

Hydrogen Production by Electrocatalysts Based on Transition Metal Dichalcogenides

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ABSTRACT

Transition metal dichalcogenides (TMDs) are a class of two-dimensional materials with intriguing physical and chemical properties. Consequently, they have attracted significant interest in various disciplines. Owing to their high catalytic activity, excellent chemical stability, and large specific surface area, TMDs are potential alternatives to precious metal-based electrocatalysts in the hydrogen evolution reaction. This review presents strategies for efficient hydrogen generation by TMD-based electrocatalysis, and discusses future challenges for these material systems.

INTRODUCTION

Hydrogen generation technologies are considered as promising alternatives to unsustainable and ecologically damaging fossil fuels. Many studies have focused on the

development of hydrogen generating water electrolysis catalysts. Precious metal-based catalysts such as Pt and Ru are the most efficient catalysts for the hydrogen evolution reaction (HER), but their scarcity, high-cost, and low stability limit their widespread industrial applications. Therefore, earth-abundant and low cost electrocatalysts that deliver the desirable electrocatalytic performance and stability are in high demand. Recently, transition metal-based electrocatalysts have shown promising potential as efficient hydrogen generating electrocatalysts, with performances comparable to those of precious metal-based catalysts. Among these materials, transition metal dichalcogenides (TMDs) deliver the prerequisite high catalytic activity, price competitiveness, and chemical stability required for HER electrocatalysts. As shown in Fig. 1, layered TMDs generally have the chemical formula MX_2 (where M is a transition metal and X is a

MX_2 (transition metal dichalcogenides)																					
M: transition metal X: chalcogen (S , Se , Te)																					
H																	He				
Li	Be															B	C	N	O	F	Ne
Na	Mg															Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr				
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe				
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn				
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo				

Fig. 1: Periodic table highlighting the representative transition metals and chalcogen elements in TMDs [1].

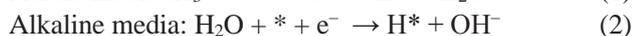
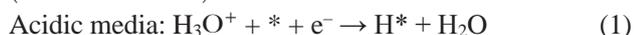
chalcogen such as S, Se, or Te). The unique characteristics of TMDs originate from their polymorphism, which depends on the atomic bonding arrangements between the transition metal and chalcogen atoms, and on the stacking order between each layer. Representative crystalline structures of TMDs are the 2H (hexagonal), 1T (trigonal), and 3R (rhombohedral) phases. The different electronic structures within each crystalline phase confer distinct catalytic activities. Density functional theory (DFT) calculations have revealed higher HER activity at the edge sites of TMDs than in the basal plane [1].

The so-called “volcano plot,” describing the exchange current density as a function of metal-hydrogen bond strength, also confirms that the edge of 2H-MoS₂ is electrochemically active whereas the basal plane remains inactive [2]. Therefore, many studies on TMD-based HER electrocatalysts have been dedicated to modulating the edge sites or surface structures of the electrocatalyst, or optimizing the physical, chemical, and electronic properties of TMDs (e.g., their conductivity, charge transfer kinetics, intermediate adsorption free energy, and reaction kinetics) [1-4]. This review briefly summarizes the representative HER processes in acidic and alkaline media, then discusses strategies for improving the performance of TMD-based HER electrocatalysts. Finally, it discusses the remaining challenges in this promising field.

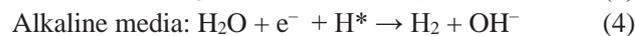
Reaction mechanism of HER

The electrocatalytic HER mechanism has been investigated in numerous experimental and theoretical studies. The HER proceeds in three steps: electrochemical hydrogen adsorption (1), electrochemical desorption (2), and chemical desorption (3). The proton source is H₃O⁺ in an acidic medium and H₂O in an alkaline medium. When a minimum external potential is applied at the electrode surface, an electron combines with a proton via the Volmer reaction (Eqs. 1 and 2), producing an adsorbed hydrogen atom (H*) on the electrode surface. Subsequently, H₂ is generated by the Heyrovsky reaction, the Tafel reaction, or both reactions. The Heyrovsky reaction (Eqs. 3 and 4) generates H₂ by combining a proton on the other electrode with an already produced H*. In the Tafel reaction (Eq. 5), H₂ is generated by combining the generated H* with a nearby H*.

(1) Electrochemical hydrogen adsorption
(Volmer reaction)



(2) Electrochemical desorption (Heyrovsky reaction)



(3) Chemical desorption (Tafel reaction)



Strategies for enhancing the HER performance of TMDs-based electrocatalysts

Phase engineering

Since the Chhowalla group reported that the exchange current density and active sites can be improved by increasing the 1T phase ratio in WS₂ [5], phase transitions of TMDs in electrocatalysts (e.g., MoS₂, WS₂, MoSe₂, and WSe₂) have been widely investigated for enhancing the HER performance of TMD-based catalysts. Owing to their intrinsic electrical conductivity and electronic structure rearrangements, metallic 1T phase and disordered 1T' phase TMDs exhibit more favorable kinetics for HER than semiconducting 2H phase TMDs. Gao et al. theoretically determined the bandgap of 2H-MoS₂ as 1.74 eV, versus 0.006 eV in 1T and 1T'-MoS₂. This finding suggests that the HER performance in metallic phase MoS₂ can be improved by increasing the charge transfer capability [6].

Putungan et al. computationally demonstrated that the H* adsorption ability and metallic phase stability are higher in the basal plane of 1T'-TMDs (M = Mo, W; X = S, Se, Te) than in 1T-TMDs [7]. Voiry et al. and Lukowski et al. experimentally determined that 1T-WS₂ and 1T-MoS₂ (synthesized by lithium intercalation) deliver higher HER performance than 2H-WS₂ and MoS₂ [5, 8], consistent with theoretical analysis. In the typical lithium intercalation-assisted synthesis process, the phase transition of TMDs occurs via electron transfer from lithium to the TMD layers, which involves quite complex processes requiring a long reaction time in an inert environment. Recently, the Park group devised novel in-situ local phase transition of TMDs by synthesizing a TMDs/perovskite oxide heterostructure, which significantly improved the HER performance of a heterostructured catalyst [9]. Electron transfer from Co to Mo in the MoSe₂/La_{0.5}Sr_{0.5}CoO_{3-δ} (LSC) heterostructure alters the electronic structure of Mo, inducing a phase transition in MoSe₂ (Fig.2).

Defect engineering

The basal plane of 2H-TMDs has a semiconducting na-

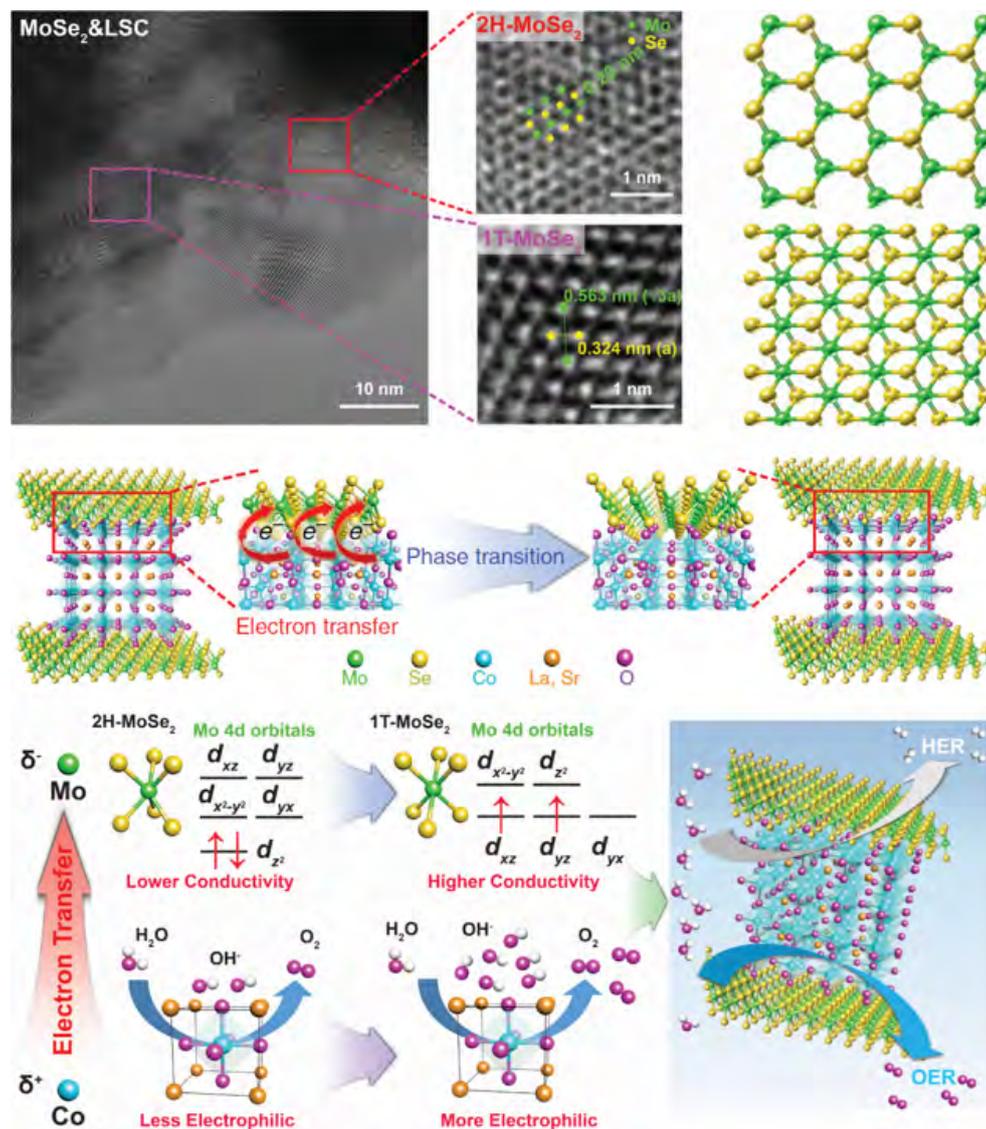


Fig. 2: Potential interaction between MoSe₂ and La_{0.5}Sr_{0.5}CoO_{3-δ}, resulting in in-situ local phase transition of MoSe₂ [9].

ture with insufficient numbers of active sites. Introducing defects in the basal plane increases the number of edge sites and modulates the Gibbs free energy (ΔG_{H^*}) of TMDs, thereby boosting the HER performance. For example, Ye et al. created hole and crack defects in pristine MoS₂ through O₂ plasma and H₂ annealing. Such defects on the treated MoS₂ surface became catalytically active sites that significantly improved the HER performance parameters, namely, the onset potential, Tafel slope, and current density, over those of pristine MoS₂ [10]. Similarly, Hong et al. modulated the S-vacancy concentration of 2H-MoS₂ by an Ar plasma treatment [11]. The DFT results demonstrated that S-vacancies provide additional active sites in the basal plane with the optimal

ΔG_{H^*} ($\Delta G_{H^*} = 0$). In addition, the S-vacancies enable direct bonding between hydrogen and Mo exposed on the MoS₂ surface, thereby optimizing the HER performance. Recently, Park's group generated in-situ chalcogen vacancies by chemical vapor deposition (CVD) in the synthesis of MoSe₂.

The HER performance of MoSe₂ was significantly improved by in-situ generated Se vacancies, with a Tafel slope value similar to that of platinum [12]. It is worth noting that their approach generates vacancy sites in TMDs without requiring post-treatments such as a plasma process. In DFT calculations, the in-situ generated chalcogen vacancy exhibited lower hydrogen adsorption

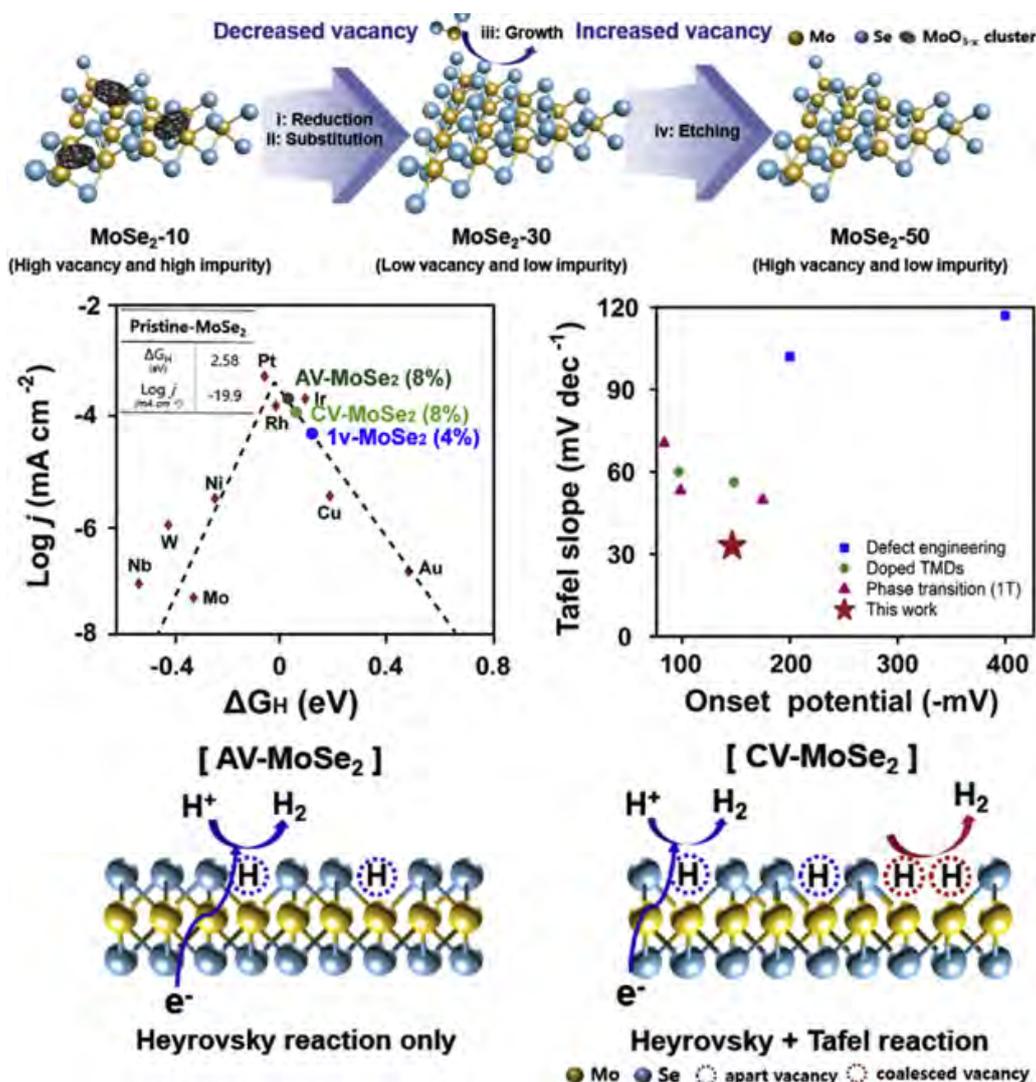


Fig. 3: Synthesis mechanism and effect of Se vacancies on the HER activity of MoSe₂ [12].

energy for HER and a lower hydrogen diffusion barrier for the Tafel reaction than pristine MoSe₂ (Fig.3).

Gao et al. theoretically demonstrated that introducing dual-native vacancies (both Mo and Se) in the basal plane and edge of MoSe₂ modulates the ΔG_{H^*} value, bringing it close to 0 eV. Their results were experimentally supported in CVD-grown MoSe₂ containing Mo and Se vacancies [13].

Heteroatom doping engineering

Heteroatom doping in TMDs is typically adopted to optimize ΔG_{H^*} of TMD-based electrocatalysts by modulating the electronic structure. Examples of TMD doping studies include non-metal doping (C, N, O, B, and P) [14-16], noble metal doping (Au, Pt, and Ru) [17-19],

and non-noble metal doping (Fe, Ni, Co, and Zn) [20-22]. Kuo et al. demonstrated that C and O doping on defected MoS₂ leads to higher hydrogen coverage [23]. Similarly, Xie's group reported that O doping in MoS₂ induces synergistic effects in structural and electronic properties, leading to improved HER performance compared to pristine MoS₂ (onset potential: -120 mV, Tafel slope: 55 mV dec⁻¹) [24]. Oxygen-incorporated MoS₂ has twice the hydrogen coverage compared to pristine MoS₂, which is attributed to optimized ΔG_{H^*} (Fig.4).

Sun et al. synthesized flower-like N-doped WS₂ via the sol-gel method. In a partial density of states analysis, the N doping induced strong hybridization between the p orbitals of the N atoms and the d orbitals of the W atoms, thereby increasing the number of charge carriers

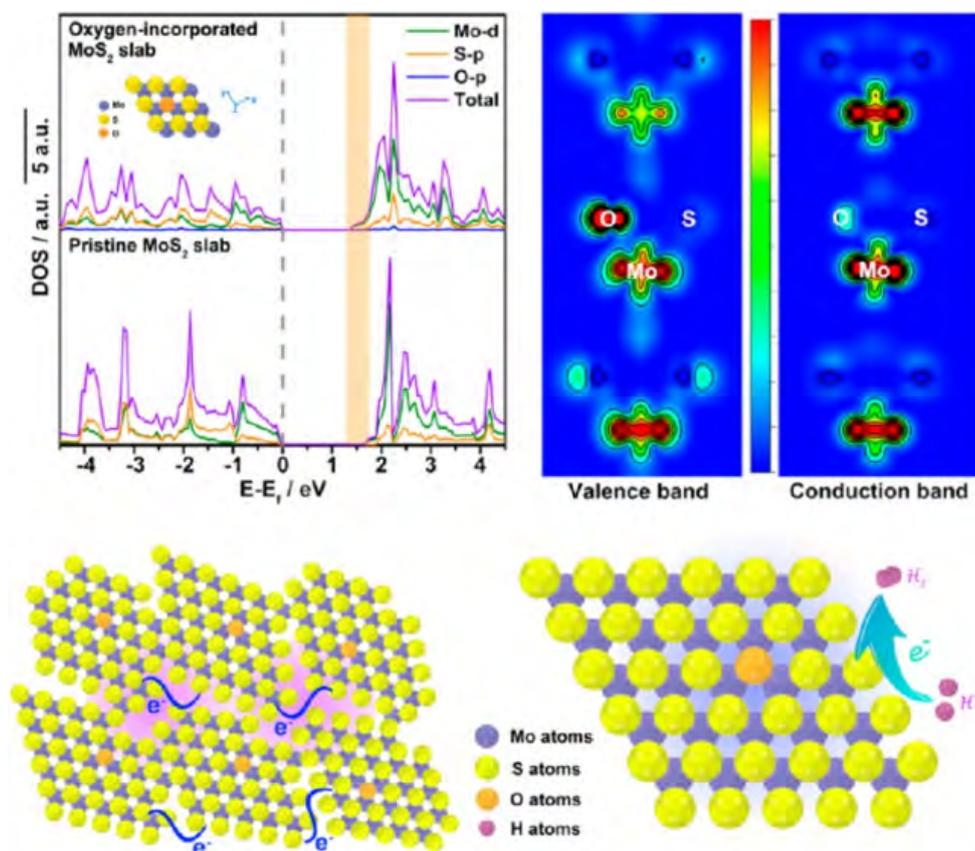


Fig. 4: Calculated densities of states and charge-density distributions of O-incorporated MoS₂ (top). Schematic of the disordered structure in O-incorporated MoS₂ (bottom) [24].

Heterostructure engineering

Although the aforementioned strategies (defect generation, doping, phase transition) improve the HER performance of TMD-based catalysts, the electrochemical properties of single type TMDs are intrinsically limited for the HER process. To improve this situation, researchers have fabricated heterogeneous catalyst structures of TMDs and catalytically active materials. Such heterostructured TMD-based catalysts have further improved the catalytic performance of single type TMDs by optimizing ΔG_{H^*} , the electron transfer pathway, the electrochemically active surface area, and the intrinsic exchange current density. Among the reported heterostructures are TMDs/sulfides [29], TMDs/selenides [30, 31], TMDs/phosphide [32], TMDs/nitrides [33], TMDs/metal oxides [34, 35],

and the intrinsic conductivity of N-doped WS₂. The HER performance is additionally enhanced by the increased surface area after N doping [25]. Bao's group synthesized Pt–MoS₂ by a one-pot chemical method. When applied as a HER electrocatalyst, Pt–MoS₂ delivered higher performance than pristine MoS₂ because it optimizes the adsorption kinetics of the hydrogen atoms at the S sites near the Pt-doped regions [26]. Bonde et al. reported that the ΔG_{H^*} of MoS₂ and WS₂ can be modulated via Co doping at the S-edge [27], but is unaffected by Co doping at the Mo-edge. That is, the Co doping forms catalytically active sites only at the S-edge. Later, Zhang et al. reported a similar doping strategy with Ni, Co, and Fe, which improves the sluggish HER kinetics in MoS₂ [28]. Among the three modifications, Ni–MoS₂ showed the best HER performance, with an overpotential of –98 mV at 10 mA cm⁻². Ni atoms doped in MoS₂ effectively reduce the kinetic energy barrier of the initial water dissociation step, and facilitate the desorption of -OH intermediates. In addition, the ΔG_{H^*} of Ni–MoS₂ was nearly 0 eV (–0.06 eV) in a computational calculation.

TMDs/rGO [36], TMDs/black phosphorus (BP) [37], and TMDs/perovskite oxides [9]. Rheem et al. devised a MoS₂/MoO₂ heterostructure with a metallic MoO₂ core surrounded by MoS₂ nanosheets [35]. The MoS₂ nanosheets improve the HER performance by increasing the overall surface area and conductivity of the composite. He et al. synthesized a MoS₂/BP heterostructure by depositing MoS₂ flakes on the surface of BP nanosheets [37]. In this electrocatalyst, the HER performance is enhanced by charge transfer at the MoS₂–BP interface. With a higher Fermi level than MoS₂, BP donates electrons to MoS₂; consequently, the intrinsic exchange current density is 22 times higher in MoS₂/BP than in MoS₂ alone. The MoS₂/BP heterostructure also delivers an excellent overpotential of –85 mV at 10 mA cm⁻² (Fig.5).

A heterostructure comprising highly conductive non-oxide materials and TMDs has also been applied as a HER electrocatalyst [38]. CoS₂ nanowires coated with MoS₂ nanosheets were synthesized by the hydrothermal method. The MoS₂/CoS₂ heterostructure produced an excellent overpotential in the HER (–87 mV at 10 mA

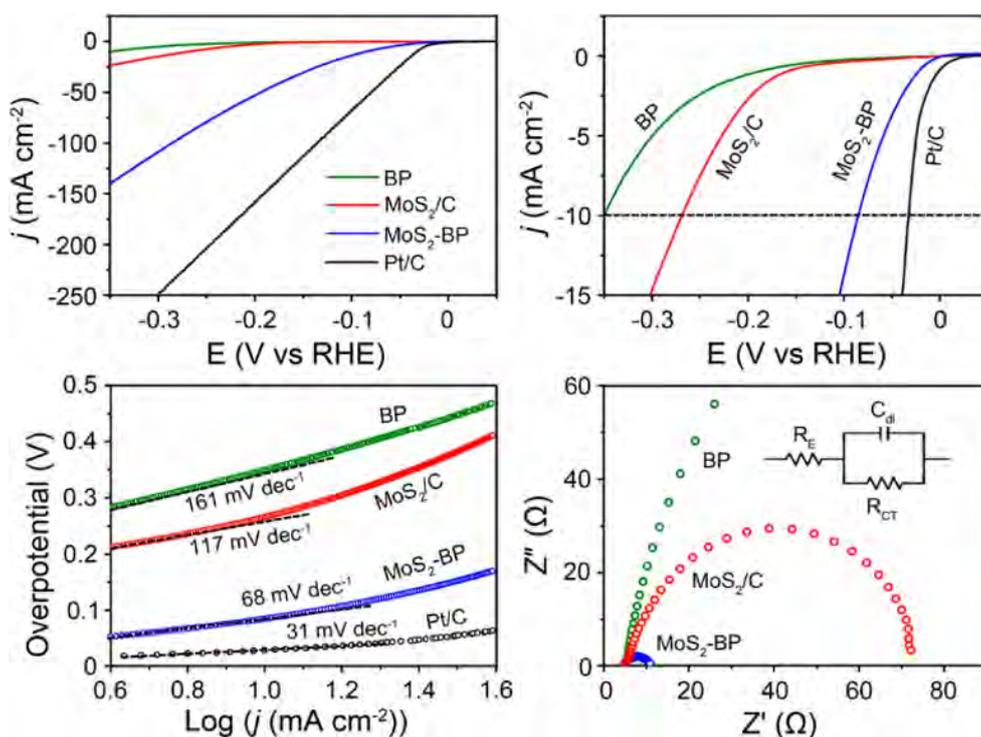


Fig. 5: Comparison of HER performances (overpotential, Tafel slope, and charge transfer resistance) of BP, MoS₂/C, and MoS₂-BP in 0.5 M H₂SO₄ [37].

cm⁻²), by virtue of the co-doped Co and O elements in the MoS₂ nanosheets, structural defects, and excellent conductivity of CoS₂ [38]. Recently, the Park group developed a novel TMDs/perovskite oxide heterostructure for HER electrocatalysts. The MoSe₂/LSC heterogeneous catalyst delivered an excellent HER onset potential (MoSe₂: -420, LSC: -330, and MoSe₂/LSC: -200 mV) and Tafel slope (MoSe₂: 237, LSC: 95, and MoSe₂/LSC: 34 mV dec⁻¹). This high performance originated from local 2H to 1T phase transitions in MoSe₂, increased surface area, and enhanced surface hydrogen adsorption capability [9].

Summary and future challenges for TMDs-based HER electrocatalysts

Although the study of TMD-based HER electrocatalysts has greatly advanced through rigorous research endeavors, the industrial viability of these materials is limited by several remaining problems. First, the HER mechanism and descriptors of TMDs in alkaline electrolytes require further investigation. A thorough understanding of the HER process in alkaline electrolytes is critical for designing efficient HER electrocatalysts and for optimizing the overall water electrolysis with TMD catalysts. Second, operational stability is as important as performance in HER

electrocatalysis. However, stability analyses of TMDs-based electrocatalysts have been rarely reported, and the exact mechanisms of stability are poorly understood. A fundamental understanding of the operational stability of electrocatalysis is a potential stepping stone for the practical industrialization of overall water electrolysis. Finally, the actual mechanism of hydrogen generation might differ from that derived in theoretical computational approaches. Therefore, establishing a concrete hydrogen generation mechanism in both acidic and alkaline electrolytes by in-situ characterization is highly desired.

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