
- 103. Wang, G.; Zhang, G.; Ke, X.; Chen, X.; Chen, X.; Wang, Y.; Huang, G.; Dong, J.; Chu, S.; Sui, M. Direct Synthesis of STable 1T-MoS₂ Doped with Ni Single Atoms for Water Splitting in Alkaline Media. *Small* **2022**, *18*, 2107238. [CrossRef] [PubMed]
- 104. Jiang, J.; Li, F.; Bai, S.; Wang, Y.; Xiang, K.; Wang, H.; Zou, J.; Hsu, J. Carbonitride MXene Ti₃CN(OH)_x@MoS₂ hybrids as efficient electrocatalyst for enhanced hydrogen evolution. *Nano Res.* 2022, *16*, 4656–4663. [CrossRef]
- 105. Chen, Y.; Tian, Z.; Wang, X.; Ran, N.; Wang, C.; Cui, A.; Lu, H.; Zhang, M.; Xue, Z.; Mei, Y.; et al. 2D Transition Metal Dichalcogenide with Increased Entropy for Piezoelectric Electronics. *Adv. Mater.* **2022**, *34*, 2201630. [CrossRef]
- 106. Kong, C.; Han, Y.; Hou, L.; Song, X.; Gao, L. Rationalizing hydrogen evolution mechanism on the slab of Zn-reduced 2H–MoS₂ monolayer by density functional theory calculations. *Int. J. Hydrog. Energy* 2022, 47, 19005–19015. [CrossRef]
- 107. Wang, Q.; Yan, L.; Wang, L.; Zhang, W.; Guo, Y.; Song, W.; Li, X. Enhanced peroxymonosulfate activation by (NH₄)₂Mo₃S₁₃ for organic pollutant removal: Crucial roles of adsorption and singlet oxygen. J. Environ. Chem. Eng. 2022, 10, 107966. [CrossRef]
- Sun, C.; Liu, M.; Wang, L.; Xie, L.; Zhao, W.; Li, J.; Liu, S.; Yan, D.; Zhao, Q. Revisiting lithium-storage mechanisms of molybdenum disulfide. *Chin. Chem. Lett.* 2022, 33, 1779–1797. [CrossRef]
- 109. Li, X.; Lv, X.; Sun, X.; Yang, C.; Zheng, Y.-Z.; Yang, L.; Li, S.; Tao, X. Edge-oriented, high-percentage 1T'-phase MoS₂ nanosheets stabilize Ti₃C₂ MXene for efficient electrocatalytic hydrogen evolution. *Appl. Catal. B* **2021**, 284, 119708. [CrossRef]
- Wang, C.; Shao, X.; Pan, J.; Hu, J.; Xu, X. Redox bifunctional activities with optical gain of Ni₃S₂ nanosheets edged with MoS₂ for overall water splitting. *Appl. Catal. B* 2020, 268, 118435. [CrossRef]
- Hsu, C.-L.; Chang, Y.-H.; Chen, T.-Y.; Tseng, C.-C.; Wei, K.-H.; Li, L.-J. Enhancing the electrocatalytic water splitting efficiency for amorphous MoS_x. Int. J. Hydrog. Energy 2014, 39, 4788–4793. [CrossRef]
- 112. Vega-Granados, K.; Gochi-Ponce, Y.; Alonso-Vante, N. Electrochemical interfaces on chalcogenides: Some structural perspectives and synergistic effects of single-surface active sites. *Curr. Opin. Electrochem.* **2022**, *33*, 100955. [CrossRef]
- 113. Chen, J.; Liu, G.; Zhu, Y.; Su, M.; Yin, P.; Wu, X.; Lu, Q.; Tan, C.; Zhao, M.; Liu, Z.; et al. Ag@MoS₂ Core-Shell Heterostructure as SERS Platform to Reveal the Hydrogen Evolution Active Sites of Single-Layer MoS₂. J. Am. Chem. Soc. 2020, 142, 7161–7167. [CrossRef] [PubMed]
- 114. Xu, Y.; Wang, L.; Liu, X.; Zhang, S.; Liu, C.; Yan, D.; Zeng, Y.; Pei, Y.; Liu, Y.; Luo, S. Monolayer MoS₂ with S vacancies from interlayer spacing expanded counterparts for highly efficient electrochemical hydrogen production. *J. Mater. Chem. A Mater.* 2016, 4, 16524–16530. [CrossRef]
- 115. Huang, H.; Xue, Y.; Xie, Y.; Yang, Y.; Yang, L.; He, H.; Jiang, Q.; Ying, G. MoS₂ quantum dot-decorated MXene nanosheets as efficient hydrogen evolution electrocatalysts. *Inorg. Chem. Front.* **2022**, *9*, 1171–1178. [CrossRef]
- 116. Wang, T.; Wang, P.; Pang, Y.; Wu, Y.; Yang, J.; Chen, H.; Gao, X.; Mu, S.; Kou, Z. Vertically mounting molybdenum disulfide nanosheets on dimolybdenum carbide nanomeshes enables efficient hydrogen evolution. *Nano Res.* 2022, 15, 3946–3951. [CrossRef]
- 117. Hua, W.; Sun, H.; Xu, F.; Wang, J. A review and perspective on molybdenum-based electrocatalysts for hydrogen evolution reaction. *Rare Metals.* 2020, *39*, 335–351. [CrossRef]
- 118. Li, Y.; Yin, Z.; Cui, M.; Liu, X.; Xiong, J.; Chen, S.; Ma, T. Interface engineering of transitional metal sulfide-MoS₂ heterostructure composites as effective electrocatalysts for water-splitting. *J. Mater. Chem. A Mater.* **2021**, *9*, 2070–2092. [CrossRef]
- 119. Han, A.; Zhou, X.; Wang, X.; Liu, S.; Xiong, Q.; Zhang, Q.; Gu, L.; Zhuang, Z.; Zhang, W.; Li, F.; et al. One-step synthesis of single-site vanadium substitution in 1T-WS₂ monolayers for enhanced hydrogen evolution catalysis. *Nat. Commun.* 2021, 12, 709. [CrossRef]
- 120. Huang, T.; Chen, W.; Liu, T.-Y.; Hao, Q.-L.; Liu, X.-H. ZnIn2S4 hybrid with MoS₂: A non-noble metal photocatalyst with efficient photocatalytic activity for hydrogen evolution. *Powder Technol.* **2017**, *315*, 157–162. [CrossRef]
- Jaiswal, M.K.; Gupta, U.; Vishnoi, P. A covalently conjugated MoS₂/Fe3O4 magnetic nanocomposite as an efficient & reusable catalyst for H2 production. *Dalton Trans.* 2018, 47, 287–291. [CrossRef] [PubMed]
- 122. Yin, L.; Hai, X.; Chang, K.; Ichihara, F.; Ye, J. Synergetic Exfoliation and Lateral Size Engineering of MoS₂ for Enhanced Photocatalytic Hydrogen Generation. *Small* **2018**, *14*, 1704153. [CrossRef] [PubMed]
- Hai, X.; Zhou, W.; Wang, S.; Pang, H.; Chang, K.; Ichihara, F.; Ye, J. Rational design of freestanding MoS₂ monolayers for hydrogen evolution reaction. *Nano Energy* 2017, 39, 409–417. [CrossRef]
- 124. Ma, F.; Wu, Y.; Shao, Y.; Zhong, Y.; Lv, J.; Hao, X. 0D/2D nanocomposite visible light photocatalyst for highly stable and efficient hydrogen generation via recrystallization of CdS on MoS₂ nanosheets. *Nano Energy* **2016**, *27*, 466–474. [CrossRef]
- Frame, F.A.; Osterloh, F.E. CdSe-MoS₂: A Quantum Size-Confined Photocatalyst for Hydrogen Evolution from Water under Visible Light. J. Phys. Chem. C 2010, 114, 10628–10633. [CrossRef]
- 126. He, H.; Lin, J.; Fu, W.; Wang, X.; Wang, H.; Zeng, Q.; Gu, Q.; Li, Y.; Yan, C.; Tay, B.K.; et al. MoS₂/TiO₂ Edge-On Heterostructure for Efficient Photocatalytic Hydrogen Evolution. *Adv. Energy Mater.* **2016**, *6*, 1600464. [CrossRef]
- 127. Guo, L.; Yang, Z.; Marcus, K.; Li, Z.; Luo, B.; Zhou, L.; Wang, X.; Du, Y.; Yang, Y. MoS₂/TiO₂ heterostructures as nonmetal plasmonic photocatalysts for highly efficient hydrogen evolution. *Energy Environ. Sci.* **2018**, *11*, 106–114. [CrossRef]
- Wang, D.; Su, B.; Jiang, Y.; Li, L.; Ng, B.K.; Wu, Z.; Liu, F. Polytype 1T/2H MoS₂ heterostructures for efficient photoelectrocatalytic hydrogen evolution. *Chem. Eng. J.* 2017, 330, 102–108. [CrossRef]

- 129. Cho, J.; Seok, H.; Lee, I.; Lee, J.; Kim, E.; Sung, D.; Baek, I.K.; Lee, C.H.; Kim, T. Activation of nitrogen species mixed with Ar and H₂S plasma for directly N-doped TMD films synthesis. *Sci. Rep.* **2022**, *12*, 10335. [CrossRef]
- 130. Koudakan, P.A.; Wei, C.; Mosallanezhad, A.; Liu, B.; Fang, Y.; Hao, X.; Qian, Y.; Wang, G. Constructing Reactive Micro-Environment in Basal Plane of MoS₂ for pH-Universal Hydrogen Evolution Catalysis. *Small* **2022**, *18*, 2107974. [CrossRef]
- 131. Bruix, A.; Lauritsen, J.V.; Hammer, B. Size-dependent phase stability in transition metal dichalcogenide nanoparticles controlled by metal substrates. *Nanoscale* **2021**, *13*, 10167–10180. [CrossRef]
- 132. Zhang, Q.; Wang, L.; Wang, J.; Yu, X.; Ge, J.; Zhang, H.; Lu, B. Semimetallic vanadium molybdenum sulfide for high-performance battery electrodes. *J. Mater. Chem. A Mater.* **2018**, *6*, 9411–9419. [CrossRef]
- 133. Shan, A.; Teng, X.; Zhang, Y.; Zhang, P.; Xu, Y.; Liu, C.; Li, H.; Ye, H.; Wang, R. Interfacial electronic structure modulation of Pt-MoS₂ heterostructure for enhancing electrocatalytic hydrogen evolution reaction. *Nano Energy* **2022**, *94*, 106913. [CrossRef]
- 134. Chang, C.; Wang, L.; Xie, L.; Zhao, W.; Liu, S.; Zhuang, Z.; Liu, S.; Li, J.; Liu, X.; Zhao, Q. Amorphous molybdenum sulfide and its Mo-S motifs: Structural characteristics, synthetic strategies, and comprehensive applications. *Nano Res.* 2022, 15, 8613–8635. [CrossRef]
- 135. Tang, M.; Yin, W.; Liu, S.; Yu, H.; He, Y.; Cai, Y.; Wang, L. Sulfur Line Vacancies in MoS₂ for Catalytic Hydrogen Evolution Reaction. *Crystals* **2022**, *12*, 1218. [CrossRef]
- 136. Tang, J.; Wei, Z.; Wang, Q.; Wang, Y.; Han, B.; Li, X.; Huang, B.; Liao, M.; Liu, J.; Li, N.; et al. In Situ Oxygen Doping of Monolayer MoS₂ for Novel Electronics. *Small* 2020, *16*, 2004276. [CrossRef]
- 137. Tayyab, M.; Hussain, A.; Syed, W.A.; Nabi, S.; Asif, Q. Effect of copper concentration and sulfur vacancies on electronic properties of MoS₂ monolayer: A computational study. *J. Mol. Model.* **2021**, *27*, 213. [CrossRef] [PubMed]

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.