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MoS_2 Electrocatalysts for Hydrogen Evolution Reaction: Progress, Challenges, and Perspectives

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ABSTRACT

Molybdenum disulfide (MoS_2) has emerged as one of the most promising non-precious electrocatalysts for the hydrogen evolution reaction (HER), owing to its earth abundance, tunable electronic structure, and high catalytic activity at edge sites. Unlike platinum-based catalysts, MoS_2 offers a cost-effective and scalable alternative, yet its performance is limited by poor electrical conductivity, low intrinsic activity of basal planes, and stability challenges under long-term operation. Recent progress in engineering strategies such as defect creation, phase modulation, heteroatom doping, and hybridization with conductive substrates has significantly improved charge transport and increased the density of active sites. Moreover, integration with carbon-based materials and development of nanostructured architectures have enhanced durability and efficiency in acidic and alkaline electrolytes. Despite these advances, challenges remain in achieving industrial-scale performance, understanding mechanistic pathways at the atomic level, and ensuring long-term stability under realistic operating conditions. This paper reviews recent developments in MoS_2-based HER electrocatalysts, highlights critical challenges, and outlines future perspectives toward designing highly active, durable, and scalable MoS_2 systems for sustainable hydrogen production.

Keywords: MoS_2, Electrocatalyst, Hydrogen Evolution Reaction, Nanostructures, Renewable Energy.

1. Introduction

International energy crisis and green issues have intensified the pursuit of renewable and sustainable sources of energy. Hydrogen has been one of the most promising alternatives because of its high energy density, eco-friendliness and abundance[1]. The electrochemical hydrogen evolution reaction (HER) is one of the most effective and clean pathways among the number of hydrogen production methods. Nevertheless, creation of low cost, highly active, and stable electrocatalysts is still a critical challenge[2]. Over the past years, molybdenum disulfide (MoS_2), a substance of the transition metal dichalcogenides (TMDs) family, has been regarded with great interest as a non-noble metal catalyst to perform the process of HER[3]. MoS_2 has a special layered structure where one plane of S atoms is on top of a plane of Mo atoms, and on the top of both these are van der Waals forces. The properties that this structure has are amazing like ability to tune the bandgap, high spin orbit coupling and high chemical stability[4]. Notably, the edge sites are the main contributors to catalytic activity of MoS_2, but basal planes are rather inactive[5]. Hence, the rationales in enhancing the HER performance of MoS_2 lie in the development of engineering approaches to reveal additional active sites and to enhance the natural conductivity of the material. Direct bandgap of monolayer MoS_2 is about 1.8 eV, whereas an indirect bandgap in multilayer and bulk MoS_2 produces a characteristic electronic and optical behavior[6]These properties have rendered MoS_2 very appealing to many applications such as electronics, sensing, energy storage, and catalysis[7]. In the case of HER, MoS_2 has been actively studied because it is abundant on earth, cheap and can be produced taxonomically through scalable routes[8]. However, pure MoS_2 has low conductivity and low availability of the active site, which limits its large-scale realistic use[9]. To overcome these difficulties, the design of MoS_2 based electrocatalysts has been largely developed. Some of the strategies are phase engineering (1T metallic phase), defect creation, heteroatom doping, vertical alignment of nanosheets, and interfaces with conductive substrates (e.g., graphene or carbon nanotubes)[10]. The methods enhance the quantity of active sites, electron transportation, and the hydrogen adsorption free energy (ΔGH), which are all fundamental to an effective HER[11].

2. Fundamentals of Her

Since the discovery of graphene oxide, the attention to 2D materials is increasing day by day. And following this attention, TMDs (Transition Metal Dichalcogenides) show emerging potential as intriguing and efficient electrocatalyst materials. TMDs are not only recognized for their catalysis action but also for their promising chemical stability [12]. It offers tailoring properties and can be tuned from semiconductors to metal like materials for a range of dynamic applications. The transition metal and chalcogen atoms are stacked with adjacent layer by week Van Der Waals forces [12].

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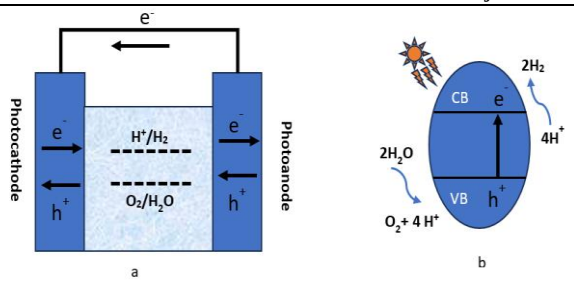

Fig. 1 Schematic representation of (a) PEC cell for H2 production (b) mechanism of h^+/e^- production.

Production of h^+ and e^- using light facilitate the reduction of reduction and oxidation of water to give H_2 and O_2 respectively. Typically, photoelectron chemical (PEC) cells can be constructed via three distinct ways; semiconductor photoanode and a metal cathode, a semiconductor cathode and a counter electrode, and a semiconductor cathode and electrode. When light strikes the electrodes, electrons are promoted to conduction band (CB) which reduce H^+ ion into H_2 from valence band (VB) leaning a hole which participates in oxidation reaction, converting water molecules into O_2.

At Photoanode (Oxidation):

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$$

At Photocathode (Reduction):

$$4H^+(aq) + 4e^- \rightarrow 2H_2(g)$$

In each case, the activity of semiconductor materials under light is crucial. Considering the property of different types of materials, TMDs offer good stability, durability and ability to harness light in different ranges enabling it to be a promising material as HER and OER photocatalyst to split water [13].

3. Synthesis and Structural Engineering of MoS_2

Hydrothermal synthesis facilitates the bottom-up growth of MoS_2 nanostructures such as nanoflowers and nanosheets with controllable morphology. It can also achieve phase control by tuning reaction parameters (temperature, precursors, duration). For example, hydrothermally synthesized 1T-MoS_2 exhibits substantially better (lower overpotential at 10 mA/cm², better stability) HER performance than 2H-MoS_2, demonstrating the advantages of controlled hydrothermal methods for engineering phases (Mazumder et al., 2025, Materials Advances)[14].

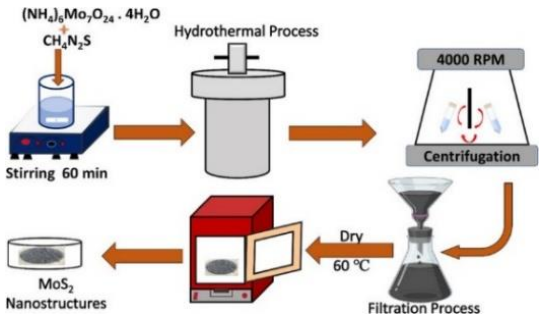

Fig. 2 Hydrothermal Synthesis of MoS_2[15].

Chemical vapor deposition makes it possible to grow large-area thin or monolayer MoS_2 which is atomically thin and has a good degree of crystallinity and uniformity which is ideal to maximize electron mobility and minimize defects which act as charge recombination sites. In an ACS-Nano Q1 publication, a CVD-grown monolayer MoS_2 on Au foils is reported to exhibit a low Tafel slope of ~61 mV/decade and high exchange current density, attributed to the dense active edge sites and robust interaction with the Au substrate[16].

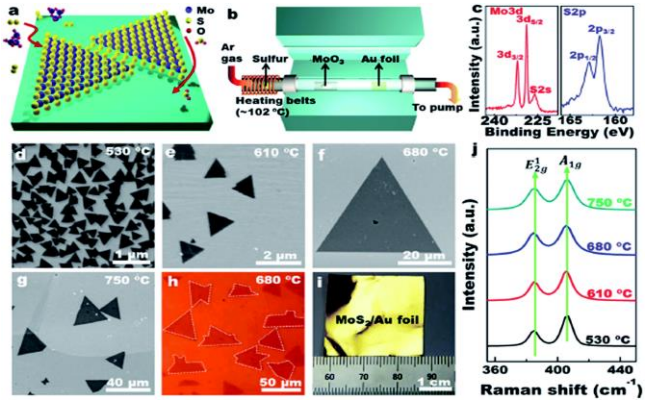

Fig. 3 CVD synthesis of monolayer MoS_2 on Au foils[17].

For instance, in the report "MoS_2 quantum dot-interspersed exfoliated MoS_2 nanosheets" (ACS Nano, 2014), the hybrid morphology of quantum dots plus few layers provided low overpotentials for HER, owing to higher active-site density and faster electron transfer[18].

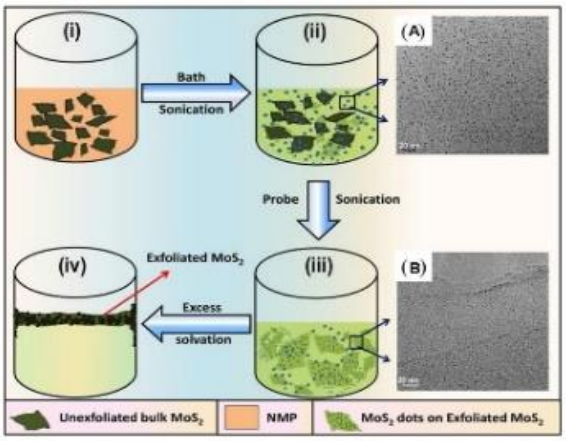

Fig. 4 Schematic diagram of 0D MoS_2[19].

4. Strategies to Enhance HER Activity

MoS_2 is an emerging candidate for HER because of being highly active and more stability than Pt. It was experimentally proven that MoS_2 layers with 2H phase, basal planes are comparatively inert but only edge have high activities of HER [20]. On the other hand, MoS_2 with 1T phase is catalytically active in both edge and basal planes. That's why, the transition of MoS_2 from 2H phase to 1T phase with the help of Lithium insertion which provides an improved performance of HER but the application of 1T phase MoS_2 is limited due to unstable nature [21]. On the other hand, amorphous, mesoporous, or nanosized 2H phase MoS_2 structures with more active sites have shown great improvements in HER, that is, higher turnover frequency, higher current density and lower overpotential [20]. Metal dopants like Co, Fe, Cu, Ni, Mn, Ru, Rh, and Ta can modify

sulfur binding at TMD edges, potentially optimizing hydrogen adsorption free energy for HER. However, recent studies by Pumera's group found that bulk p-doped TMDs (MoS_2 and WS_2 with Nb or Ta) showed lower catalytic activity than undoped materials [22]. First-principles calculations indicate that strain strongly affects hydrogen adsorption on 1T WS_2: Gibbs free energy is 0.28 eV without strain and reaches 0 eV at 2.7% strain. It is uncertain if a catalyst sheet can sustain such non-zero strain [23].

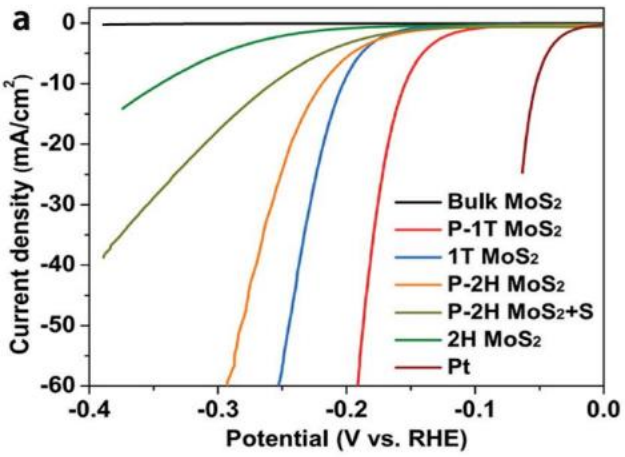

Fig. 5 Current density Vs Overpotential Graph for different phases of MoS2 and Pt [24].

MoS_2 nanosheets with 34–40% disorder showed HER activity close to Pt, with an overpotential ~160 mV higher than Pt. Integrating metal chalcogenides with graphene or doped graphene improves conductivity and HER kinetics. Notably, MoS_2/NGO achieves 10 mA cm^{-2} at just 56 mV overpotential, making it one of the best non-noble metals nanosheet catalysts, with a Tafel slope of 41.3 mV/dec, approaching that of commercial 20% Pt/C (30 mV/dec) [25]

Table 1 Electrochemical performance of different forms of MoS_2 [25].

Catalyst	Electrochemical Performance
Hierarchical MoS2 nanosheets	Overpotential @10 mA cm^2: 0.167 V Tafel slope: 70 mV dec^{-1}
Metallic-phase MoS2 nanosheets	Overpotential @ 10 mA cm^2: 0.175 V Tafel slope: 41 mV dec^{-1}
MoS2/mesoporous G	Overpotential @ 10 mA cm^2: 0.14 V Tafel slope: 42 mV dec^{-1}
MoS2/N-doped G	Overpotential @ 10 mA cm^2: 0.056 V Tafel slope: 41.3 mV dec^{-1}
MoS2/G	Overpotential @ 10 mA cm^2: 0.11 V Tafel slope: 67.4 mV dec^{-1}

5. MoS_2-Based Electrodes Architecture

The electrode design significantly determines the catalysis efficiency of MoS_2 based systems for HER. Since the intrinsic activity of MoS_2 originates predominantly from their edge sites, the way they are constructed as a nanosheet, film or composite is a key factor that controls how efficiently these active sites could be accessed [26], [27]. Smart electrode design could achieve both maximal exposure of catalytic sites as well as effective electron transport and promote mass transfer of reactants while ensuring good mechanical stability under the electrochemical environment [28].

5.1. 2D Nanosheets and Thin Films

MoS_2 nanosheets are one of the simplest electrode designs using these methods. Due to the high surface area and ultrathin morphology, more catalytic sites can be exposed compared to bulk MoS_2. They are not only conveniently assembled as thin films on conductive supports (e.g., glass carbon, nickel foam, graphene) but can also offer uniform and smooth catalytic surfaces [29]. The main benefits are short electron transport distances and the potential to tune the film-thickness to balance conductivity and catalytic access[30]. For example, vertically stacked MoS_2 thin films present relatively more edge sites to the electrolyte than randomly packed ones, which leads to improved catalytic activity toward the HER [31].

5.2. Comparative Evaluation

Each kind of electrode structure has its own advantages and disadvantages. Two-dimensional nanosheets are easy to fabricate with tunability, but they may aggregate[32]. The 3D framework maximizes the exposure of the active site and should benefit mass transfer whereas being more complicated to synthesize [33]. Flexible electrodes provide mechanical flexibility but may sacrifice surface area, however. Optimum strategies frequently rely on hybrid materials that incorporate several aspects such as flexible 3D structures, or vertically oriented nanosheet networks on porous substrates [32].

Table 2 Comparative Analysis of Different MoS_2 Based Electrodes.

Electrode architecture	Key features	Advantages	Limitations	Typical applications
2d nanosheets / thin films	Ultrathin layers deposited on conductive substrates [29]	High surface area, tunable thickness, short electron paths [31]	Restacking reduces activity; limited bubble release [30]	Lab-scale studies, fundamental mechanistic investigations [29]
3d porous frameworks	Hierarchical, interconnected pore networks [34]	Maximized edge exposure, fast mass transfer, efficient bubble removal [35]	More complex synthesis, scalability challenges [36]	Large-area electrodes, industrial hydrogen generation [36]
Flexible & binder-free electrodes	Direct growth on carbon cloth, foils, or polymers [37]	No binder resistance, high conductivity, mechanical flexibility [38]	Moderate surface area; may require optimization for durability [39]	Portable/wearable hydrogen devices, flexible electrolyzes [38]

6.Challenges in MoS_2 Electrocatalysis

There are several challenges for the use of MoS_2 as an electrocatalyst. As there is great potential for use of MoS_2 as energy storage, this has no large-scale production with a lower cost. 2H MoS_2 has low conductivity, and 1T MoS_2 has less stability. Further research is needed to enhance the doping performance of MoS_2. It gives better performance with MoS2 for use in composite sites. So, further research will help to increase the efficiency of MoS_2 composites. It needs better control to maintain the purity, particle size, and crystal structure. MoS_2 also has an agglomeration problem. The surface structure of MoS_2 is complex, which is why it has fewer characteristics than noble metals. The selective cation, anion of MoS_2, also creates effects on the mechanism of the electrolyte [40].

7.Future Perspectives

Hydrogen Evaluation Reaction (HER) is helpful for high-range production of Hydrogen. Non-acidic HER is now a focusing topic for MoS_2 electrocatalysis, because it has low corrosion, eco-friendliness, safety, and is also economical for electrolysis by using seawater. MoS_2 is used as an HER catalyst without any noble metal. Non-acidic HER is a slow process, because there is a unique mechanism. The catalytic efficiency of MoS_2 depends on its phase and electronic structure. It needs to clarify the relationship between structure, physicochemical properties, and HER activity. It needs to track all the steps of HER by using Spectroscopy, advanced microscopy, in situ techniques, and atomic-scale simulation [41]. To increase HER performance, it needs to increase the intrinsic catalytic activity, enhance electronic conductivity, create more active sites, etc. High-entropy composition and core-shell structure techniques help to enhance HER performance. New structures, such as structure design, composites, and doping, will help to increase the performance of MoS_2. So, further research is needed to enhance the work performance of MoS_2 for many electrical, industrial and economical applications [42]

8. Conclusion

Through this article a constructive and comprehensive discussion on recent advancement and development on hydrogen evaluation reaction using MoS_2 is built up. Over the article, the fundamental reaction and mechanism of hydrogen HER, synthesis and structural engineering of MoS_2, strategies to enhance HER activity of MoS_2, MoS_2-based electrode architectures, electro-chemical performance of MoS_2 HER catalysts, challenges in MoS_2 electrocatalysis and future perspectives are discussed thoroughly. TMDs are well recognized for their photocatalysis activity. MoS_2 is specially known for its good chemical stability and tailoring properties. Though it faces some challenges like overall high-cost installation, charge recombination and agglomeration problem. Non-acidic HER is a sluggish process. To improve catalytic activity, structural modification, modification of catalytic activity, electronic activity and increased active site need to be considered. So, scientists and engineers have a large room to work to mitigate these issues. Further intensive research and investigation on MoS_2 based hydrogen evaluation reaction (HER) can make this a potential solution for renewable energy technology.

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