

Recent Advances in 2-Dimensional Transition Metal Dichalcogenides as Photoelectrocatalyst for Hydrogen Evolution Reaction

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This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1002/jctb.6335

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Keywords: 2D-TMDs, photoelectrochemical, photocatalyst, water splitting, HER

Abstract

Hydrogen gas has been attracting significant interest as an emerging energy source that is clean, sustainable, and renewable. Primarily, it can be produced via photoelectrochemical (PEC) splitting of water using solar energy. Among the various catalysts employed for the photoreduction of water, two-dimensional transition metal dichalcogenides (2D-TMDs) are inarguably the best candidates toward industrialization because they have extraordinary physical, optical, and electric properties, and are solution-processable at low costs. In this review, we focus on the development of 2D-TMDs and their photoelectrochemical properties toward the hydrogen evolution reaction. First, the synthesis and properties of 2D materials are summarized and discussed. Next, the strategies for improving the photocatalytic activity of the 2D material-based catalysts for water splitting are thoroughly investigated. Finally, the remaining challenges and direction for the future development of 2D-TMDs in photoelectrochemical catalysis-derived hydrogen evolution reaction are addressed.

Introduction

Advancements in modern life require a significant amount of energy for powering industries, agricultural processes, and transportation.¹ However, traditional energy sources, such as oil and charcoal, are limited and nonrenewable.² Furthermore, the burning of fossil fuel causes severe environmental issues, including pollution and global warming. Therefore, the search for clean, renewable, and sustainable energy is paramount. Among the new generation of energy sources, hydrogen energy is one of the most promising alternatives to traditional fossil energy. In brief, hydrogen is abundant, has a large energy density, and can be easily obtained via a water-splitting reaction.^{3,4} Moreover, the combustion of hydrogen to generate electric current is an environment-friendly reaction, which only produces water as the by-product. In principle, hydrogen gas can be obtained via an electrochemical or photoelectrochemical hydrogen evolution reaction (HER).⁵⁻⁷ The electrochemical process requires an electric current source to achieve the reduction potential of water,⁸ whereas the photoelectrochemical process can employ visible light to generate electric current for the reduction of hydrogen.⁹ Although the photoelectrochemical (PEC)-HER consumes zero energy, its practical application is not viable due to its relatively low performance, which does not satisfy the requirements for industrial application. Thus, further exploration and investigation of low-cost catalysts with high photocatalytic activity toward the HER are necessary for the near future.

Recently, the evolution of two dimensional (2D) materials, such as graphene, has profoundly impacted the development of electronic devices, optoelectronic devices, and

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catalysis due to their extraordinary properties, such as high strength, high conductivity, very thin layer, high transparency, and high stability.¹⁰⁻¹⁶ Along with the development of graphene, other 2D materials like transition metal dichalcogenides (2D-TMDs), which have graphene-like structures, have also been thoroughly investigated.^{17, 18} Specifically, each layer of the TMD material, MeX_2 , (Me: transition metal atom, X: chalcogenide atom) consists of a Me atom sandwiched between two X atom layers and bonds to other layers by weak van der Waals interaction.¹⁸ Therefore, materials can be easily exfoliated to a few single layers, which, in this size range, have superior properties to bulk materials. The reduction in the thickness of 2D-TMDs generally results in enhanced conductivity, strength, and stability.^{19, 20} These properties of thin layer 2D-TMDs give rise to their numerous applications, including in solar cells, organic light-emitting diodes, transistors, photodetectors, and gas sensors.²¹⁻²⁹ In addition, they are attractive for application in catalysis due to the high sensitivity of the electronic structure in transition metals.¹⁷ Many recent studies have revealed that the indirect bandgap of 2D-TMDs can be converted to a direct bandgap as their thickness is reduced to few atomic layers, leading to significant enhancement in optical properties, thus enabling their application in photocatalysis.³⁰ Furthermore, the conduction band and valence band of 2D-TMDs are well-matched with the reduction and oxidation potential of water, indicating that they are capable of catalyzing the water-splitting reaction.³¹

This review focuses on the recent developments of 2D-TMDs as catalysts in the PEC-HER. We first summarize and discuss the synthesis methods and catalytic properties of 2D-TMDs for their application in the HER. Next, the advances in the strategies for improving the

catalytic activity of 2D materials, including surface functionalization, structure engineering, and compositional engineering toward highly efficient PEC-HER are highlighted. Finally, the challenges and opportunities associated with the future development of 2D-TMDs for application as catalysts in the PEC-HER are provided.

Structure and properties of TMDs materials

As aforementioned, the TMDs consist of the hexagonal layers formed by sandwiching a transition metal atom layer between 2 chalcogenide layers. Theoretically, the thickness of each layer was about 6-7 Å and the arranging of these layers determines the structure and property of these materials.¹⁸ Typically, the most common structures of TMDs are attributed to 1T, 1T', 2H and 3R polymorphs which correspond to trigonal, hexagonal, and rhombohedral structure (**Figure 1a-b**).³² These structures are formed by the electron filling of the valence d-orbitals of transition metal atoms and p orbitals of chalcogen atoms.³³ **Figures 1c-d** show the bandgap alignment of TMDs and the origin of conduction band minimum and valance band maximum.³¹ The electronic structure and optical bandgap of these materials largely depend on the coordination environment of the transition metals and their d-electron numbers.³⁴ As can be observed from **Figure 1c** that either bandgap or energy level of MX₂ was changed when M or X element in MX₂ was replaced. Notably, most sulfide and selenide based TMDs compounds are semiconductors; however, telluride based TMDs are metallic,

paramagnetic or superconducting (PdTe₂).¹⁸ Herein, we only consider the TMDs that exhibit a good catalytic activity toward HER (the combination of Mo, W and Ti with S and Se). Among TMDs polymorphs, the 1T and 1T' structures are reported to be octahedral and distorted octahedral, respectively. Meanwhile, the 2H phase has two hexagonal layers in the crystallographic unit cell, while the 3R phase contains three rhombohedral layers in its unit cell.³⁵ The 1T and 1T' phases show the metallic behavior as a high conductivity; whereas, the 2H and 3R phases of TMDs are semiconductors with bandgap ranges 0.3–2 eV in bulk.^{34, 36}

Synthesis of 2D-TMDs

Top-down methods

As aforementioned, 2D-TMDs materials have a structure similar to that of graphene, where each layer is bonded to other layers by weak Van der Waals force.¹⁸ The simplest method of cleaving them into thin layers is the scotch tape method.³⁷ Specifically, the surfaces of thin-film pure TMDs are attached to the tape and pulled out many times to obtain the thinnest film, which is a single/few-layer TMDs, as shown in **Figure 2a**.³⁸ However, the materials obtained from this technique are only suitable for surface, structure, and some characterization studies to provide insight into the early development processes. For practical applications, more facile and scalable approaches such as the ball milling method, liquid sonication method, and chemical exfoliation should be developed. To produce atomically thin 2D-TMDs on a large scale, Coleman and his colleagues proposed a liquid sonication method that could effectively exfoliate various 2D-TMDs in various solvents.³⁹ The transmission electron microscopic images (TEM) of the obtained products including single-layer

nanosheets of BN, MoS₂, and WS₂, which were exfoliated using an ultrasonic tip in N-methyl-2-pyrrolidone (NMP) solvent, are shown in **Figure 2b**. The typical setup for the experiment can be seen in **Figure 2c**. Moreover, 2D-TMDs can also be exfoliated using a chemical exfoliation method, which is primarily based on the intercalation of lithium ions into the boundary of interlayers and the expansion of lithium-ion in the presence of water (**Figure 2d**).^{40, 41} Notably, lithium intercalation renders a large amount of electron charge onto the surface of 2D-TMDs, which, in turn, induces the phase transformation from 2H to 1T phase.⁴² The role of the crystal phase of the 2D-TMDs on the performance of the PEC-HER will be thoroughly discussed in the next section.

Bottom-up methods

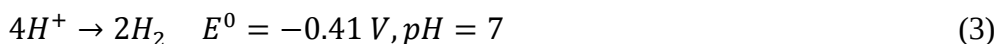
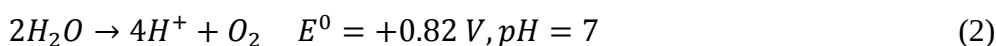
Contrary to the top-down method, the bottom-up method is not initiated with bulk 2D-TMDs materials but precursors containing transition metal sources and chalcogenide sources. Chemical vapor deposition (CVD) is one of the most powerful techniques to obtain high-quality 2D-TMDs with controllable thickness.^{43, 44} The typical procedures for the fabrication of 2D-TMDs using CVD are shown in **Figures 3a–b**.^{29, 45} As can be seen, the ultrathin 2D-TMDs can be achieved by a CVD method with or without the pre-deposition of a transition metal source on the target substrates. When a bare substrate is used in the CVD synthesis, precursors such as metal oxides and chalcogenides evaporate simultaneously and react with each other in the gas phase to form 2D structures (**Figure 3a**). Conversely, for the CVD with pre-deposition substrates, only chalcogenide sources are evaporated and react with the transition metal precursor film for the growth of the 2D-TMDs (**Figure 3b**). Notably, both

CVD methods require a high temperature, from 700–1000 °C.⁴⁴⁻⁴⁹ Depending on the synthetic condition, 2D-TMDs can be fabricated in different morphologies, such as thin films,⁵⁰ triangular nanoflakes,⁵¹ and nanoflowers.⁵² In contrast to the CVD method, the solvothermal approach can be performed at a considerably low reaction temperature range, from 200 to 400 °C (**Figures 3c–d**) For example, Altavilla *et al.* achieved MoS₂ and WS₂ nanosheets at a temperature of 360 °C through the thermal reduction of (NH₄)₂MeS₄ in a long-chain organic ligand and high boiling point solvent (oleylamine/n-octadecene).⁵³ However, the materials produced by this method are not applicable in practical catalysis due to the presence of long-chain organic ligands on the surface, which, in turn, reduces the contact between the active sites and reactants. In contrast to the solvothermal method, the hydrothermal method does not require long-chain organic ligands and solvents. Therefore, it has been widely adopted for the synthesis and engineering of the structure, morphology, and composition. For instance, Zhang *et al.* used a hydrothermal method for synthesizing different MoS₂ morphologies, such as nanospheres and nanoflowers, from MoO₃ and Na₂S.9H₂O as precursors at a temperature range of 200–300 °C.⁵⁴ Chen *et al.* obtained a MoS₂ nanoflake/graphene composite with Na₂.MoO₄.9H₂O, SC(NH₂)₂ and graphene oxide as starting materials ⁵⁵. Interestingly, MoS₂ was formed in the 1T phase at a synthesis temperature lower than 180 °C. At temperatures higher than 210 °C, the 1T phase is converted to 2H phase. Similarly, Yang and coworkers achieved a WS₂/rGO hybrid catalyst through a hydrothermal method by reducing WCl₆ in thioacetamide (C₆H₅NS).⁵⁶ Wang *et al.* used a hydrothermal method to fabricate MoS₂ quantum dots using sodium molybdate

(Na₂MoO₄) and L-cysteine as precursor materials.⁵⁷ These results indicate that the hydrothermal synthesis is a facile method for engineering the nanostructure, size, and morphology of 2D-TMDs, which are critical parameters in the PEC-HER.

Photoelectrochemical catalyst mechanism

Basically, in a semiconductor, the distribution of valence electron wave function creates an energy band that separates the valence band (where the electron is full filled) and the conduction band (where the electron is unoccupied). In a photoelectrolysis process, when photons of visible light are irradiated to the semiconductor, the electrons in the valence band received the photon energy to form electron–hole pairs.⁵⁸ These electron–hole pairs will be separated into electrons and holes, which in turn take part in the electrocatalysis of water to generate hydrogen gas and oxygen gas at the cathode and anode, respectively.⁵⁹ **Figure 4a-b** shows the PEC-HER mechanism where the photoinduced electrons and holes participate in HER to produce O₂ and H₂ on the surface of the catalysts by the following process:^{60, 61}



In the PEC system, the electron and hole are collected via connecting with a conducting electrode. Therefore, the recombination of electron-hole is significantly reduced and the efficiency of the photocatalytic process is improved.⁶² In addition, the external potential was generally employed to manipulate the flow of hole or electron, thus only reduction or

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oxidation process occurs on the working electrode to generate hydrogen or oxygen, respectively. On the counter electrode, the rest process of oxidation or reduction is operated which corresponds to oxygen or hydrogen generation. Thermodynamically, the minimum energy required for the redox process of water is 1.23 eV (Equation 1). At the valence band, the holes contribute to the oxidization of water, giving rise to O₂; meanwhile, at the conduction band, the electrons reduce water to produce H₂. The potentials for the reaction are shown in Equations 2 and 3, respectively.^{63, 64} To achieve a high performance of the water-splitting process, the semiconductor requires a bandgap energy that is close to the redox potential of water. The bandgap of TMDs has been reported to be in alignment with the H₂O redox potential, which is suitable. The energy bandgap can be adjusted using some techniques, including doping, quantum size control, and combining a co-catalyst with a supported catalyst.³¹

Catalytic properties of TMDs

2D materials, especially, transition metal compounds have shown outstanding potential as stable catalyst and high conductivity such as transition metal nitrides, oxides and chalcogenide.^{65, 66} Primarily, the conductivity and sulfur-terminal active sites are two major factors that affect the catalytic properties of TMDs in the HER.^{67, 68} The conductivity of 2D-TMDs is determined by their structure, including 1T, 2H, 3R, and 1T' (as shown at **Figure 1a-b**).^{33, 69-73} The bandgap of TMDs was calculated and measured at low value and indirect bandgap, therefore, it is hard to have effective charge-carrier creation and recombination. In fact, the bulk 2D-TMDs materials have been found to be effective catalysts for

hydrodesulfurization; however, they are inert to the HER and PEC-HER due to the conductivity limitation, low number of active sites, and the indirect bandgap of ~ 1 eV.^{18, 74} Fortunately, the bandgap and active sites of the 2D-TMDs can be tuned via structure and composition engineering, thus enabling their potential in the PEC-HER. In particular, their bandgaps can be tuned in the range 1.7–2 eV, and the band structure can be changed from an indirect to a direct bandgap.^{75–78} The utilization of 2D-TMDs in photocatalysis was first developed by Ho et. al in 2004.⁷⁹ Typically, they combined MoS₂ and WS₂ with TiO₂ and applied them as efficient photocatalysts for the photodegradation of methylene blue, thereby demonstrating their potential for photocatalytic applications. The performance of 2H and 3R phased 2D-TMDs as catalysts in the PEC-HER has been demonstrated; however, their performance is relatively low due to the low number of active sites, low optical absorption in the UV-vis region, and high electron–hole recombination rate.^{17, 80} Interestingly, the 1T-phase 2D-TMDs exhibit a pronounced enhancement in catalytic activity toward the HER compared to that of the 2D-phase 2D-TMDs.⁸¹ The catalytic activity of the 1T-phase 2D-TMDs originates from their affinity for binding H at the surface S sites.⁸² Consequently, the active sites of the 1T-phase 2D-TMDs are on the basal plane instead of the edge sites, as seen in the 2H-phase 2D-TMDs. Moreover, the catalytic activity of 2D-TMDs toward the HER can also be improved through phase engineering,^{83, 84} defect engineering,^{85, 86} metal doping,^{87, 88} and composition engineering.^{89–91}

Improvement of the catalytic performance of TMDs

2D-TMDs/p-Si p-n junction for PEC-HER

P-type silicon (p-Si) is a well-known semiconductor with a low bandgap of 1.1 eV; it is able to absorb a wide range of UV-visible light (UV-vis) for generating electron-hole pairs for use in various photovoltaic devices, such as solar cells or photodiodes.⁹² Conversely, n-type TMDs such as MoS₂ and WS₂ have a much wider bandgap of 1.7–2 eV and high transmission (> 90%), as their thickness is low as single and few layers. Therefore, the presence of a thin 2D-TMD layer does not cause any significant drop in the photovoltaic performance of the bottom p-Si. Furthermore, the combination of 2D-TMDs with p-Si provides not only better electron-hole pair separation by forming p-n junctions but also numerous active sites with appropriate energy potential for the HER. The use of p-Si in photocatalysis was first reported by Hou *et al.* in 2011.⁹³ Typically, in their work, they used an incomplete cubane-like Mo₃S₄ cluster on p-Si as a photocathode for the HER with a current density of 10 mA cm⁻² at 0 V. Thus, this result confirms the importance of p-Si in the PEC-HER. More recently, Kwon *et al.* achieved wafer-scale MoS₂/p-Si and WS₂/p-Si materials as efficient photocathodes for the PEC-HER.^{94, 95} In their study, the wafer-scale MoS₂ thin-film exhibited high transparency, which highly depended on the thickness of the thin film. These highly uniform MoS₂ nanosheets with controllable thickness were synthesized by a CVD process and transferred to the surface of p-Si using a wet transferring approach. It was confirmed that p-Si functioned as a charge generator, which mainly contributed to the generation of electron-hole pairs. Subsequently, these electrons were transferred to MoS₂ and participated in the PEC-HER at the active sites on the surface of MoS₂. Due to the efficient charge generation of p-Si under light illumination, the PEC-HER performance of the photocathode was highly improved with a positive onset voltage at 0.17 V

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and a high photocurrent density of 24.6 mA cm^{-2} at 0 V. The overall performance of $\text{MoS}_2/\text{p-Si}$ as photocathode for PEC-HER is shown in **Figure 5a-f**. However, the reproducibility of this method is very low due to the damage of MoS_2 upon transferring; thus, it is not suitable for large-scale production. To counter this problem, Seo et al. proposed the direct synthesis of MoS_2 , WS_2 , WSe_2 , and the multi heterojunction of these materials on p-Si via pulsed laser deposition.⁹⁶ This report also proved the high performance of the 2D-TMD layer on p-Si as a catalyst for the PEC-HER. More recently, Hasani *et al.* reported the direct synthesis of MoS_2 and WS_2 on p-Si by a CVD process, thus solving the major problem of reproducibility in Kwon's work.^{97, 98} These results indicate that p-Si is an important combination for boosting the efficiency of 2D-TMDs toward a high-efficiency PEC-HER.

TMDs co-catalysts for PEC-HER

The common TiO_2 photocatalytic material is always under consideration for application in the HER due to its high oxidation potential, physical and chemical stability, and its absorption efficiency.⁹⁹ However, the energy band alignment of TiO_2 is not suitable for efficiently producing hydrogen through photoreduction reaction.¹⁰⁰⁻¹⁰⁴ On the contrary, the absorption of 2D-TMDs is weak; however, the band alignment is suitable for the redox potential of water. Therefore, the composites formed by 2D-TMDs with TiO_2 are expected to be promising catalysts for high performance PEC-HER.¹⁰⁵⁻¹⁰⁷ The mechanism of $\text{TiO}_2\text{-MoS}_2$ co-catalyst is shown in **Figure 6a**.¹⁰⁸ Through this approach, Liu and coworkers obtained an effective catalyst for the PEC-HER from a core-shell structure comprised of $\text{N-TiO}_2\text{-x@MoS}_2$; the obtained catalyst exhibited a high rate of hydrogen reduction ($1.88 \text{e mmol h}^{-1}$

g⁻¹).¹⁰⁹ The high catalytic performance of this composite material originates from the synergistic effect of N and Ti³⁺ co-doped, and the narrow bandgap of MoS₂, which restrains the recombination of the electron-hole pairs. Similarly, Shen *et al.* successfully achieved a very high hydrogen generation rate of 16.7 mmol h⁻¹ g⁻¹ (**Figure 6b**) from a co-catalyst constructed by MoS₂ nanosheets and 1D TiO₂ nanowire.¹¹⁰ Apart from MoS₂, the composite catalysts of other 2D-TMDs such as MoSe₂, WS₂, and WSe₂ are also produced with enhanced performances toward the PEC-HER compared to the case with bare 2D-TMDs.¹¹¹⁻¹¹³ Apart from TiO₂, other metal oxides such as WO₃, Fe₂O₃, ZnO, MoO₃, SnO₂, and Cu₂O have also been considered.¹¹⁴⁻¹¹⁹ For example, Yang and coworkers have reported a WO₃/WS₂ composite as a catalyst with excellent kinetics toward the PEC-HER.^{120, 121} Moreover, 2D-TMDs can also be combined with other light absorbers such as CdS, CdSe, CdLa₂S₄, and carbon nitride (g-C₃N₄) to form co-catalysts for the PEC-HER (**Figures 6c-d**).¹²²⁻¹²⁵ For example, Andrew et al. used the composite of CdSe nanoribbons and MoS₂ for improving the PEC-HER performance in an aqueous sodium sulfite/sulfide solution, showing a quantum efficiency of 9.2%.¹²⁵ Tekalgne *et al.* attempted to decorate the CdSe quantum dots on WS₂ nanoflowers via a hydrothermal method for improving the performance of the PEC-HER.¹²⁶ They suggested that the CdSe quantum dots with 10 nm sizes and a mixture of 10 wt% with WS₂ nanoflowers could offer the best catalytic activity toward the PEC-HER.

2D-TMDs heterojunction for PEC-HER

Apart from paring with other materials to form n-p junction catalysts, the 2D-TMDs can be combined with each other to construct a p-n heterojunction for the PEC-HER. It is well-

known that most of the 2D-TMDs exhibit n-type behavior due to the abundant electrons of chalcogenide atoms. Nevertheless, a typical 2D-TMD, namely WS₂, shows p-type behavior.^{127, 128} Thus, the formation of a p–n heterojunction based solely on 2D materials is possible. For example, Xiao *et al.* successfully fabricated a MoS₂/WSe₂ bilayer heterojunction and used it as an efficient photocathode for the PEC-HER.¹²⁹ For a uniform distributed p–n junction, either WSe₂ or MoS₂ was fabricated via a CVD method and transferred layer by layer onto an Au electrode using polystyrene as the supporting polymer. The bandgap and band alignment of the thin-films of MoS₂, WS₂, and WSe₂ with p-Si are shown in **Figure 7**. The use of stacking heterojunction MoS₂/WSe₂ as PEC cathode exhibited an improved photo-to-current conversion efficiency of about 50% in the range of 400–680 nm compared to that of the bare WSe₂ electrode. Seo and coworkers also proved that charge-transfer in the multi-heterojunction MoS₂/WS₂/WSe₂ for Si-based PEC-HER is significantly improved compared to that of the homo-catalysts due to the multitargeted gap.⁹⁶ These results demonstrated that 2D-TMDs can form p–n heterojunctions for use as efficient photocatalysts in the PEC-HER.

TMDs and carbon-based 2D materials for PEC-HER

Graphene is the first famous 2D material that exhibits extraordinary physical, electronic, optical properties. This material was widely used in various applications and devices as the transparent conductive electrodes or enhance the strength of materials for constructions, components or architectures. Interestingly, reduced graphene oxide (an imperfect graphene structure) can combine with a catalyst to improve the conductivity and separation of the

electron/hole to minimize the recombination of charges.¹³⁰ Practically, MoS₂ and WS₂ has been composited with rGO to enhance electrocatalytic and photocatalytic performance in hydrogen production.¹³¹⁻¹³³ While the graphene mostly acts as conductive materials for support of the charge-carrier transferring, the graphitic carbon nitride (g-C₃N₄) is a type of semiconductor that can be used as a catalyst for PEC. In specific, g-C₃N₄ exhibits many advantages such as physical, chemical stability, wide range of visible light absorption, simple fabrication by pyrolysis.⁶⁶ Recently, Pramoda et al. have combined 1T MoS₂/g-C₃N₄ and nitrogenated rGO as a co-catalyst for hydrogen evolution reaction.¹³⁴ The covalent cross-link of these composite materials indicates their potential for the application in PEC.

Defect engineering TMDs for PEC-HER

The active site of TMDs is not only presented at the edge sites but also the defects and vacancies on the surface of these materials. By using DFT calculation, Ouyang et al. proposed that the intrinsic defects in the MoS₂ layer create more S vacancies and some typical defects. These vacancies and defects can contribute as active sites for PEC-HER such as V_{MoS3}, MoS₂ point defects, 4|8a, S bridge, Mo–Mo bond grain boundaries.¹³⁵ The roles of defect structures and edge configuration on the stability and catalytic property of MoSe₂ for HER were experimentally demonstrated by Shu and co-workers.¹³⁶ Typically, the introduction of defects to MoSe₂ could facilitate the adsorption of H atoms and the desorption of H₂, therefore, enhance the efficiency of hydrogen production. Besides, MoS₂, MoS₂, WS₂, and WSe₂ have also been engineered in terms of increasing the defects through crumbling the large materials into small particles or doping foreign element into the lattice of TMDs such as

metal dopant or S dopant.¹³⁷⁻¹⁴³ Nevertheless, the number of publications about these surface modification and defect engineering on TMDs for PEC-HER is still limited. The unstable state of TMD surface due to the defects generally resulted in the short durability of catalyst under working condition, therefore, it still need more practical and theoretical method to solve this problem.

Conclusion and outlook

A green, eco-friendly fuel such as hydrogen is a promising candidate for replacing traditional fossil fuels such as charcoal and oils. By using an unlimited natural energy resource from sunlight, photoelectrocatalysis is a promising method for producing hydrogen in the near future. However, most of the development of catalyst material and build-up the system for PEC-HER is still limited in the laboratory scale. Nonetheless, it is clearly observed through the review that the nanomaterials and nanotechnology are dramatically developing. Thus, the 2D materials such as TMDs with superior physical properties, good chemical stability, high catalytic activity, low cost, and earth-abundant are viable for the utilization in large scale PEC-HER, targeting industrialization.

The development of TMDs for PEC-HER is currently focusing on improving light absorption, charge transfer efficiency, phase stability, scalability and reproducibility, targeting industrial scale. In specific, the combination of TMDs with some large bandgap materials showing the improvement of light absorption. Nonetheless, the engineering of band alignment is needed to optimize the range of absorption. Moreover, the contact of these material surfaces also creates the charge trapping point which can reduce the charge transfer

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efficiency. Also, the adhesion of 2D materials onto an electrode needs to be taken into account for improving the stability of the device. Furthermore, phase-engineering is also an important approach to improving the catalytic activity of 2D-TMDs. Generally, the 1T-phase 2D-TMD materials are the most active for the HER; however, this phase is not stable enough for practical application compared to the 2H phase of 2D-TMDs. Therefore, more investigations on the phase-engineering of 2D-TMDs are required. Furthermore, employing a fabrication method with high reproducibility and scalability, and at a low cost is crucial for commercialization. Therefore, future development of 2D-TMDs for application in the PEC-HER should focus on (1) improving the visible light absorption to maximize the light to electricity efficiency; (2) improving the catalytic activity of 2D materials via functionalization, structure engineering and compositional engineering; (3) improving the stability of materials under working condition; (4) improving the scalability and reproducibility of the synthetic methods targeting commercialization.

In summary, this review provides the most recent significant advances in the design and utilization of TMD materials as photocatalysts in the HER. In particular, the developments of synthetic methods such as mechanical exfoliation, solvothermal growth, and chemical vapor growth were discussed. Next, the strategies for improving the performance of TMDs in the PEC-HER through paring with photo-active materials such as p-Si, transition metal oxide, and quantum dots materials are summarized and discussed. Some breakthroughs in 2D-TMDs as catalysts for the PEC-HER are highlighted. For example, the p-n-junction-based photocatalyst formed by MoS₂ thin-films with p-doped Si exhibited excellent photocatalytic

activity with a high current density of 24.6 mA cm⁻² at 0 V. Nevertheless, many challenges still need to be resolved before these 2D materials can be practical.

Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government (MSIT) (NRF-2018R1A1A1A05018332).

Notes

The authors declare no conflict of interest

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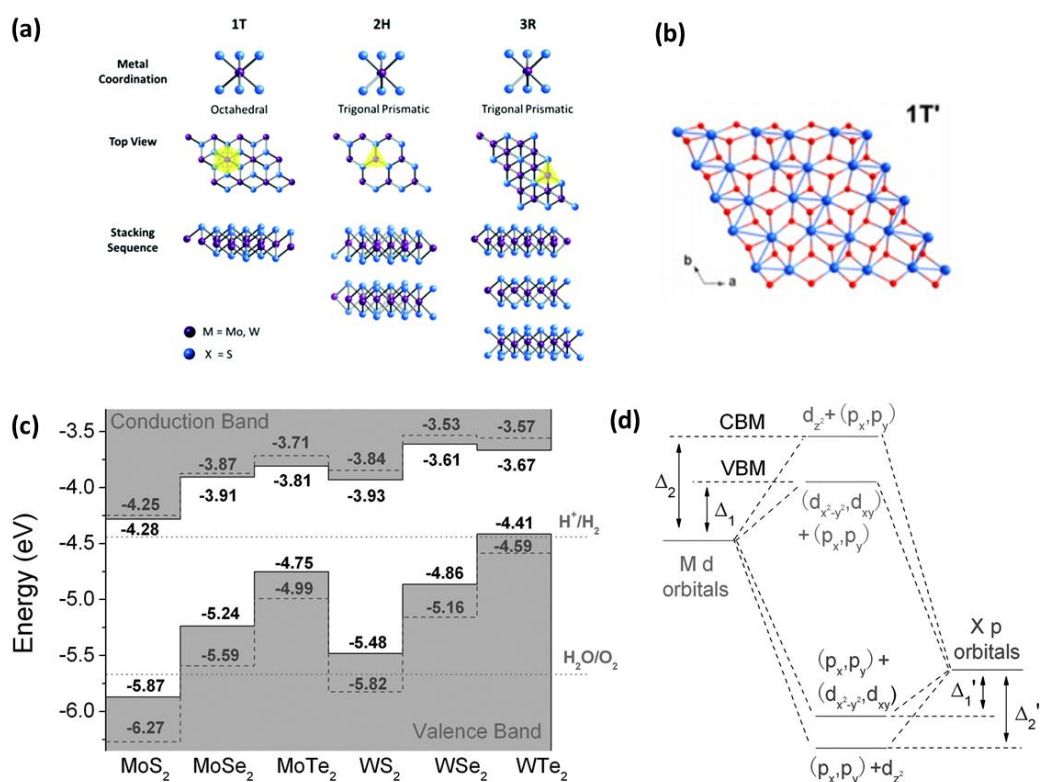


Figure 1. (a) 1T, 2H, 3R phases of TMDs materials (reproduced with permission).³⁵ (b) 1T' phase TMDs (reproduced with permission).³⁶ (c) Band alignment of monolayer TMDs, and (d) schematic of the origin of CBM and VBM in MX₂ (reproduced with permission).³¹

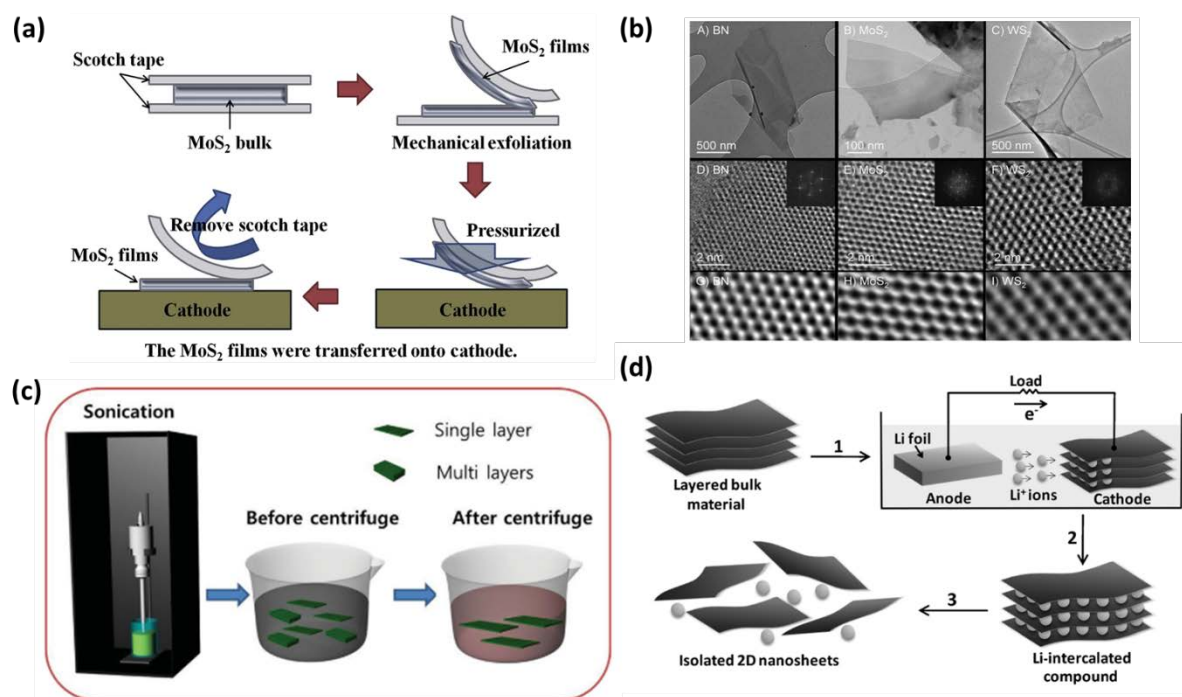


Figure 2. Top-down synthetic method of 2D-TMD materials: (a) scotch tape method (reproduced with permission).³⁸ (b) TEM images of some TMDs materials (BN, MoS₂, WS₂) obtained by the sonication method (reproduced with permission).³⁹ (c) Sonication method (reproduced with permission).²⁴ (d) Lithium intercalation method (reproduced with permission).⁴¹

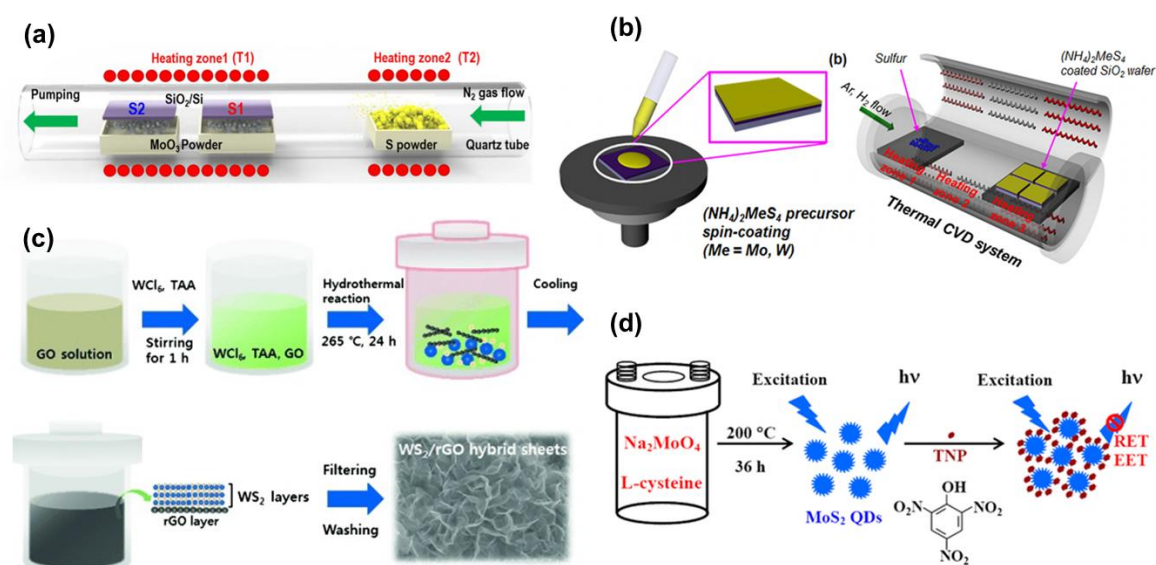


Figure 3. Bottom-up synthetic method of 2D-TMDs: (a) chemical vapor deposition method without pre-deposition of transition metal film on substrates (reproduced with permission).⁴⁵ (b) Chemical vapor deposition method without pre-deposition of transition metal film on substrates (reproduced with permission).²⁹ (c) Hydrothermal method for WS₂ nanoflower/graphene oxide (reproduced with permission).¹⁴⁴ (d) Hydrothermal method for MoS₂ quantum dots (reproduced with permission).⁵⁷

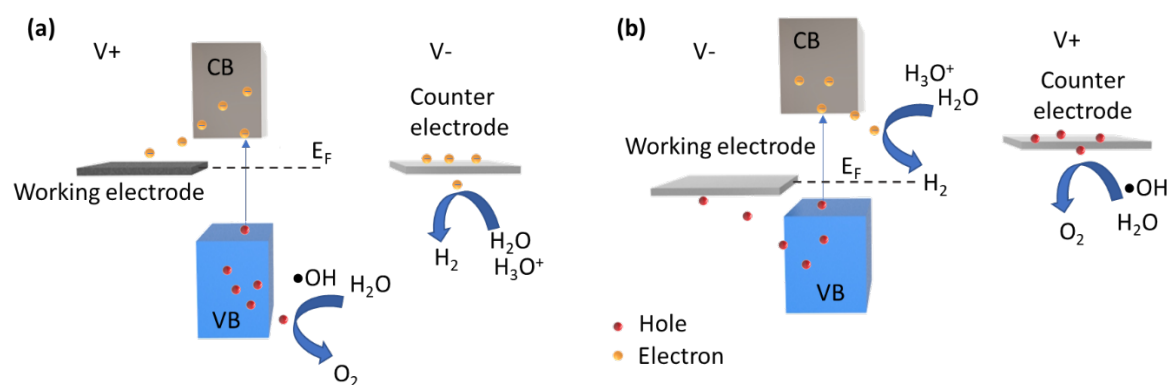


Figure 4. Redox mechanism of the photoelectrocatalyst (a) n-type semiconductor and (b) p-type semiconductor in band alignment of materials with conductive working electrode.

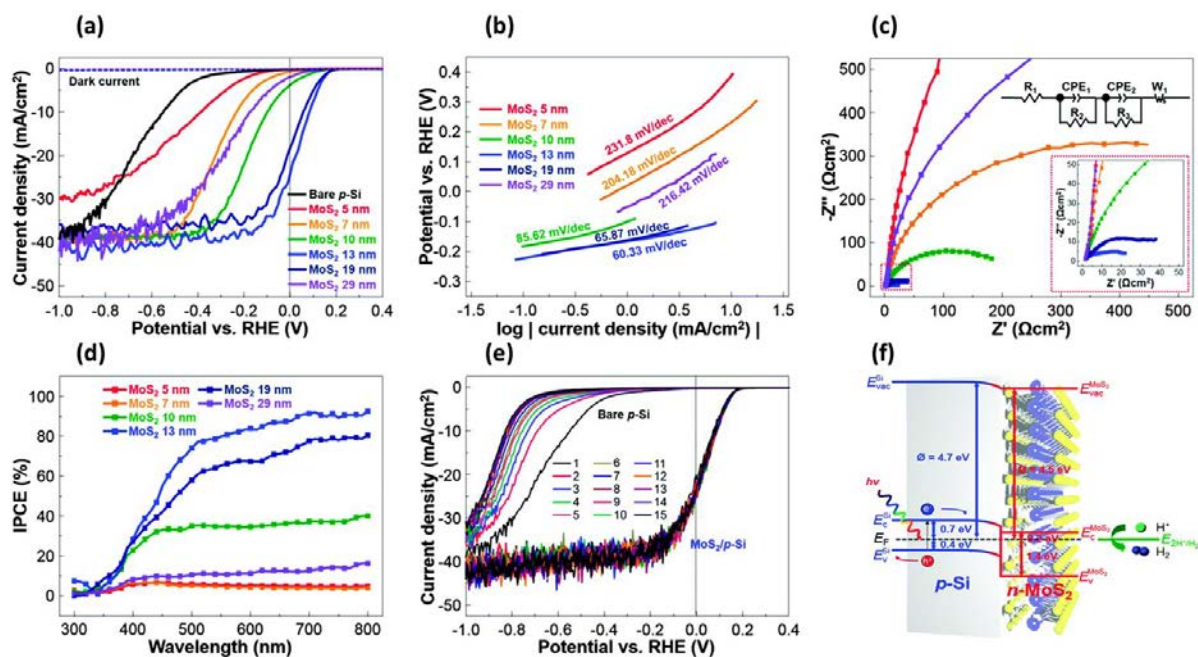


Figure 5. (a) PEC performance shown as polarization J-V curves of MoS₂ films of different thicknesses. (b) Tafel slopes of MoS₂ layers plotted as log (j) against potential vs. RHE. (c) EIS analysis of MoS₂/p-Si heterostructures. (d) IPCE measurement of various thicknesses MoS₂/p-Si photocathodes. (e) Cyclic test over 15 cycles. (f) Schematic of the energy band diagram of MoS₂/p-Si heterojunction (reproduced with permission).⁹⁴

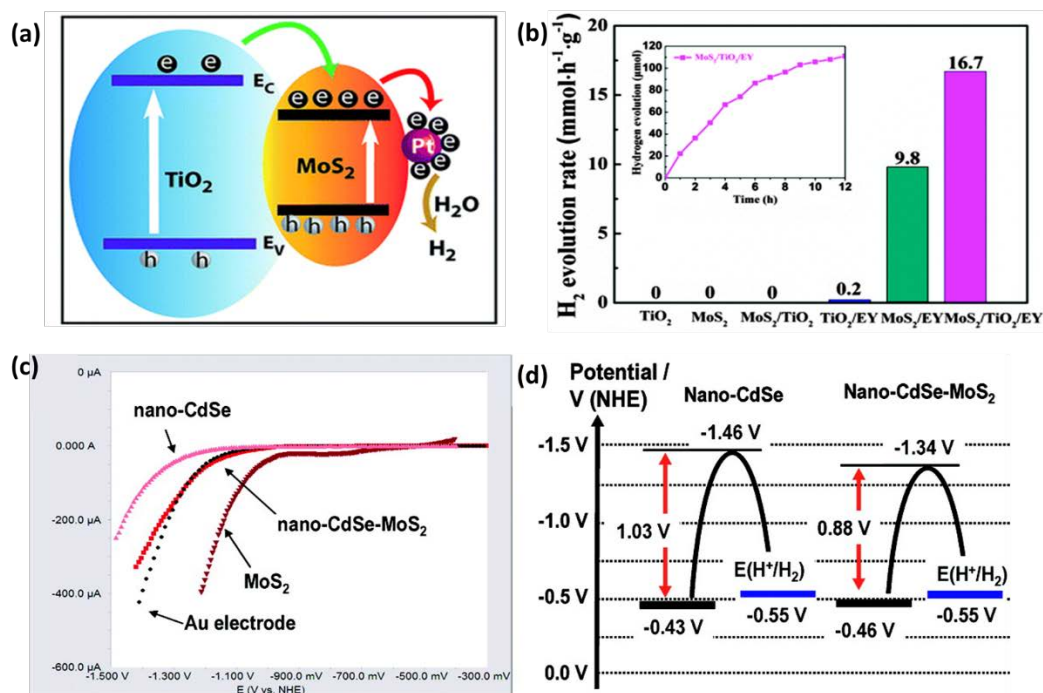


Figure 6. (a) Mechanism of co-catalyst MoS₂/TiO₂/Pt for hydrogen production (reproduced with permission).¹⁰⁸ (b) Different photocatalytic hydrogen evolution rates within 3 h with some catalyst compared to the case with the MoS₂/TiO₂ nanowire (reproduced with permission).¹¹⁰ (c) Cyclic voltammograms in 0.1/0.1 M Na₂S/Na₂SO₃ solution (pH = 9.3), and (d) band energy diagram for nano-CdSe and CdSe–MoS₂ (reproduced with permission).¹²⁵

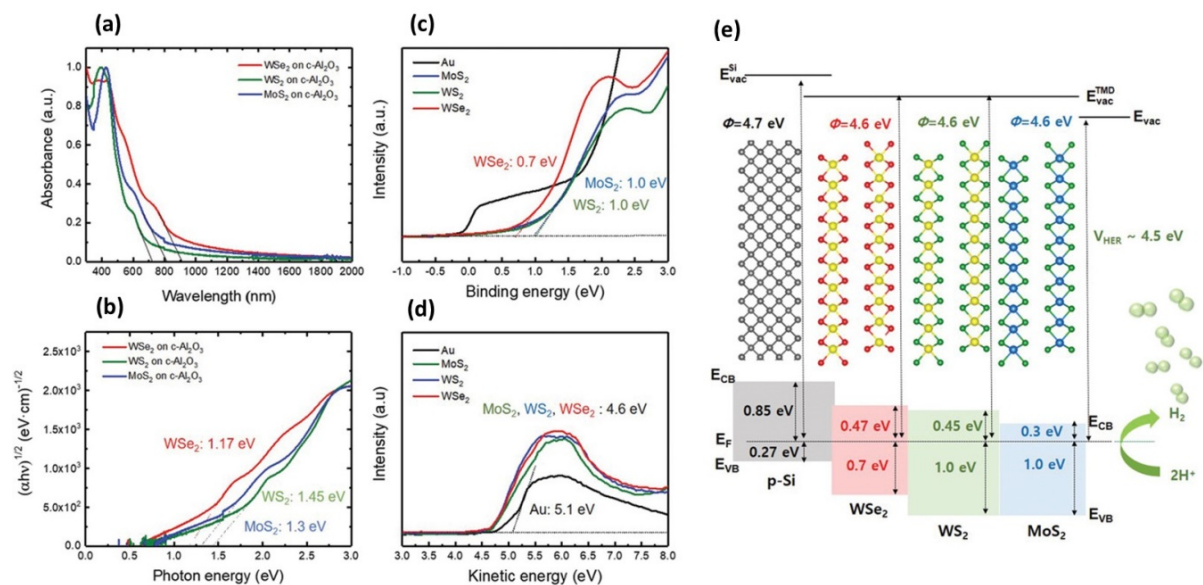


Figure 7. (a) Absorption spectra and (b) Tauc plot of MoS₂, WS₂, and WSe₂ for determining the optical bandgap energy. Ultraviolet photoelectron spectrum data for determination of (c) valance band maxima and (d) work function. (e) Schematic diagram of the energy band alignment with p-Si (reproduced with permission).⁹⁶