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Engineered 2D Transition Metal Dichalcogenides - A Vision of Viable Hydrogen Evolution Reaction Catalysis

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ABSTRACT: The hydrogen evolution reaction (HER) is an emerging key technology to provide clean, renewable energy. Current state-of-the-art catalysts still rely on expensive and rare noble metals, however, the relatively cheap and abundant transition metal dichalcogenides (TMDs) have emerged as exceptionally promising alternatives. Early studies in developing TMD-based catalysts laid the groundwork in understanding the fundamental catalytically active sites of different TMD phases, enabling a toolbox of physical, chemical, and electronic engineering strategies to improve the HER catalytic activity of TMDs. This report focuses on recent progress in improving the catalytic properties of TMDs towards highly efficient production of H₂. Combining theoretical and experimental considerations, we provide a summary of the progress to date and conclude a pathway forward for viable hydrogen evolution from TMD driven catalysis.

Keywords: hydrogen evolution reaction; catalysis; transition metal dichalcogenides; energy conversion; 2D materials

1. Introduction

Tackling global climate change and the energy crisis requires novel approaches in clean energy generation and efficient manufacturing.^[1] Hydrogen (H₂) is one of the most popular clean energy sources, providing the highest energy output of any known fuel (gravimetric energy density of 120-142 MJ kg⁻¹).^[2,3] Currently, the global H₂ production required to meet the industry need is around 0.1 gigatons, which is mainly consumed in ammonia production (54%), chemical production (35%), electronics processing (6%), metals processing/refining (3%), and food industry (2%).^[4] The global need for H₂ as a fuel will continue to grow, as

implementation into broader society *via* domestic consumption (*e.g.* power generation and heating) and transport industry (*e.g.* fuel driving vehicle) is accelerated. This growing need requires developments in H₂ storage, transport, and production techniques. While great progress has been made in H₂ storage and transport, the utilization of the H₂ energy is stymied by the lack of inexpensive and efficient production methods.

Current technologies producing H₂ are hydrocarbon reforming, pyrolysis of fossil fuels (*e.g.* natural gas, oil and coal) and biomass conversion, which are expensive and unsustainable with significant greenhouses emissions.^[2,3] An attractive alternative technique is water splitting which produces only H_{2(g)} and O_{2(g)} *via* direct thermolysis (> 2500 °C), photocatalytic, or electrolytic routes. All of these water splitting techniques involve suitable catalysts to improve the production of H₂ and reduce the energy consumption, yet electrolysis is the most encouraging technique owing to its high efficiency and relatively low cost.^[2–4] The half reaction of water splitting to produce H_{2(g)} *via* electrolysis is called the electrochemical hydrogen evolution reaction (HER).

It is believed that the electrochemical HER will be key to meeting global challenges of the energy crisis and anthropogenic climate change, giving uninterruptable H_{2(g)} fuel supplies with low energy consumption.^[5,6] Currently, the most efficient HER catalysts are precious metal (*e.g.* Pt and Pd) based which are expensive and scarce. Recently, a new class of catalytic materials, layered transition metal dichalcogenides (TMDs), have emerged with several advantages over noble metal catalysts, notably the lower cost and higher abundance. Results showed that these sustainable materials are promising catalysts for the HER.^[7,8] Early studies on developing these catalytic materials were stymied by the low efficiency due to the scarcity of metal edge sites and the poor electron transport efficiency in multilayered TMDs.^[9,10] In recent years, research progress in using TMDs as HER catalysts has developed rapidly, led by improved fundamental understandings in the catalytic process and advancements in chemical, electronic, and structural tuning of TMDs. In this progress report,

we provide a background to key concepts for the electrochemical HER and discuss how TMDs can be manipulated through size, strain, defect, and phase engineering; edge-enrichment strategies; chemical doping; and hybrid structures to unlock their potential as the next-generation of HER catalysts.

2. Key Concepts of Electrochemical HER

2.1. HER at Electrodes

Complete water splitting can be described by the overall reaction (1):

where the full reaction includes two half-reactions, the reduction reaction to generate H_2 (HER) at the cathode electrode and the oxidation reaction to generate O_2 (oxygen evolution reaction/OER) at the anode electrode. Conventionally research is driven in the acidic regime (*anode*: $\text{H}_2\text{O} \rightarrow 2\text{H}^+ + \frac{1}{2}\text{O}_2 + 2e^-$; *cathode*: $2\text{H}^+ + 2e^- \rightarrow \text{H}_2$), and the HER in this case normally involves three steps:

- the Volmer reaction on the electrode surface, giving the reaction between a proton and the transferred electron to generate an adsorbed hydrogen atom (H_{ads}^*);
- the Tafel reaction which combines two adsorbed H atoms to generate H_2 gas, or
- the Heyrovsky reaction involving the reaction between one adsorbed H atom, one electron and one proton to yield H_2 gas.

The Volmer reaction is the first reaction to generate the necessary adsorbed intermediate, and is typically rate-limiting step of HER. In principle, electrochemical water splitting (or HER) requires a thermodynamic electrochemical potential of ~ 1.23 V at room temperature. This value increases under experimental conditions when the high activation energy (E_a) is required to form reaction intermediates on the electrode surface. This is where the catalyst provides value by minimizing the overpotentials (energy cost) at the electrodes for both HER and OER by reducing the thermodynamic barriers, and thus accelerates the overall reaction.

2.2. Key Principles for the HER (in Acidic Media)

In electrochemical HERs, the catalytic performance of a catalyst is normally measured by the HER current density (j) at certain overpotentials. A good HER catalyst should exhibit high j at low overpotentials. This HER performance is a synergic result of both the catalytic activity and the number of the active sites.^[10] In practical cases, the reaction kinetics (*e.g.* the activation energy, E_a) and mass transfer are also affect the HER process greatly. As we have introduced above, the Volmer and Heyrovsky reactions all perform the proton-electron transfer process which are highly dependent on the electrode potential. The electrode potential changes with the electrostatic potential of the water-solid interface, and highly depends on different hydrogen atoms added on the electrode.^[11-13] Triggering the Volmer, Tafel or Heyrovsky reactions requires overcoming the particular energy barrier for that specific reaction at the electrode, and the E_a can be extrapolated to the limit where the potential does not change.^[12,14-15] Building on this principle, Jiang *et al.* calculated the reaction energy (ΔE between the final and initial states), the E_a of the above three elementary steps of 1T MoS₂, and suggested that the full HER is rate limited by the desorption of the H since the E_a of the Heyrovsky reaction ($E_a = 0.62$ eV) is much higher than that of the Volmer step ($E_a = 0.16$ eV), and lower than that of the Tafel reaction ($E_a > 0.89$ eV).^[12]

Nevertheless, the Volmer reaction is the rate limiting step in most HERs, and the Sabatier principle provides good guidance in designing suitable materials with the consideration of the free-energy of adsorbed H on the active site (ΔG_{H^*}) during an equilibrated reaction.^[7] With this principle, a good HER catalyst should satisfy the criterion of suitable ΔG_{H^*} which is closest to that of the reactant or product ($\Delta G_{H^*} \approx 0$). The reaction is rate limited by the adsorption of H^{*} if ΔG_{H^*} is too high (insufficient binding), and in turn is H₂-desorption limited provided a too negative ΔG_{H^*} (binding is too strong).

In most literature, the HER catalytic activity of a material is usually described by the parameters of Tafel slope, j_0 , turnover frequency (TOF) and onset overpotential. The former

two represent the relationship between the overpotential (η), current density (j) and j_0 as the following equation:^[16]

$$|\eta| = \frac{2.3RT}{\alpha nF} \log \frac{j}{j_0} \quad (2)$$

where R , T , α , n and F are the ideal gas constant, the absolute temperature, the electrochemical transfer coefficient, the number of electrons involved in the reaction and the Faraday constant, respectively. The Tafel slope is defined as the value of $\frac{2.3RT}{\alpha nF}$ (mV dec⁻¹).^[16] The HER can be rate-limited by the Volmer, Heyrovsky, or Tafel reactions when the Tafel slope is about 120, 40, and 30 mV dec⁻¹, respectively.^[17] j_0 is the value of the current density from the Tafel plot at the overpotential of 0 V, reflecting the intrinsic catalytic activity of the catalyst under equilibrium conditions.^[16] The turnover frequency (TOF) is the value describing how many molecules are generated per active site per second (s⁻¹), which is frequently used in the research of catalysis. In the HER, this value highly depends on the working potential. Since the polarization curve of the HER is the synergic result of different active sites, the TOF is an average of catalytic activity of all active sites. As for the onset overpotential, it is the overpotential of the HER activity begins, and can be extrapolated from Tafel plot and the cathodic Tafel line.^[10,18] However, many reports in literature use the overpotential as the onset overpotential where a defined current density (*e.g.* 10 mA cm⁻²) is reached, which is unsuitable as this value changes with the catalyst loading as well as the active site coverage. In this case, the term of catalytic performance might be used to distinguish with the catalytic activity, and more direct, suitable methods (*e.g.* Faradaic and energy efficiencies) should be introduced to estimate the total catalytic performance.

Building on these key principles, the best HER catalyst developed so far are still noble metal based. For example, except the high exchange current density (j_0 , also represents the kinetics toward the redox reaction of the catalyst),^[16] Pt has ΔG_{H^*} around -0.09 and -0.03 eV at pH=0 with a 25% and 100% H coverage, respectively (**Figure 1a-b**).^[19] Nevertheless, with

an abundance of chemistries, electronic structures, and properties, the cheap and abundant TMDs, have emerged as leading materials for the next generation of HER catalysis.^[7-10,20-24]

TMDs can have a ΔG_{H^*} close to 0 eV, a high j_0 (**Figure 1c-f**, will be further introduced), and a fundamental competitive advantage over competing emerging HER catalysts in that they have rich tunable 2D surface chemistries, and more importantly, precisely tunable properties based on size, defects, strain, doping, and heterostructure formation on the 2D planar crystals.

The progress in tailoring TMDs *via* these strategies forms the basis for our discussions within the progress report. Building on the progress we have achieved so far, comparison of the TMDs with other state-of-the-art HER catalysts, and the future possibilities on developing highly efficient TMD based HER catalysts are also included in this report.

Figure 1. a-b) The Sabatier plot shows the j_0 against the ΔG_{H^*} and E_{ads} of different metals with (a) 25% and (b) 100% H coverages at pH=0. Data was taken from references.^[8,19] Materials near the top and close to the ΔG_{H^*} of 0 eV are expected to be most active in HER. The j_0 of many reported MoS₂ materials is also highlighted in figure a, which is similar to some other TMDs.^[8,19] c-f) Plots of the ΔG_{H^*} as a function of the HX adsorption free energy (ΔG_{HX^*} , X=S or Se) at 2H edge (c), 1T edge (d), 2H plane (e) and 1T plane (f). Data in figures c-d is taken from refs.^[22-24]. MAE is the mean absolute error. The dotted lines are guides for the eye. Figures e-f are reproduced with permission.^[24] Copyright 2015, Elsevier.

Figure 2. a) The periodic table with TMD elements highlighted. Reproduced with permission.^[21] Copyright 2013, Springer Nature; b) the three most common crystal structures for TMDs, 2H – hexagonal, 1T – octahedral, and 1T' – distorted octahedral, each with different electronic properties. Reproduced with permission.^[31] Copyright 2016, Springer Nature; c) i) electron hopping in multilayered 2H-MoS₂ and the ΔG_{H^*} at basal plane and edge sites. ii) the number of catalytically active sites as a function of size for equal amount of material; d) Methods to tune the chemistry, electronic, and catalytic properties of TMD monolayers by defect engineering, band-gap engineering, and heterostructure formation. Reproduced with permission.^[32] Copyright 2018, Royal Society of Chemistry.

3. TMD Materials as Catalysts for the HER

TMDs are materials having chemical composition of MX₂ (M and X are the transition metal and the chalcogen, respectively, including similar chalcogenides with more than one TM atom and corresponding X atoms) with two-dimensional (2D) building blocks (*e.g.* S-Mo-S)

weakly bonded to each other by van der Waals forces (**Figure 2**). There are three crystal phases that most TMD monolayers are thermodynamically stable (**Figure 2a&b**); 1H for most group VI TMDs (D_{3h} point group, each M center is prismatically coordinated by six surrounding X atoms); 1T phase for group IV, VII, and X TMDs (D_{3d} group, M atom is octahedrally coordinated to six neighboring X atoms); and 1T' (or T_d) for WTe_2 where the 1T lattice is distorted.^[21-24] However, TMDs can be switched between phases and 'locked' into a meta-stable phase, for example MoS_2 into 1T *via* lithium exfoliation and charge injection^[25] or WSe_2 into 1T' by controlled cooling rates and ligand selection.^[26] The earliest reports of TMDs for electrochemical water-splitting come from the late 1970s.^[27] The explosion of interest in TMD materials corresponds to the development of exfoliation^[28] and synthesis^[29,30] techniques that have enabled the production and stabilization of monolayers. These monolayers enable a higher per mass catalytically active surface area, and thus more catalytically active basal-plane, defect, and edge sites available for the HER to occur.

Bulk TMDs can be stacked from the monolayers and commonly have three polymorphs (1T, 2H and 3R/rhombohedral), depending on the crystal phase and stacking arrangement. The number in these three polymorphs means how many M-X-M units in the unit cell of the bulk crystal. The physical properties of the bulk TMDs are varied.^[22-24] For example, group 5 TMDs could be either 1T or 2H structured. For group 4, 7 and 10 bulk TMDs in the periodic table (**Figure 2a**), it prefer the 1T phase, whereas the group 6 TMDs prefer the 2H phase.^[22-24] Some TMDs such as groups 4 and 5 are metallic, and some are semiconducting (groups 6, 7, and 10).^[22-24]

The HER catalytic activity and mechanism of metallic and semiconducting sites of TMDs are significantly different from each other. Although the basal plane of 1H/2H-TMDs such as MoS_2 , WS_2 , $MoSe_2$ and WSe_2 are HER inert (ΔG_{H^*} is ~ 2 eV uphill),^[22] the ΔG_{H^*} at the metallic edge (the edge performs metallic features) in some cases is close to that of Pt and is thermo-neutral (**Figure 1c**).^[7] It was revealed that the ΔG_{H^*} of 2H- MoS_2 's edge is close to

0.08 eV with 50% H coverage (the j_0 of some reported 2H MoS₂ is also high).^[7] The result has been further refined, giving the best edge configurations of MoS₂ (0.06 eV of ΔG_{H^*}) and WS₂ (-0.04 eV of ΔG_{H^*}) with 50% S coverage, *versus* ΔG_{H^*} of -0.45 and -0.06 eV respectively in both cases with 100% S edges.^[22]

Figure 1c&d are the plot of ΔG_{H^*} of various TMDs at different edges against the absorption free energy of H-X (ΔG_{HX^*} , X is the chalcogen) based on the data reported by Tsai *et al.*^[22-24] The reaction tends to form H₂X along with the desorption of H-X group when $\Delta G_{HX^*} > 0$; whereas it would be more stable upon decreasing the ΔG_{HX^*} . Besides MoS₂, several other TMDs such as MoSe₂, WS₂, WSe₂ and TaS₂ are also highly promising for HER with 2H or 1T edges (**Figure 1c&d**). Tsai *et al.* have further calculated the ΔG_{H^*} and ΔG_{HX^*} at both the edge and basal plane of various TMDs to estimate the HER catalytic activity and relating stability.^[22,23] ΔG_{H^*} at the edge of TMDs are all close to 0 eV and highly suited for HER, whilst the ΔG_{HX^*} of all 1T and most 1H/2H edges are negative (**Figure 1c&d**).^[24] The ΔG_{H^*} on the basal plane of semiconducting TMDs is normally high and unsuitable for HER (*e.g.* ΔG_{H^*} of ~ 1.92 eV of the 2H MoS₂).^[24] Replacing the Se by S (electronegativity: 2.58 of S *vs* 2.55 of Se) in TMDs can slightly tune the ΔG_{H^*} close to more thermo-neutral states, but which on the other hand reduces the stability significantly (**Figure 1e**). The stability of the semiconducting basal plane should be carefully considered during the activation for an efficient HER. Like that on the semiconducting basal plane, the ΔG_{H^*} on the metallic plane has also the inverse relationship with ΔG_{HX^*} (**Figure 1f**).^[24] Nevertheless, the metallic planes are more active for the HER with similar stabilities comparing with the semiconducting basal plane, *i.e.* the ΔG_{H^*} of 0.12 eV on the plane of 1T-MoS₂ *versus* the 1.92 eV on that of the 1H/2H-MoS₂.^[24] In this case, improving the electronegativity of the X atoms (*e.g.* replacing the Se by S) can be more efficient to improve the HER activity than that on the semiconducting TMDs (at the basal plane), and the basal plane of some metallic TMDs are actually suited for catalytic HER (**Figure 1f**), *i.e.* both the 1T-MoS₂ and 2H-NbS₂ have the

ΔG_{H^*} of around 0.12 eV on the basal plane, which is close to the 2H edges of some TMDs (e.g. MoS₂, **Figure 1c**). Some TM sulfides are not chemically stable in aqueous media (ΔG_{HX^*} of 0.21 and -0.09 eV on the basal plane of 1T-VS₂ and 1T-TiS₂, respectively, **Figure 1f**), however if they can be stabilized the ΔG_{H^*} values are highly promising for efficient HER (e.g. 0.05 eV of 1T-VS₂ and 0.38 eV of 1T-TiS₂).^[24] These features open new avenues to robust and stable HER, if the ΔG_{H^*} and ΔG_{HX^*} can be further adjusted (e.g. by the chemical doping) towards more stable surfaces with a ΔG_{H^*} more close to 0.

Despite these theoretical calculations, research on the experimental HER performance of TMDs is rather limited before 2010 because of the very poor catalytic activity. Such poor performance was mainly due to at least the following two reasons:

- the scarcity of edge sites, which are the only catalytically active part of the material in most cases, and
- the low electrical conductivity of the most TMDs.^[6,9]

for example, the HER catalytic activity of 2H MoS₂ decreases by a factor of ~4.5 with each additional layer due to the poor electron hopping efficiency in multi-layers (**Figure 2c**).^[9] The understanding of these limitations, in combinations with the ability to tune the electronic and chemical properties of TMDs, provides a clear direction to improve and use TMDs as HER catalysts. It is from these tuning methods that tailored strategies to improve the HER catalytic activity can be developed (**Figure 2d**).

4. Progress on Strategies to Improve the HER Catalytic Activity of 2D TMDs

The fundamental understanding gained over the past few years in the catalytically active sites, reaction limiting factors, and the importance of precise chemical and structural control of TMDs has opened a clear set opportunities to manipulate their properties towards increased catalytic activity. These include precise phase control, defect generation, size control and edge enrichment, chemical doping, heterostructuring, and any combination of these (**Figure 2d**).

Before the discussion of this progress, we briefly revisit the development on multi-layered

TMDs as the HER catalyst over the last decade. Improvements on the catalytic performance have been realized *via* the following strategies:

- the formation of nanomaterials and amorphous phases;^[33-41]
- the edge-aligned TMDs,^[42-51] and
- three-dimensional (3D) porous TMDs.^[52-59]

Although the formation of the TMDs nanoparticle can directly improve the edge ratio, the catalytic performance is still quite poor due to the poor electron hopping between the multilayers (**Figure 2c**).^[33-37] The poor charge transport might be alleviated in amorphous TMDs, while the density of the active site also increased dramatically. Some amorphous TMDs have exhibited outstanding catalytic performance,^[38-41] comparable to lately developed 2D TMDs. Nevertheless, their poor stability/durability associated with the amorphous nature is still needed to be addressed suitably. Besides, both the edge aligned and 3D TMDs have been introduced in terms to improve the catalytic performance. These approaches have been further modified by expanding the layer distance and introducing strain into the lattice,^[51,54] but the performance is still unsatisfactory. Technical challenges limiting these approaches are the inert plane on the 3D channel, and the poor charge transport issue between the edge aligned multi-layered TMDs.

Unlike these multilayered TMDs, the 2D TMDs (*e.g.* monolayers) are more active owing to the increased charge transport efficiency (**Figure 2c**), the higher exposed surface areas, and the rich surface chemistry, which enables various strategies (discussed below) to improve the catalytic performance.

4.1. Phase Engineering

As we mentioned above, TMDs are unique layered materials. The 2D monolayered building blocks of TMDs exist in one of three phases (1H, 1T, and 1T', **Figure 2b**). All of these 2D TMDs have dramatically different electronic properties and catalytic activity. The thermodynamically stable form of MoS₂, WS₂, MoSe₂, and WSe₂ is 1H (or 2H), and for all of

these materials 1H (or 2H) is semiconducting and hence has quite poor electrical conductivity. Manipulation of these materials can lead to the formation of the 1T metallic TMDs which has different catalytically active sites and significantly improved electron transport efficiency. Further, theoretical calculations have suggested that the basal plane of some 1T TMDs (*e.g.* MoS₂, NbS₂, VS₂, TaS₂, WS₂, TiS₂) are catalytically active for HER, whereas the basal plane of their 1H/2H phases are usually inert due to the high ΔG_{H^*} (**Figure 1c-f**).^[22-24] The key challenges to explore for 1T TMDs monolayers are the stability and cheap methods of production.

In 2013, Chhowalla *et al.* reported the HER of chemical exfoliated WS₂ monolayers with both 1T and 1H structures (**Figure 3**).^[60] Testing thin films of 1H WS₂ showed with onset overpotentials of 150-200 mV and a Tafel slope of 110 mV dec⁻¹ or higher. Increasing the 1T WS₂ concentration (1H WS₂ ratio decreased) gradually improved the HER performance (**Figure 3a-d**).^[60] Among different WS₂ samples, 1T WS₂ monolayers exhibited the best HER performance, giving the Tafel slope of 55 mV dec⁻¹ (was 60 mV dec⁻¹ without *iR* correction), onset overpotential of 80-100 mV and a j_0 of 2×10^{-5} A cm⁻².^[60]

This HER performance of WS₂ monolayers (particularly the 1H monolayers) might be underestimated since the catalyst was mounted on the glassy carbon electrode with the thickness larger than five monolayers.^[60] For 1H semiconducting monolayers, the thickness of the catalyst on the electrode should be ideally as thin as the monolayer to sustain the rapid charge transport between the electrode and the top-most surface of the catalyst. Re-stacking of the monolayers would degenerate the HER performance.^[10] Therefore, the relationship between the catalytic performance and the loading amount of monolayered Mo-S nanocrystals (NCs) on the glassy carbon electrode is crucial.^[10] The double layer capacitance (C_{dl}) (reflects the effective surface area of the total active sites) divided by the catalyst mass gradually decreased by increasing the catalyst loading.^[10] With a mass density larger than $\sim 100 \mu\text{g cm}^{-2}$, the C_{dl} was decreased by adding more catalyst. All these features meant that the re-

stacking/agglomeration of monolayered NCs highly suppressed the catalytic performance, *i.e.* the Tafel slope was also increased.^[10]

Figure 3. a) Atomic force microscopy (AFM) image of WS₂ monolayers; b-c) High-angle annular dark-field scanning TEM (HAADF-STEM) images of the WS₂ monolayer with distorted 1T (b) and 1H structure (c); d) Polarization curves of bulk and WS₂ monolayers (both 1T and 1H phases), sub-monolayered WS₂ and Pt nanoparticles. Figures a-d are reproduced with permission.^[60] Copyright 2013, Springer Nature; e) Schematic shows the synthetic procedure of monolayered ultrasmall 1T TMDs from their 2H bulk crystals; f-g) AFM (f) and HAADF-STEM images (g-h) of the prepared monolayered WS₂ NCs; h) The corresponding L2D-WF-ABSF filtered image of WS₂ NCs in figure g; i) Brightness profiles along the dotted lines in (h) (top, line 1; bottom, line 2); j) Schematic shows the structure of 1H/2H and 1T TMDs; k-l) Polarization curves (k) and corresponding Tafel slopes (l) of different monolayered NCs. Figures e-l are reproduced with permission.^[69] Copyright 2018, John Wiley & Sons.

The HER performance of 1H WS₂ monolayers with different sizes (edge lengths of 400-800 nm) has also been explored.^[61] The monolayers were fabricated on Au foil by a chemical vapor deposition (CVD) method, and were directly used for the HER. Tafel slopes and j_0 of these monolayers were 102-104 mV dec⁻¹ and 6.31-17.78 $\mu\text{A cm}^{-2}$, respectively. Such exchange current density (j_0) is comparable to that of 1T WS₂ nanosheets ($2 \times 10^{-5} \text{ A cm}^{-2}$),^[60]

owing to the interaction between the Au foil and WS₂.^[61] In comparison, 1H MoS₂ monolayers grown on Au foils has the Tafel slope of 61 mV dec⁻¹ and the j_0 of 38.1 $\mu\text{A cm}^{-2}$, a significant improvement compared to WS₂ with smaller size.^[62]

1T MoS₂ nanosheets produced by LiBH₄ exfoliation have the lateral size up to 1 μm and the 1T content > 80%.^[25,63] When the 1T nanosheets were converted to 1H phase by annealing, the Tafel slope increased from 40 mV dec⁻¹ to 75-85 mV dec⁻¹ and the onset overpotential became higher. The high HER performance of 1T MoS₂ sheets was mainly owing to the low ΔG_{H^*} at the basal plane (around 0.12 eV), closing to the ΔG_{H^*} at the edge of 1H/2H MoS₂ (0.08 eV).^[7,22-24]

Combining phase engineering and edge-enrichment, 1T MoS₂ monolayers with smaller sizes have also been prepared for HER. In 2017, Li *et al.* applied the intercalant of butyl lithium (n-butyllithium) to exfoliate MoS₂.^[64] With the assistance of ultrasonication treatment, the few-layered MoS₂ sheets was exfoliated, cracked and converted to 1T MoS₂ nanosheets (> 70% phase content, ~100-200 nm in lateral size). The Tafel slope and onset overpotential of the as-prepared 1T MoS₂ nanosheets were 42.7 mV dec⁻¹ and 156 mV respectively. This performance is worse than the above 1T MoS₂ sheets due to the lower ratio of the 1T : 1H phases and the fact that multi-layered sheets were commonly found in the sample.^[64] Nevertheless, the demonstrated performance is already dramatically improved from that of many 1H-MoS₂ monolayers.^[10,62,65-67]

To expose the maximum surface active sites, He *et al.* proposed a solvothermal approach to preparing vertically aligned 1T WS₂ sheets (phase content was around 70%) with a lateral size of several micrometers.^[68] The vertically aligned 1T WS₂ sheets exhibited a Tafel slope of 43 mV dec⁻¹ and onset overpotential of 118 mV (at the j of 10 mA cm⁻²). By contrast, the flat 1T WS₂ sheets on glassy carbon electrode has only the Tafel slope of 52 mV dec⁻¹ and onset overpotential of 230 mV. Such an improvement is owing to the improved exposure of the 1T basal plane.

In 1T TMDs, the exposure of the basal plane becomes crucial to an efficient HER, which is different with that of most 1H/2H TMDs with only catalytically active edges. Monolayered 1T TMDs NCs have also been reported recently (Zhang *et al.* 2018).^[69] Bulk TMDs (size around tens of micrometers) were initially reduced to micro-sized particles (size around 1 μm) with ball-milling, and then intercalated by n-butyllithium producing various monolayered TMDs nanodots (MoS_2 , WS_2 , MoSe_2 , $\text{Mo}_{0.5}\text{W}_{0.5}\text{S}_2$ and MoSSe) (sub-5 nm, **Figure 3e-l**) with a high percentage of 1T phase (67-80%). As suggested in **Figure 3k-l**, the Tafel slope of these TMDs varies from 40-63 mV dec^{-1} . The lowest Tafel slope was achieved on the MoSSe dots owing to possibly the Se-depleted sites formed during the preparation (see **Table 1**).^[69] The Tafel slope of the 1T MoS_2 NCs was actually inferior to that of 1H monolayered NCs and 1T monolayered sheets,^[10,67] and the underlying reason is still unclear (preparations and purifications of the 1T NCs may need to be improved further).

Table 1. HER catalytic performance of various monolayered 1T-TMDs NCs.^[69]

Parameters	MoS_2	WS_2	MoSe_2	$\text{Mo}_{0.5}\text{W}_{0.5}\text{S}_2$	MoSSe
Tafel Slope (mV dec^{-1})	53	63	54	58	40
Onset overpotential (mV)	58	139	101	95	49

One important consideration of the phase engineering for TMDs is the confusion between 1T and 1T' phases which have dramatically different electronic properties and hence HER pathways. A recent work by Sokolikova *et al.*^[26] demonstrated the solution phase synthesis of kinetically stabilized 1T' WSe_2 on arbitrary substrates (**Figure 4**). The Tafel slope of 1T' WSe_2 at ultralow mass loadings of $40 \mu\text{g cm}^{-2}$ was 150 mV dec^{-1} which increased dramatically to 232 mV dec^{-1} upon the thermal conversion to 1H/2H WSe_2 (**Figure 4f**). While the performance of the Tafel slope and the j at 10 mA cm^{-2} were significantly improved from other optimized TMDs (**Figure 4f-g**), this approach shows the power of phase engineering to enhance catalysis when applied intelligently. To further improve the catalytic performance, additional approaches are also suggested, that will be further discussed below.

Figure 4. a) Annular dark-field scanning TEM image of a WSe₂ branched nanoflower illustrating ultra-thin nature of individual nanosheets (scale bar: 100 nm), inset—an overview image of an ensemble of the WSe₂ nanoflowers (scale bar: 200 nm); b-d) zoomed in image (scale bar: 0.5 nm) with an overlaid crystal model of the 1T' (b) and 2H (d); c,e) fast Fourier transform (FFT); f) Polarisation curves of the 1T' and 2H WSe₂ nanosheets grown on the carbon paper, inset shows corresponding Tafel slopes; g) Comparison plot summarising the reported group VI TMD electrocatalysts for HER (exf-NSs – exfoliated nanosheets; syn-NSs synthesised nanosheets; NPs – nanoparticles). Figures a-g are reproduced with permission.^[26] Copyright 2019, Springer Nature.

4.2. Defect Engineering

4.2.1. Size Control and Edge Enrichment

The catalytic activity of monolayers, in principle, can be rationally improved by the lateral size reduction to improve the density of edge sites (**Figure 2c**). We developed a method to produce monolayered 1H MoS₂ NCs with a lateral size around 12.5 nm (**Figure 5**).^[10,70] The Tafel slope and onset overpotential of the 1H MoS₂ NCs (on glassy carbon electrode) were 51 mV dec⁻¹ and 120-140 mV respectively (**Figure 5i-j**), which are clearly better than

monolayered 1H MoS₂ sheets (on Au foil electrode),^[62] and similar to the monolayered 1T WS₂ nanosheets (on glassy carbon electrode).^[60] Theoretical calculations (**Figure 5f-g**) demonstrated that the 1H MoS₂ NC also have a metallic surrounding region that wraps the semiconducting core, improving the charge transport at the catalytically active sites.^[10,71]

The formation of pores within larger monolayers can also enrich the catalytically active edge sites. Ajayan *et al.* has demonstrated this concept with 1H MoS₂ monolayer triangles prepared from a CVD method.^[72] These highly crystallized 1H monolayers were large in size (up to 100 μm), and nearly inactive for HER (Tafel slope of 342 mV dec⁻¹ and onset overpotential around 500 mV).^[72] The samples were activated for HER by O₂ plasma pore generation leading to a Tafel slope and onset overpotential of 162-171 mV dec⁻¹ and 400 mV respectively. The newly formed inside edges consisted of both S and Mo terminated structures. Another strategy is annealing MoS₂ monolayers with H₂ to create pores/edges inside the monolayer. The Tafel slope and onset overpotential of these edge-rich monolayers were 117 mV dec⁻¹ and 300 mV, respectively. With smaller starting crystal sizes (100-200 nm), the HER performance can be improved further with a Tafel slope of 50 mV dec⁻¹ and onset overpotential of 120 mV.^[65]

Ultrathin TaS₂ sheets have also been treated by O₂-plasma to generate internal pores (Li *et al.* 2016).^[73] The initial highly crystallized TaS₂ sheets were created by chemical exfoliation, and have the lateral size about 15 μm with a thickness of 1-3 layers.^[73] After the pore generation, the Tafel slope and onset overpotential were both reduced from 215 mV dec⁻¹ and 310 mV, to 125-142 mV dec⁻¹ and 225 mV, respectively.^[73]

Besides, H₂O₂ oxidation can be combined with the traditional liquid exfoliation process for MoSe₂ to introduce chemically induced pores.^[74,75] During this process, the thin exfoliated MoSe₂ sheets were oxidized and etched to generate pores with high density. Whilst the Tafel slope (80 mV dec⁻¹) did not change significantly, the onset overpotential of the porous MoSe₂ was greatly reduced to 75 mV from 220 mV by this pore generation process.^[75]

Both edge-enrichment and creating monolayered NCs with small lateral size (*e.g.* 5-10 nm) are promising approaches, however, the small lateral size systems show better HER performance, even for the multilayered TMDs NCs with partial 1T phase.^[69] With ongoing developments in synthesis techniques^[10,69,71,76–79] the formation of the monolayered TMDs NCs is a highly promising strategy to achieve optimal HER catalytic performance. The edge enrichment and size control, at least, can be complimented with the phase engineering we have discussed above, although the stability of the 1T/1T' TMDs is still need to be appropriately addressed. Beyond this phase engineering, the following sections suggest that more strategies can be adapted together with the edge and size control, to further improve the HER performance.

Figure 5. a) Schematic shows the preparation of monolayered MoS₂ NCs. Reproduced with permission.^[71] Copyright 2017, Elsevier; b) The AFM image of the monolayered MoS₂ NCs; c) The optical image of the monolayered Mo-S NCs before (left) and after S-depletion (right); d-e) TEM images of the Mo-S NCs before (d) and after S-depletion (e). Insets are relating FFT patterns; f) Calculated density of state (DOS) of MoS₂ in the core and/or edge region, and the entire NC; g) Decomposition of the total DOS of MoS₂ in the core with S vacancies (S depletion) and edge regions into partial DOS of the Mo and S orbitals; h) Schematic shows the metallic edge, near-edge regions, and semiconducting core of the MoS₂ NCs; i-j) Polarization curves (i) and Tafel plots (j) of different catalysts in 0.5 M H₂SO₄. Figures b-j are reproduced with permission.^[10] Copyright 2016, American Chemical Society.

4.2.2. Defect and Strain Engineering

While phase engineering is a powerful tool to unlock catalytic potential for TMDs, there is significant value in exploring the optimization of thermodynamically stable 1H/2H TMDs for HER. A key consideration is that, as we have described previously, the basal plane of 1H/2H TMDs is relatively inactive for HER, and this contributes a huge amount of the surface area. By calculating the ΔG_{H^*} during the Volmer reaction, Wang *et al.* suggested that various types of the S vacancies could activate the HER activity on the basal plane of MoS₂, with these new S-depleted sites being suited for both Tafel and Heyrovsky reactions.^[80] Although precise control of these S vacancies is still difficult, several reported literatures suggest that some favorable S vacancies could be formed on MoS₂ monolayers.^[81-85]

In 2016 the HER catalysis of the monolayered MoS₂ NCs was studied (see **Figure 5**).^[10] These fresh-prepared 1H MoS₂ NCs (the lateral size around 12.5 nm) were treated with a cation exchange resin to gain S-depleted MoS_{1.65} NCs. The HER catalytic activity was highly improved from pure MoS₂ NCs (Tafel slope of 51 mV dec⁻¹, onset overpotential of 120-140 mV of pure NCs). These S-depleted NCs had a very low Tafel slope of 29 mV dec⁻¹, low onset overpotential of 60-75 mV (extrapolated from the Tafel plot and the cathodic Tafel line), and high j_0 of 4.13×10^{-3} mA cm⁻².^[10] The low Tafel slope around 30 mV dec⁻¹ suggested a Volmer-Tafel pathway reaction of the Mo-S NCs, which is highly promising and is among the best Mo-S base catalysts developed so far. Density functional theory (DFT) calculations showed addition effects of the defect generation including induced lattice strain, and new electronic states below the conduction band enhancing electron transport efficiency and promoting HER activity.

Figure 6. a) Schematic shows the top (top) and side (bottom) views of MoS₂ with strained S-vacancies on the basal plane; b-c) Theoretical calculations show the ΔG_{H^*} versus the reaction coordination of HER upon the S-vacancies (b), and the ΔG_{H^*} versus the x-strain with S-vacancies (c); d) The aberration-corrected (AC) TEM image of MoS₂ monolayer (4 × 4 nm) with about 43 S-vacancies (~11.3% S-vacancy) shows the Mo atoms, the pair of S atoms (2S, one S atom above the other below the Mo plane), the single S atoms (1S, only one S below the Mo plane) and the zero S atoms (0S, both the S atoms above and below the Mo plane were depleted); (e-f) Polarization curves and Tafel slopes of different samples. S-MoS₂, V-MoS₂ and SV-MoS₂ are the MoS₂ monolayer with 0% S vacancy, $12.5 \pm 2.5\%$ S vacancies, and both the $1.35 \pm 0.15\%$ strain and $12.5 \pm 2.5\%$ S vacancies, respectively. Figures a-f are reproduced with permission.^[86] Copyright 2016, Springer Nature.

Controllable S-depletion and the relating HER catalytic activity should also be established to guide further improvements. In 2015, Zheng *et al.* systematically investigated the relationship between the point S-vacancies of MoS₂ and the HER catalytic activity on the defected sites (**Figure 6**).^[86] The calculated ΔG_{H^*} on the basal plane without surface S-depletion is around 2 eV (catalytic insert for HER) which decreases to 0.18 eV with 3.12% surface S-depletion (**Figure 6b**), and reaches ± 0.08 eV with 9.38-18.75% S-vacancies. Fine control of the S-vacancies can generate more suitable ΔG_{H^*} to thermos-neutral, which is better than that of the best configured edge sites. The ΔG_{H^*} on the basal plane can also be tuned to be negative and close to 0 eV, giving better adsorption of the H atoms during the Volmer reaction (**Figure 6b**). Considering that the strain on the basal plane has also improved the HER catalytic performance owing to the strengthened hydrogen binding,^[60,87] the ΔG_{H^*} of the MoS₂ monolayers with uniaxial elastic strain was further simulated. As suggested in **Figure 6c**, the ΔG_{H^*} decreased with the strain for any investigated concentrations of the S-vacancy. This result is useful since the MoS₂ monolayers are less stable with more S-depletions, and the small applied strain could improve the stability with few S-depletions for the best HER.

Modeled electronic structures showed that the S-depletion has introduced the defect level between the gap and under the bottom of the conduction band minimum.^[71,86,88] In a *n*-type semiconductor such as 1H MoS₂ monolayer, the Fermi level should close to the conduction band.^[71,89] The hydrogen adsorption on the S-depleted Mo sites of the basal plane is induced by these newly formed gap states (localized around the S-vacancy). The bands move closer to the Fermi level (the number of gap states also increased) with more S-vacancies, which rationally explained the gradual improved H binding (**Figure 6b-c**). Tensile strain has also such effect to the gap states, and strengthened the hydrogen binding.^[60,86,87]

Building on these theoretical understandings, Zheng *et al.* prepared large 1H MoS₂ monolayer sheet with the minimized edge ratio.^[86] Both strained ($1.35 \pm 0.15\%$) and unstrained MoS₂ monolayers were produced with controlled S-vacancies (*e.g.* 21.88%, 18.75%, 12.50%, 8.00% and 6.25%, to the total S atoms).^[86] Theoretical calculations have further suggested that the strained ($1.35 \pm 0.15\%$) MoS₂ monolayer with 12.5% S vacancies has the best matched ΔG_{H^*} to 0 eV.^[86] The HER catalytic activity of the strained pure MoS₂ sheets was poor, with onset overpotential higher than 350 mV (determined by the current density at 10 mV cm⁻²) and Tafel slope of 90 mV dec⁻¹. This HER performance was better than the pure MoS₂ without the strain (*e.g.* Tafel slope of 98 mV dec⁻¹). Both the onset overpotential and Tafel slope of the MoS₂ monolayer were firstly reduced to 250 mV and 82 mV dec⁻¹ upon the S-depletion (12.5% S vacancies), which further reduced to 170 mV and 60 mV dec⁻¹ respectively with additional $1.35 \pm 0.15\%$ strain (**Figure 6e-f**). The demonstrated best HER catalytic activity is below previously reported phase engineered and edge enriched TMDs,^[51,60,67,90,91] but the performance improvement induced by the S-depletion and strain opens an attractive future pathway for HER optimization. As suggested in **Figure 1e-f**, the ΔG_{H^*} on the basal plane of both 1H and 1T 2D-TMDs are all higher than 0 eV. Surface chalcogen vacancies could also improve the H binding and reduce the ΔG_{H^*} to be more thermodynamically neutral. Such an improvement has already been demonstrated on the 2D

MoSe₂ and MoSSe₂ NCs with Se vacancies.^[69] Noteworthy, both the surface vacancies and strain have led to a decrease in the stability of TMDs, which restricted further exploitations of the strategy. To address this, other techniques such as surface doping can be introduced to stabilize the structure as well as to reach the optimized ΔG_{H^*} .

4.3. Chemical Doping

The approaches discussed thus far have focused on manipulating the electrical properties and edge states of TMDs. However, more marked effects can be achieved by substituting either the transition metal or the chalcogen in a TMD structure, yielding new chemistries, band structures, and lattice strain towards optimized HER catalysis. Chemical doping of TMDs by various elements such as Pt, Co, Fe, Ni, O, Cl and Se can effectively tune the electronic structure and improve the HER catalytic activity.^[92-104] The external atoms could replace or bind with the M/X atoms on both the basal plane and edge of TMDs, depending on the reaction dynamics and the stability of the doped structure. Chemical doping could regulate the electronic structure of TMDs, resulting in high electrical conductivity.^[105] The HER catalytic activity of TMDs could also be finely tailored by changing the ΔG_{H^*} in the Volmer reaction and providing new active sites of the dopant itself.

4.3.1 Doping with Metals

Among various doping approaches, the incorporation of a metal atom was frequently used to tune the ΔG_{H^*} . For example, Jiang *et al.* investigated the shift of the ΔG_{H^*} of 1T MoS₂ by substitutional doping of the Mo site with different elements (V, Cr, Mn, Fe, Co, Ni, Nb, Ta, W, or Re), with DFT calculations.^[12] The doping of Mn, Cr, Cu, Ni, and Fe all reduced the ΔG_{H^*} in close to 0 eV. However, realization of such substitutional doping is challenging since the surface of 1T TMDs is highly reactive towards surface covalent functionalization and the surface of 2H/1H TMDs is relatively chemical inert.^[106,107] Investigations have implied that the doping of MoS₂ is tend to be the functionalization on the active surface and the position at the S vacancy, resulting stable structures with different HER promotion effects.^[106,107]

In 2012, Merki *et al.* demonstrated the doping of MoS₂ with various metals *via* electrochemistry.^[92] They used the amorphous MoS₃ with rich edge sites to hold the dopants of Mn, Fe, Co, Ni, Cu and Zn elements. The initial amorphous MoS₃ film has the onset overpotential of 171-203 mV, j_0 of 8.9×10^{-4} mA cm⁻² and Tafel slope of 86 mV dec⁻¹ at pH = 7.^[92] It was found that the Fe, Co and Ni doping significantly improved the intrinsic activity of the catalyst under equilibrium conditions (j_0) and the Mn, Cu, Zn doping showed slightly improvement on j_0 . The ΔG_{H^*} at the Mo- and S edges were calculated as 0.08 and 0.18 eV (associated with a single lowest energy site) respectively, basing on the model with the best H coverage. Incorporation of Co did not change the ΔG_{H^*} at the Mo-edge, but lowered the ΔG_{H^*} at the S-edge.

It is crucial to determine the optimal amount of dopants using DFT calculations as it highly affects the ΔG_{H^*} . Zheng *et al.* investigated the ΔG_{H^*} to understand the binding behavior of the whole surface of both 1H/2H and 1T WS₂ as a function of the concentration of substitutional Co dopants (calculation models are shown in **Figure 7a-b**, 4×4 unit cell).^[108] Doping of Co with very high concentrations is thermodynamically unfavorable since the incorporation of Co into the WS₂ lattice is an endergonic process.^[108] Similarly to the results reported by Merki *et al.*,^[92] it was shown that the Co doping improves the HER catalytic activity by increasing the H adsorption on the S-sites neighboring the dopant.^[108] The ΔG_{H^*} of the plane site of 1H/2H WS₂ shift to increasingly orange exergonic values (-0.98 eV) with more Co dopants (before 13% dopant), and then transit to increasingly blue endergonic values until the Co dopant's concentration of 25% (**Figure 7**). The optimized concentrations of Co doping on 1H/2H and 1T WS₂ are 6% (1 Co atom per unit cell) and 13% respectively, giving the best ΔG_{H^*} at around -0.12 eV for the 1H/2H and -0.05 eV for the 1T WS₂. Comparing with the pristine WS₂, these two values are more suited for HER with higher catalytic activities (**Figure 7c**).

Figure 7. ΔG_{H^*} of 2H and 1T WS_2 with increasing Co-dopant concentrations (W: turquoise; S: yellow; Co: light pink): a-b) Stable geometry (left) and activity map (right) as a function of Co doping concentrations. In the middle color scale bar, dark blue, red and yellow correspond to weak, strong and the optimal range for H adsorption; c) Plot of the minimum ΔG_{H^*} across the basal plane of 2H- WS_2 (i) and 1T- WS_2 (ii) as a function of doping concentrations. Figures a-c are reproduced with permission.^[108] Copyright 2018, The Royal Society of Chemistry.

Other DFT calculations (summarized in **Table 2**) have also suggested the similar doping effect on the HER performance of TMDs, which agree well with some of experimental works.^[12,93,99,108-112] Recently, Tsang *et al.* reported the Co and Ni doped thin MoS_2 nanosheets for HER.^[113] They introduced Fe, Co, Ni and Ag dopants into the structure of MoS_2 nanosheets (1-3 layers) *via* a solvothermal reaction.^[113] Successful doping of the metal atoms have been confirmed by the HAADF-STEM observations. All these metal atoms can bind with the S atom, but only the Ni atom can also bind with Mo atoms to form metal-metal bond,^[113] which is in consistent with the previous theoretical calculations.^[109] The un-doped thin MoS_2 nanosheets have an onset overpotential of around 300 mV (at the j of 10 mA cm^{-2}) and Tafel slope of 94 mV dec^{-1} . The Ag, Fe, and Ni doping have led to the larger onset overpotential, and the Co-doped MoS_2 showed much improved HER catalytic performance (onset overpotential at around 220 mV). Although the pristine and Co-doped MoS_2 all exhibited the Volmer-Heyrovsky pathway of the HER with similar Tafel slope $\sim 92\text{-}94 \text{ mV dec}^{-1}$, the evidently lowered onset overpotential meant that the reaction barrier has been much alleviated. In 2017, Hu *et al.* also reported the improved HER on TMDs by Co doping.^[114] They fabricated the 2D $MoSe_2/CoMoSe_2$ heterostructures *via* a two-step CVD method with Co doping at the margin (edge). Onset overpotential (at the j of 10 mA cm^{-2}) and Tafel slope

of the doped heterostructures were 305 mV and 95.2 mV dec⁻¹, respectively, greatly reduced from the 378 mV and 134 mV dec⁻¹ of the initial MoSe₂ sheets owing to the tuned ΔG_{H^*} at the edge position.^[114]

Table 2. Catalytic performance of doped TMDs. The best matched ΔG_{H^*} of atoms near dopants or the active dopants was taken from literatures with suitable H coverage. X and M in this table are the chalcogen and the transition metal, respectively.

TMDs	Pristine ΔG_{H^*} (eV)			Dopants and Specification	ΔG_{H^*} (eV) after doping			Ref.
	Edge	Plane			Edge	Edge	Plane	
	X	M	X		X	M	X	
1H-MoS ₂	-0.45	0.06	--	Fe/Co/Cu (interstitially dope the S edge)	0.04/0.01/0.05	unaffected	--	[109]
				Ni (interstitially dope the Mo edge)	-0.08	0.15		
				Ni (interstitially dope the S edge)		--		
				Pt/Co/Ni/Ag/Zn/Pd/Au (replace Mo)	0.1/--/--/--/--	--	0/-0.07/-0.28/0.01/-0.05/-0.04/-0.07	[93]
			2.2	P (substitutional replace S)	layer expanded		0.43 (0.04 at P sites)	[110]
			2.11	N (substitutional replace S)	improved the electrical conductivity		0.71 (-1.43 at N sites)	[115]
			--	O (substitutional replace S)	improved the electrical conductivity			[105]
1T-MoS ₂	--	--	0.13	Cr/Mn/Cu/Ni/Fe (replace Mo)	(W/Re/Nb/Ta/Co doping increase the $ \Delta G_{H^*} $ on the plane)		0.03/0.1/-0.07/-0.08/-1.2	[12]
1H-WS ₂	--	--	2.4	Co (replace 6% Mo atoms)	--	--	-0.12	[108]
1T-WS ₂	--	--	0.9	Co (replace 13% Mo atoms)	--	--	-0.05	[108]
1H MoSe ₂	0.51/0.28 (1/2 H _{ads})	0.08/-0.18 (1/2 H _{ads})	2.1	B replace Se atoms	-0.05/-0.12 (1/2 H _{ads})	-0.04/-0.24 (1/2 H _{ads})	1 (-0.15/-0.05 on the 1/2 B sites)	[111]
Ni ₂ S ₃	S (100): 1.086, Ni (100): 0.583			N (replace S atoms)	--	--	0.036	[112]

4.3.2 Doping with Non-metals

Besides the transition metals, the doping of non-metals such as O, B, Cl, Se, P, N and C have also been investigated to improve the catalytic performance on HER.^[95,97-99,101,105,115]

Theoretical calculations suggested that the P dopants (substitutional replace S, **Table 2**) can be the new active site (ΔG_{H^*} of 0.04 eV) and offer the reduced ΔG_{H^*} (0.43 eV *vs* 2.2. eV of pristine one) of the neighboring S atoms favoring for the HER.^[110] The ΔG_{H^*} can be further reduced to -0.11 eV by considering the layer expansion induced by the P dopant.^[110] With controlled P doping, a Tafel slope of 34 mV dec⁻¹ and an extremely low onset overpotential of 43 mV was achieved for thin, layer expanded, MoS₂.^[110] Other measurements on the P doped

2D MoS₂ (also the WS₂) have further confirmed the improved catalytic performance on HER.^[99,116,117]

In 2017, Li *et al.* revealed that the N doping (through the substitution of S) can lead to the decrease of the ΔG_{H^*} at the basal plane S atoms (0.71 eV vs 2.11 eV of pristine one, **Table 2**), while the N atom is inactive (ΔG_{H^*} of -1.43 eV).^[115] Although the ΔG_{H^*} at the S atom is still high (0.71 eV), the N doped MoS₂ nanosheets showed a low Tafel slope of 45 mV dec⁻¹ and low onset overpotential of 168 mV (at the *j* of 10 mA cm⁻²), which were largely improved from the pristine MoS₂.^[115] Unlike the P doped MoS₂/WS₂ with significantly reduced ΔG_{H^*} ,^[110] the good catalytic performance on the HER of the N doped MoS₂ was also ascribed to the improved electrical conductivity upon the regulation of the electronic structure.^[115] The increased density of the charge carrier has also been found in the O-doped MoS₂ sheets.^[105] Other similar works have also demonstrated this improved electrical conductivity and the relating good HER performance of 2D TMDs.^[98,101,118] Nevertheless, for different TMDs, the change of the ΔG_{H^*} upon the N doping may be varied, *i.e.* the low ΔG_{H^*} of 0.036 eV at the basal plane of Ni₂S₃ (also named as TMDs in this report), which is more close to 0 eV comparing with that of the 1H edge of MoS₂, WS₂ and MoSSe (**Table 2**).^[112]

Other non-metal dopants such as B, Cl, Se and C have also been investigated.^[95,97,111,119] They can either tune the electronic structure to improve the electronic transport or tune the ΔG_{H^*} for a better HER, *i.e.* the ΔG_{H^*} of -0.05 eV at the plane B site of the B doped MoSe₂ sheet and the highly improved catalysis of the Cl doped MoS₂.^[95,111] With the same principle, using alternating layers of different chalcogen atoms within a single mono-layer TMD can also improve HER performance. In 2015, Ren *et al.* investigated the HER of the Se-doped MoS₂ nanosheets and presented a Tafel slope of 55 mV dec⁻¹ and an onset overpotential of 140 mV which were much improved from the un-doped MoS₂ nanosheets.^[97] More careful preparations and experiments have been conducted on the *Janus* TMDs with controlled chalcogen substitution where one chalcogen layer is fully replaced by a different

chalcogen.^[120-126] One of the most studied version of these, the monolayered S-Mo-Se, can be considered as the MoS₂ monolayer with one Se substitutional doping layer (**Figure 8a**).^[122] In the *Janus* structure, the breaking of structural symmetry gives large intrinsic lattice strain, and has significant effects in altering the band-structure for distinctive physical and chemical properties. The emergence of the in-gap states and the shift in the Fermi level of the *Janus* structure owing to the structure asymmetry largely effects the hydrogen adsorption.^[123] Predictions have showed that the vacancy at the basal plane of the *Janus* S-W-Se monolayer is highly active for HER with the ΔG_{H^*} (0.015 eV vs 0.18 eV of the plane of MoS₂ with S vacancy)^[86] close to that of Pt, achieving the same result as through defect and strain engineering without sacrificing the structural stability.^[123]

In 2017, Lou *et al.* prepared *Janus* S-Mo-Se monolayers (**Figure 8b-d**) via a CVD method.^[120] Measurements on the patterned device (edges were covered to be inert) showed the HER performance of Se-Mo-S (S faces the substrate and Se is exposed for HER) > S-Mo-Se > MoSe₂, were significantly improved compared to MoS₂. The observed improvement in HER performance was ascribed to the presence of S or Se vacancies on the surface of the TMDs. The ΔG_{H^*} on the plane was calculated as 0.007, 0.060, 0.063, 0.161 eV for Se-Mo-S (with single Se vacancy), S-Mo-Se (with single S vacancy), MoSe₂ (with single Se vacancy) and MoS₂ (with single S vacancy), respectively.^[120] These results mean that the *Janus* Se-Mo-S is more promising than the MoS₂ monolayer, with fewer surface vacancies required for highly efficient and stable HER.

Although the experimental HER performance on *Janus* TMDs has not been well established (owing to the difficulty on large scale fabrications), these results showed a promising path forward. The underlying mechanism for HER performance upon element doping and/or substitution can be used to guide further improvement of the HER catalytic performance. Nevertheless, comparing with NCs and nanosheets of some TMDs we discussed above, the doped TMDs actually have not showed outstanding catalytic performance. There

are also several other factors which should be carefully addressed during the preparation of the catalyst electrode, such as the precise control of the doping and the clean surface of the TMDs after the doping treatment.

Figure 8. a) Schematic shows the Janus structure of S-Mo-Se triangular sheet (top) and corresponding optical (left bottom)/AFM (right bottom) images. Reproduced with permission.^[122] Copyright 2017, Springer Nature; b-d) Time-of-flight secondary ion mass spectrometry (TOF-SIMS) of the Janus S-Mo-Se triangular sheet. Reproduced with permission.^[120] Copyright 2017, American Chemical Society; e) Schematic of the Mo₂C/MoS₂ hybrid nanosheets. Reproduced with permission.^[127] Copyright 2017, American Chemical Society; f) Schematic of the HER on the hybrid structure of Mo₂N and MoS₂. Reproduced with permission.^[128] Copyright 2019, American Chemical Society.

4.4. Hybrid Structures

Unlike precise element doping, the fabrication of hybrid structures of TMDs and co-catalysts is more feasible. Systematic investigations suggested that the TMDs layer can be converted to other phases, *i.e.* the carbonization and nitridation of the MoS₂ to form MoC_x and MoN_x,^[127-129] which have the outstanding catalytic performance on HER owing to the hybridization between the *d*-orbitals of Mo and the *s*- and *p*-orbitals of C/N, giving similar *d*-band electronic structure with Pt.^[130-132] The synergistic effect (*e.g.* the improved charge injection from the co-catalyst) and the tuned ΔG_{H^*} at the interface of the hybrid structure offer additional opportunities in improving the HER performance.^[127,128] Recently, Zhao *et al.* fabricated the hybrid nanosheets (average thickness of 9 nm) of the MoS₂/Mo₂C (**Figure 8e**), with nanodomains of Mo₂C or a mixture of S and C incorporated in the MoS₂ sheet.^[127] DFT calculations suggested that some interfaces between the MoS₂ and Mo₂C (Mo-S-C) have the

ΔG_{H^*} very close to 0 eV, giving the efficiently improved catalytic performance on HER (Tafel slope of 53 mV dec⁻¹, and onset overpotential of 89 mV at j of 10 mA cm⁻²) over pure MoS₂ and Mo₂C nanosheets.

Such positive effect of the interface is also applicable in various reported hybrid structures such as the MoS₂/Mo₂C on N doped carbon nanotubes (CNTs),^[133] the WS₂/W₂C on N- and S-decorated carbon matrix,^[134] the S-decorated Mo₂C,^[135] and the N, S co-doped Mo₂C nanosheets.^[136] According to the previous DFT calculations, the formation of the hybrid interface between multilayered TMDs (*e.g.* MoS₂) and carbon materials is exothermic and favorable,^[129] giving the tuned ΔG_{H^*} to favor for the H adsorption/desorption, and the “ohmic contact” to low down the charge transfer resistance. This phenomenon explains well why the HER catalytic performance of some hybrid structures of TMDs and carbon materials, such as the MoSe₂ and CNTs,^[137] the MoS₂/MoSe₂ and graphene,^[138,139] were significantly superior to their pure phases or mixtures.

As we have discussed above, TMDs and their carbides, hybrid structures of TMDs and their nitrides have also been investigated for the improved catalytic performance on HER. Such improvement has been demonstrated by a report of Ojha *et al.*, where the Mo₂N nanostructures conjugated with few-layer MoS₂ sheets on the surface were fabricated for HER (**Figure 8f**).^[140] Ojha *et al.* then concluded that the interfaces and junctions between the Mo₂N and MoS₂ contributed significantly in the promoted HER. Ang *et al.* explained that the boundary of Mo₂N and MoS₂ generates the cleavage of H-O bond of the H₃O⁺ cation, resulting the improved H₂ generation.^[136] Additional DFT calculations by Yang *et al.* showed an interfacial electric field between the Mo₂N and MoS₂ domains, driving the force to facilitate the charge transfer for an efficient HER.^[141] The charge transfer issue has also been considered in building other hybrid structures for the promoted HER, such as the Ag₂S/MoS₂ and MoO₂/MoS₂ nanocomposites.^[142,144]

Further, other hybrid structures building on the TMDs have also been investigated to offer the multi-functions (*e.g.* both the HER and OER), which will be further examined in the following sections on the progress on the HER in alkaline electrolyte. Although the HER catalytic performance of these hybrid structures is still un-comparable to other engineered 2D TMDs (*e.g.* edge enriched, phase engineered, NCs with surface vacancies), they have exhibited remarkable merits towards practical applications, that are the feasible fabrication, the low-cost, and the potential high robust structure. For example, these hybrid structures can be grown on the 3D robust support (*e.g.* carbon cloth, carbon paper and carbon foam) for direct use.^[127,145]

4.5. Strategies for the HER in the Alkaline Media

The catalytic reactions discussed above were mainly driven in the acid media. Nevertheless, the high potential of the overall water electrolysis is mainly raised from the sluggish four-electron transfer kinetic of the OER, which requires the alkaline media to accelerate the reaction. In this case, the adsorption of the OH⁻ on the surface of TMDs (particularly the 2D phase) make them dispersible/soluble in the electrolyte.^[71] Besides, the HER pathways in alkaline electrolytes (*anode*: $2\text{OH}^- \rightarrow \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2\text{e}^-$; *cathode*: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$) also changed from that in acidic conditions, and the OH⁻/H₂O adsorption/dissociation (rather the ΔG_{H^*} alone) on the catalyst surface become crucial.^[146-148]

The stabilization of TMDs on the electrode can be realized by direct binding with other robust support such as carbon fibers and carbon papers.^[148-151] The key challenge of developing 2D TMDs for alkaline-based HER is how to improve the adsorption/dissociation of OH⁻ and H₂O molecules on the surface. Progress in this field suggested two main techniques, that are the chemical doping and the formation of a hybrid structure to tune the liquid/solid interface.^[148-151] Recently, Zhang *et al.* reported the C doped MoS₂ (C-MoS₂) sheets with exceptional capability of alkaline HER (1.0 M KOH), giving low Tafel slope of

46 mV dec⁻¹ and overpotential of 45 mV at 10 mA cm⁻² (vs 129 mV dec⁻¹ and 228 mV of pure MoS₂ sheets).^[152] Such outstanding performance was ascribed to the change of the electronic and coordination structures of MoS₂ upon C doping (**Figure 9a-c**). Specifically, the C dopants prefer to form the sp^2 hybrid orbitals, vacating an un-hybridized $2p_z$ orbitals perpendicular to the basal plane of MoS₂. The perpendicular $2p_z$ orbitals potentially offered active sites for water adsorption and activation, which was supported by the DFT calculations and absent in the case of pure MoS₂ (**Figure 9a-b**). The C dopants served as the site for H₂O adsorption, and the nearby S sites assisted the water dissociation by attracting the H, resulting significantly lower potential energy for the water adsorption and dissociation on the surface of C-MoS₂ than that on the pure MoS₂ (**Figure 9c**), Mo₂C and also S-depleted Mo-S sheets.^[152] With similar considerations of the electronic modulation, Huang *et al.* fabricated the metallic 1T MoS₂ with co-doping of O and Ni.^[151] The doped 1T-MoS₂ has the hexagonal arrangement with the Ni center and surrounding Mo atoms (**Figure 9d**). This catalyst has a positive onset overpotential of ~ 0 V and a low overpotential of 46 mV at j of 10 mA cm⁻² for the alkaline HER (1 M KOH), which is comparable to Pt-based catalyst.^[151] DFT calculations suggested that all the Fe, Co, and Ni doping reduced the ΔG_{H^*} at the basal plane of 1T MoS₂, while the Ni doping has the best configurations ($|\Delta G_{H^*}|$). The $\Delta G(H_2O)$ on the Ni doped 1T-MoS₂ is also reduced to 0.925 eV from 1.65 eV of pure 1T-MoS₂, which is further reduced to 0.324 eV when O is introduced to form Ni-O-Mo configurations, benefiting the dissociation of H₂O to H^{*} intermediates.^[151]

Figure 9. a,b) The top-view electrostatic potential of the water adsorbed on the basal plane, and the corresponding side-view bonding and non-bonding orbitals of C-MoS₂ (a) and MoS₂ (b); c) The relative energy diagram along the reaction coordinate, including the first (left panel) and second (right panel) water dissociation process on the basal plane of MoS₂ and C-MoS₂, respectively (R: reactant, RC: reactant complex, TS: transition state, IM: intermediate). Figures a-c are reproduced with permission.^[152] Copyright 2019, Springer Nature; d) The monolayer structure of XO@1T-MoS₂ (XO: metal heteroatom), showing the hexagonal XMo₆ units in XO-doped 1T-MoS₂ (X = Fe, Co, Ni). Reproduced with permission.^[151] Copyright 2019, Springer Nature; e) HAADF-STEM and relating elemental mapping images of the 1T-MoS₂ nanosheets with Ni-based co-catalyst loaded on the surface. Reproduced with permission.^[153] Copyright 2017, John Wiley & Sons; f) Schematic shows the interfacial synergy between Ru and MoS₂ for enhanced alkaline HER. Reproduced with permission.^[148] Copyright 2017, Royal Society of Chemistry; g) Schematic shows the alkaline HER in the interface of MoS₂ and LDH. Reproduced with permission.^[149] Copyright 2017, Elsevier; h) Photograph of the electrochemical microcell; i-j) Onset potential (i) and Tafel slope (j) of MoS₂ as a function of contact resistance. Figures h-j are reproduced with permission.^[154] Copyright 2016, Springer Nature.

Besides the doping strategies, formation of the hybrid structures has also been considered to offer multi-functions of the 2D TMD-based catalyst.^[153] For example, Zhang *et al.* reported the hybrid structure of nickel hydr(oxy)oxide nanoparticles and the 1T MoS₂ nanosheets. The Ni-based nanoparticles were homogenously loaded on the MoS₂ sheets (**Figure 9e**), facilitating the adsorption and dissociation of H₂O, and supplying protons for subsequent HER reactions at nearby active sites on the 1T-MoS₂. As a result of this “synergistic effect”, the hybrid catalyst showed a Tafel slope of 75 mV dec⁻¹ and the overpotential of 73 mV at 10 mA cm⁻² for alkaline HER (1 M KOH), which were greatly improved from the pristine 1T-MoS₂. Similar “synergistic effect” has also been observed in many other reports.^[148-150] In the work of Liu *et al.*, Ru nanoparticles were loaded on the MoS₂, giving the Tafel slope of 60 mV dec⁻¹ and the overpotential of 13 mV at 10 mA cm⁻² (1 M KOH, **Figure 9f**). In the acidic electrolyte, the improvement on the HER performance by the Ru nanoparticles was neglectable and even worse since the OER was sluggish at low concentration of OH⁻.^[148] In 2017, Hu *et al.* reported the nano-hybridization of MoS₂ with layered double hydroxides (NiCo-LDH), and demonstrated the Tafel slope of 76.6 mV dec⁻¹ and overpotential of 78 mV at 10 mA cm⁻² (1 M KOH, **Figure 9g**).^[149] This hybrid structure has the MoS₂ core and the thin LDH outer layer (**Figure 9g**), where the LDH served as the acceptor of the OH⁻. The above demonstrated “synergistic effect” suggests that many other OER catalysts can be rationally designed to bind with TMDs for an improved alkaline HER.

In hybrid structures, nevertheless, engineering TMDs still need to be considered to further improve the HER once the dissociation of H₂O (or the adsorption of the OH⁻) is secured by the co-catalyst in the interface of the hybrid structure. Comparisons between the doped and hybrid TMDs also suggested that the alkaline HER performance of the TMD-based hybrid structures are not outstanding; whilst the careful tune of the structure of 2D-TMDs (*e.g.* precise doping) is slightly difficult at this stage.

4.6. Other Strategies and Factors

Beyond the fundamental manipulation of TMDs, there are several other pathways to control and engineer their HER performance, including electron transfer and substrate binding, intrinsic charge engineering, and the formation of TMDs heterostructures. Tsai *et al.* calculated the ΔG_{H^*} at the edge of MoS₂ nanosheets on different substrates, demonstrated that the best adhesion energy between MoS₂ and the substrate should be -0.30 eV for the optimal H adsorption.^[24] On the other hand, charge transport between the electrode and the catalyst is important as it governs the Volmer and Heyrovsky reactions. Many 1H/2H TMDs are semiconductors with poor electrical conductivity, thus to drive the electrons to the active sites with additional electrical potential. This extra driving force can be minimized by size reduction, percolation, the addition of conductive fillers and intimate contact with a conductive substrate.

Intrinsic charge engineering is one strategy to consider this charge transport during the HER. It can facilitate electron injection from the electrode and transport to the catalyst by improving the electrical coupling between the substrate and the catalyst. Voiry *et al.* covered the edge of the MoS₂ by poly-methylmethacrylate (PMMA) for pure HER measurements on the basal plane (**Figure 9h-j**). They used phase engineering to locally tune the contact resistance,^[154-156] demonstrating that both the Tafel slope and the onset overpotential of the basal plane of 2H/1T MoS₂ nanosheets are highly depended on the contact resistance. Building on the improved charge injection on the basal plane and the existence of some S vacancies, the 2H MoS₂ nanosheets exhibited the low Tafel slope of 50 mV dec⁻¹ and low onset overpotential of 100 mV.^[154] Besides this intrinsic charge engineering, improvement on the charge transport to tune the ΔG_{H^*} has also been achieved *via* the TMDs heterostructures. For example, Vikraman *et al.* demonstrated the improved HER performance using MoS₂-WS₂ heterostructures owing to the elevation of electron-hole separation at the layer interfaces and sharing of active edge sites through the interface.^[157] Kwon *et al.* have improved the HER catalytic performance of MoS₂ through the formation of n-TMD/p-TMD heterojunctions to

use the high electric fields in the *p-n* junction.^[158] Although the fabrication of these materials is not simple enough, the concept of the adhesion energy and charge injection can be well employed in building the hybrid structure that we have discussed above.

5. Comparison with other HER Catalysts

Our discussions suggest that 2D TMDs can be potentially well used in both acidic and alkaline HER. In recent years, several other state-of-the-art noble metal-free HER catalysts have also been developed, including alloys, heteroatom-doped carbon materials, metal phosphides, 2D metal oxides and MXenes (*e.g.* metal carbides and metal nitrides). In 2006, Nørskov *et al.* calculated the ΔG_{H^*} of many pure metals and their bi-metallic alloys (**Figure 10a**), and suggested that many alloys are highly active for HER.^[159] However, only a small fraction of these alloys were predicted being stable in acidic HER environments, including surface alloys of BiPt, PtRu, IrRe and PtRh.^[159] These stable catalysts are still expensive and unsuitable for large scale implementations. Other noble metal free alloys (*e.g.* NiMo) have also been reported being highly active in alkaline electrolyte, but their corrosion in acidic solution is still common.^[160-161] Alloys with reduced cost (*e.g.* tri-metallic) and the monatomic/monolayered catalyst have also been reported,^[162-165] which unfortunately still face either poor catalytic performance or challenging fabrication routes for large surface coverage (*e.g.* high loading of Pt on carbon support). In this regard, 2D TMDs exhibit significant advantages on the high exposure of the surface, which can be activated for both acidic and alkaline HER based on our discussions.

With the advantages of the low cost and easy fabrication, several heteroatom-doped carbon materials have been reported for HER in recent years, including N, O, S and P doped carbon nanomaterials.^[166-170] Nevertheless, the HER catalytic performance of these materials reported so far are still poor (most Tafel slopes were larger than 100 mV dec⁻¹) comparing with that of 2D TMDs. Besides, like the alloy and heteroatom-doped carbon catalysts, several 2D TMDs are also highly conductive, *i.e.* the electrical conductivity of 10-100 S cm⁻¹ of monolayered 1T

MoS₂ sheet at room temperature, comparable to the best-performing reduced graphene oxide sheet.^[25] Even for the semiconducting 1H 2D TMDs, their poor charge transfer can be readily solved by intact contacting 2D TMD NCs onto the conductive substrate (*e.g.* the surface of 3D graphene).^[171]

Like 2D TMDs, metal phosphides, such as Co₂P, MoP and FeCoP, have the $|\Delta G_{H^*}|$ very close to 0 eV (**Figure 10b**).^[172] They exhibited outstanding HER performance even superior to many 2D TMDs, *i.e.* the Tafel slope of 33 mV dec⁻¹ and overpotential of 23 mV at $j = 10$ mA cm⁻² of the Ni₅P₄ NCs (in 0.5 M H₂SO₄),^[173] and the Tafel slope of 32 mV dec⁻¹ of FeP nanoparticles (in 0.5 M H₂SO₄).^[174] Some metal phosphides showed good alkaline HER performance, and also good oxidation resistance in both the acidic and alkaline electrolytes owing to relatively strong bonds between the metal and phosphide atoms.^[173-175] Nevertheless, metal phosphides are typically non-layered materials which increases the materials usage in the catalysis. The full exposure and participation of the surface and edges in the HER render particular advantages of 2D TMDs, although significant modifications of the materials (*e.g.* doping and hybrid structure) and relating engineering works of the electrode (*e.g.* 3D electrode) are still required to improve the HER performance.

Besides TMDs, many metal oxides and (oxy)hydroxides such as V₂O₅ and δ -MnO₂ are also layered. Exfoliation of these materials can fully take the advantages of the high surface exposure for electrocatalysis. Although these 2D materials are highly promising in both the OER and oxygen reduction reaction (ORR), their HER performance are too poor to comparable with that of most advanced 2D TMDs.^[177-179]

Other 2D layered materials beyond TMDs, the MXenes (*e.g.* metal carbides and metal nitrides), have also been investigated as outstanding HER catalyst. They have also very low ΔG_{H^*} close to 0 eV, and sometimes performed better HER performance over the advanced 2D TMDs.^[180] Differing from the active edge of 2D TMDs, the basal plane of many 2D MXenes

(except the Hf_2N , V_2N , and W_2N) are HER active.^[180] Nevertheless, the use of 2D MXenes in HER is highly stymied by their limited fabrication techniques, *i.e.* the fabrication of Sc_2C and Hf_2N which showed more optimized ΔG_{H^*} than Mo_2C .^[180] Even for the 2D MoC_2 , their top-down fabrication normally involve the selective etching process from their corresponding MAX phases with toxic fluoride chemicals,^[180,181] whilst that of 2D TMDs are highly successful, including the CVD (as well as the epitaxial growth),^[61] solvothermal synthesis,^[182] liquid phase exfoliation^[74], chemical exfoliation,^[60] tandem intercalation^[79] and the controlled explosion technique.^[10] Nevertheless, taking both the advantages, and the “synergistic effected interface” (see section 4.4) between these materials, the improved HER performance can be readily achieved by forming the hybrid structure of the 2D TMDs and MXenes.^[127,128,136]

Figure 10. a) $|\Delta G_{\text{H}^*}|$ on 256 pure metals and surface alloys. The rows indicate the pure metal substrates, and the columns indicate the solute embedded in the surface layer of the substrate (the solute coverage is 1/3 layer, and the adsorbed hydrogen coverage is also 1/3 layer. Reproduced with permission.^[159] Copyright 2019, Springer Nature; b) Activity volcano for the HER showing the electrochemical active surface area normalized current density from at $\eta = 100$ mV as a function of ΔG_{H^*} . Reproduced with permission.^[172] Copyright 2015, Royal Society of Chemistry; c) Summary of the different approaches to optimizing TMDs HER catalytic activity by control of electronic structure and active sites in a 3D electrode, leading to a future where these can be synergistically applied to achieve cost-effective HER catalysis.

6. Conclusion and Prospect

Table 3. Comparison of various approaches for improving the HER catalytic activity of TMDs (mainly the MoS₂ as examples). In most literatures, a 0.5 M H₂SO₄ electrolyte was used (pH value should not equal to 0), and the j_0 was usually affected by the amount of catalyst used in the test. We not conclude these differences in the table.

TMDs	Strategy	Tafel Slope (mV dec ⁻¹)	η (mV)	j_0 (mA cm ⁻²)	Stability (cycles/time)	Specification	Ref.
2H-MoS ₂	nanoparticles (2 nm)	82-163	<160	--	stable (1000)	limited improvement, poor performance	[182]
MoS ₂	amorphous	41-63 (1M H ₂ SO ₄)	--	$10^{-4.7} - 10^{-3.2}$	unstable (6)	unstable catalytic performance	[38]
MoS ₂	amorphous	40 (1M H ₂ SO ₄)	<170	1.3×10^{-4}	unstable (18)		[39]
MoS ₂	amorphous	29	0	5.6×10^{-1}	unstable (1000)		[41]
2H-MoS ₂	edge-aligned	86	--	2.2×10^{-9}	stable (1000)	promising, but the basal plane is inactive, edge can be enriched with small aligned sheets	[48]
2H-MoSe ₂	edge-aligned	75	--	2.0×10^{-9}	slight change (1000)		[183]
2H-MoS ₂	edge-aligned	36	119	--	stable (1000)		
2H-MoS ₂	edge-aligned, interlayer expanded	56-73	133	$0.56-0.93 \times 10^{-3}$	--	edge exposed, charge transport is challenge	[51]
2H-MoS ₂	3D porous	50	<150	--	--	edge contribution is limited, inactive basal plane	[52]
1H-MoS ₂	monolayer sheet	75-85	--	--	--	inactive basal plane	[63]
1H-WS ₂	monolayer sheet	110	<150	--	--	promising, edge contribution limited or basal plane need to be further optimized	[60]
1H-MoS ₂	size reduced	51	<120	$\sim 37 \times 10^{-3}$	--	promising, edge contribution limited or basal plane need to be further optimized	[10]
1T-MoS ₂	phase change	40	-100	--	--		[63]
1T-WS ₂	monolayer sheet	55	<80	$\sim 2 \times 10^{-2}$	stable (10000)		[60]
1T-MoS ₂	edge-aligned, interlayer expanded, phase change	43-47	113	$0.13-0.25 \times 10^{-3}$	stable (1000)	promising, performance can be further improved, fine control of the doping is challenge	[51]
1T-MoS ₂	phase change and size reduction	53	58	--	--	promising, need to be further improved	[69]
1T-MoSSe	phase change, size reduction and doping	40	49	--	--		[97]
1H-MoS ₂	size reduction and surface vacancy	29	<60	4.13×10^{-3}	stable (3000)		
2H-MoS ₂	doping, nanosheet	55	140	--	stable (9000 s)	conceptual promising, the demonstrated performance is poor, fabrication need to be further explored	[86]
1H-MoS ₂	surface vacancy, strain	60	170	$> 10^{-3}$	--	conceptual promising, challenges in the fine control of the structure and doping.	[114]
2H-MoSe ₂	2D sheet, doping	95.2	305	--	stable (12 h)		[154]
1H/1T-MoS ₂	electron injection, monolayer, few vacancies	40-50	50	$1-17 \times 10^{-3}$	--		
MoS ₂ -WS ₂	heterostructure	72	129	4.36×10^{-1}	stable (20 h)	low mass loadings	[149]
1T'-WSe ₂	phase change	150	300	--	--		[26]

TMD materials are highly promising as HER catalysts as they are relatively cheap, and highly tunable with phase-engineering, defect-engineering, chemical doping, hybrid and 3D structuring, as summarized in **Table 3**. These strategies all have both advantages and disadvantages, with the path forward utilizing a combination of these techniques. Ideally, a good HER catalyst for practical uses should have the following key features:

- A matched theoretical thermodynamic activity;
- A high density of catalytically active sites
- High electrical conductivity for efficient charge transport;
- High stability; and
- Simple fabrication pathways, efficiency utilization of material uses for low cost manufacture.

It is still highly challenging to manufacture TMD based catalysts satisfying all these features. For example, owing to the abundant active sites adjacent to each other, amorphous MoS₂ film with outstanding catalytic activity comparable to that of Pt has been demonstrated.^[41] However, the catalyst durability of the film was too poor to support the practical use.^[41] Some reported strategies for the TMD crystals with higher structure stability are more promising, but the demonstrated HER performance do not pass the threshold for commercial applications. Nevertheless, there are clear pathways forwards to enable TMD catalysts for the efficient HER, and it is likely a combinational approach of size, defect, phase, hetero- and hybrid engineering, and coupled with electrode structuring to account for fluid and gas diffusion for the optimal performance of these materials.

In a structural view, a porous 3D electrode instead of the flat 2D substrate would be suggested. This electrode should have both the high electrical conductivity and good mechanical strength to bear the long-time impact of rapid H₂ bubble movement in the mass production of H₂, *i.e.* the edge aligned nanosheets of TMDs (with expanded interlayer space) on the structural strengthened 3D graphene (or other similar supports). In this structure, edge ratio can be improved by reducing the lateral size, whilst the HER improvement from the interlayer expansion may be questionable since the mass diffusion and gas (bubble) release in such a small interlayer (~ 1 nm) is considerable poor comparing with that on the surface and edge exposing to the electrolyte directly. To expose the full surface, TMDs branches built by monolayered NCs on highly conductive stander like that of vertically aligned structure

may be useful. Nevertheless, the formation of TMDs monolayer perpendicular to the 3D channel is highly challenging at the current stage. This structure also cannot promise the high mechanical strength of the active layer (*e.g.* desquamation from the substrate). With this consideration, the hybrid edge aligned nanosheets with thin TMDs layers outside the electrically conductive layers (**Figure 10c**) may be more promising. The TMD nano-domains could also hybrid with the conductive part at the outermost layer to improve the charge injection efficiency to the catalytically active site (**Figure 10c**). Fabrication of this hybrid structure is accessible, for example, the insufficient and controlled sulfuration of the monoclinic MoO₂ (metallic) sheets. The above structures on the 3D support may be too ambitious, and the structure on the surface of alternative mechanical robust and electrically conductive support (*e.g.* the carbon cloth) can be used (**Figure 10c**). Alternatively, to alleviate the negative effects from the electron hopping between multi-layers and give more exposed active sites, rationally designed monolayered TMDs NCs (*e.g.* with high density of the active site, low E_a and suitable ΔG_{H^*}) could also layer-by-layer stacked with the internal channel of the 3D electrode (**Figure 10c**), if the interaction to the conductive substrate can be finely tuned for more efficient charge transport and the best matched ΔG_{H^*} . In many reported literatures, 3D graphene have been frequently used to build HER catalyst owing to the large pore size and high electrical conductivity. Some functionalized 3D-G materials have the improved mechanical strength, whilst the electrical conductivities were normally degenerated.^[184,185] Functionalization of the 3D-G with conducting polymer is also difficult in this case when the molecular of these conducting polymers are generally rigid (*e.g.* pyrrole). Rare works have been conducted to improve the mechanical strength, toughness and maintain the good electrical conductivity of such kind catalyst supports for efficient HER. The influence of these catalyst supports on the catalytic performance is still need to be well established.

Building on the rationally designed structure of the electrode, the active part of the catalyst then can be further modified to follow the discussed strategies or their combinations (**Figure 10c**). Specifically, the activation of the surface could be realized by both the phase change and the surface vacancy/doping. As for the metallic 1T TMD monolayers reported so far, the demonstrated HER catalytic performance was actually not so good as expected.^[22–24,63,64] More significantly improved HER performance was achieved on their small NCs (*e.g.* sub-5 nm).^[69] Nevertheless, the Tafel slopes of these 1T TMD NCs ($\sim 40 \text{ mV dec}^{-1}$, according to the slow Heyrovsky reaction) are still higher than the 29 mV dec^{-1} of the S-depleted 1H MoS₂ NCs ($\sim 12.5 \text{ nm}$) and amorphous MoS₂,^[10,41] due to likely the still high ΔG_{H^*} (*e.g.* 0.12 eV of MoS₂ monolayers) on the basal plane and the low ratio of the 1T monolayers in those as-prepared samples. Activation of the Tafel dominated reaction may need more adjacent active sites on the surface or the tuned reaction barriers by forming both the surface vacancy and doping. Improving the 1T ratio in a preparation may be realizable by taking the repeatedly and controlled insertion reaction with Li/Li⁺ based on the small size and strong diffusion ability of the Li/Li⁺ (repeat diffusion and insertion into the structure of TMDs to form a metastable phase), though it needs to be experimentally confirmed. Besides, the 1T TMDs are principally unsuitable for long-term operation due to the metastable nature. In this point, precise single-atom doping of the TMD can be considered as a pathway to adjust the structure stability, whilst the dopants can also serve as the highly active sites.^[186,187] Although DFT calculations suggested that the some types of the doping, in particular the precious metals, on the pure TMDs (**Table 2**) are difficult,^[93,108,109] the progress on the chalcogen-depletion of TMDs offers more possibility,^[110,83–86] *i.e.* the stabilization of the Pt atoms on the chalcogen vacancy. More theoretical modeling is therefore highly anticipated to assist understanding the catalysis and the stability associated with these doping modifications. Although 1H S-depleted MoS₂ NCs were believed having metallic feature from theoretical calculations,^[10,71] their 1T counterparts are still considered more promising. Nevertheless, further modifications

of the 1H monolayered TMDs NCs may be necessary, if the phase stability of 1T TMDs cannot be well addressed. Whilst the precise estimation of the catalytic activity is highly success with some conceptual devices,^[154,188] development of the direct evaluation of the catalyst's stability is slightly behind. Upon the chemical doping at the atomic-level, the slight change of the catalyst may not be detectable by the frequently used "long-term" (*e.g.* hours or days) polarization curves of the power samples and *ex-situ* characterizations. Other *in-situ* observations of the catalyst may need to be involved by integration with the conceptual device, such as the electrochemical scanning tunneling microscope (ECSTM),^[189] the scanning transmission electron microscopy (STEM),^[190] the tip-enhanced Raman-SPM/AFM (SPM: scanning Probe Microscopy) combined microscopy and beyond.^[191]

To tune the HER catalytic performance of TMDs, other techniques such as the formation of *Janus* structure, the creation of heterostructures and the interaction control between the TMDs and substrate would be also considered, though some preparations are still not feasible and cost-effective. These preparations would be more complex in practical cases when more than one sensitive factors are involved to tune the catalytic performance. Another powerful aspect of TMD catalysis that can be used in complement to the techniques we have discussed is the fabrication of chemically functionalized TMDs, these functionalities can include noble metals as we have discussed above, and also the metal organic frameworks, layered perovskites, hybrid structures or organic group functionalization.^[156-158,192-196] This is an emerging a powerful field as it opens a whole new set of possibilities to active the catalytically active sites of TMDs and add catalytic activity, *via* the functional moiety, to inactive sites on the pristine TMD for both acidic and alkaline HER. Since heterostructuring is hugely flexible owing to van der Waals stacking, unique electronic band structures (*e.g.* tune the ΔG_{H^*} and enable improved charge injection between interfaces) can be fabricated and tested in an extremely simple and controllable manner.^[127-128,133-136] Together with some doping strategies, it also supports the alkaline HER of TMDs based materials.^[156-158] While

heterostructuring will need to be supported by robust DFT calculations.^[197] It unlocks a plethora of potential material combinations and a whole new field of potential HER catalysts. While TMD heterostructures for electrocatalysis are only few and far between,^[149,150] recent reports on improved synthesis techniques for photocatalysis show the promise and power of this approach.^[197-200] On the catalytic activity scale, the emerging twistrionics may be introduced to precisely control the electronic structure of TMD bilayer heterostructures, where just by changing the angle of stacking significantly changes in band-structure emerge.^[201,202] As studied between a wider variety of TMDs or incorporated into machine learning theory,^[203,204] it is anticipated to be another powerful tool for optimized HER catalysis.

Therefore, building on the rational design of the electrode structure, and combining all of the techniques described above, TMDs can be highly promising catalysts to replace precious metals in efficient electrochemical HER (**Figure 10c**). This can be realized by building on more experimental and theoretical investigations on both TMDs and catalyst supports, as well as complementary 3D spatial electrode design.

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References

- [1] W. A. Braff, J. M. Mueller, J. E. Trancik, *Nat. Clim. Chang.* **2016**, 6, 964.
- [2] I. Dincer, *Int. J. Hydrogen Energy* **2012**, 37, 1954.
- [3] P. Nikolaidis, A. Poullikkas, *Renew. Sustain. Energy Rev.* **2017**, 67, 597.

- [4] L.-C. Ma, B. Castro-Dominguez, N. K. Kazantzis, Y. H. Ma, *Int. J. Greenh. Gas Control* **2015**, *42*, 424.
- [5] M. S. Dresselhaus, I. L. Thomas, *Nature* **2001**, *414*, 332.
- [6] J. A. Turner, *Science* **2004**, *305*, 972.
- [7] B. Hinnemann, P. G. Moses, J. Bonde, K. P. Jørgensen, J. H. Nielsen, S. Horch, I. Chorkendorff, J. K. Nørskov, *J. Am. Chem. Soc.* **2005**, *127*, 5308.
- [8] T. F. Jaramillo, K. P. Jørgensen, J. Bonde, J. H. Nielsen, S. Horch, I. Chorkendorff, *Science* **2007**, *317*, 100.
- [9] Y. Yu, S.-Y. Huang, Y. Li, S. N. Steinmann, W. Yang, L. Cao, *Nano Lett.* **2014**, *14*, 553.
- [10] L. Lin, N. Miao, Y. Wen, S. Zhang, P. Ghosez, Z. Sun, D. A. Allwood, *ACS Nano* **2016**, *10*, 8929.
- [11] H. Helmholtz, *Ann. Phys. Chem.* **1853**, *165*, 353.
- [12] Q. Tang, D. Jiang, *ACS Catal.* **2016**, *6*, 4953.
- [13] E. Skúlason, G. S. Karlberg, J. Rossmeisl, T. Bligaard, J. Greeley, H. Jónsson, J. K. Nørskov, *Phys. Chem. Chem. Phys.* **2007**, *9*, 3241.
- [14] J. Rossmeisl, E. Skulason, M. E. Bjorketun, V. Tripkovic, J. K. Nørskov, *Chem. Phys. Lett.* **2008**, *466*, 68.
- [15] E. Skúlason, V. Tripkovic, M. E. Bjorketun, S. Gudmundsdottir, G. Karlberg, J. Rossmeisl, T. Bligaard, H. Jonsson, J. K. Nørskov, *J. Phys. Chem. C* **2010**, *114*, 18182.
- [16] J. O. Bockris, E. C. Potter, *J. Electrochem. Soc.* **1952**, *99*, 169.
- [17] B. E. Conway, B. V. Tilak, *Electrochim. Acta* **2002**, *47*, 3571.
- [18] Y. Zhou, S. Xu, L. Guo, S. Zhang, H. Lu, Y. Gong, F. Gao, *RSC Adv.* **2015**, *5*, 14804.
- [19] J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov, U. Stimming, *J. Electrochem. Soc.* **2015**, *152*, J23.
- [20] H. I. Karunadasa, E. Montalvo, Y. Sun, M. Majda, J. R. Long, C. J. Chang, *Science*

- 2012**, 335, 698.
- [21] M. Chhowalla, H. S. Shin, G. Eda, L.-J. Li, K. P. Loh, H. Zhang, *Nat. Chem.* **2013**, 5, 263.
- [22] C. Tsai, K. Chan, F. Abild-Pedersen, J. K. Nørskov, *Phys. Chem. Chem. Phys.* **2014**, 16, 13156.
- [23] C. Tsai, F. Abild-Pedersen, J. K. Nørskov, *Nano Lett.* **2014**, 14, 1381.
- [24] C. Tsai, K. Chan, J. K. Nørskov, F. Abild-Pedersen, *Surf. Sci.* **2015**, 640, 133.
- [25] M. Acerce, D. Voiry, M. Chhowalla, *Nat. Nanotechnol.* **2015**, 10, 313.
- [26] M. S. Sokolikova, P. C. Sherrell, P. Palczynski, V. L. Bemmer, C. Mattevi, *Nat. Commun.* **2019**, 10, 712.
- [27] H. Tributsch, *A J. Phys. Sci.* **1977**, 32, 972.
- [28] V. Nicolosi, M. Chhowalla, M. G. Kanatzidis, M. S. Strano, J. N. Coleman, *Science* **2013**, 340, 72.
- [28] F. Reale, P. Palczynski, I. Amit, G. F. Jones, J. D. Mehew, A. Bacon, N. Ni, P. C. Sherrell, S. Agnoli, M. F. Craciun, S. Russo, C. Mattevi, *Sci. Rep.* **2017**, 7, 1.
- [30] Y. H. Lee, X. Q. Zhang, W. Zhang, M. T. Chang, C. Te Lin, K. Di Chang, Y. C. Yu, J. T. W. Wang, C. S. Chang, L. J. Li, T. W. Lin, *Adv. Mater.* **2012**, 24, 2320.
- [31] Y. Li, K. A. N. Duerloo, K. Wauson, E. J. Reed, *Nat. Commun.* **2016**, 7, 10671.
- [32] X. Zhang, Z. Lai, Q. Ma, H. Zhang, *Chem. Soc. Rev.* **2018**, 47, 3301.
- [33] V. W. Lau, A. F. Masters, A. M. Bond, T. Maschmeyer, *Chem-Eur. J.* **2012**, 18, 8230.
- [34] S. Fletcher, *J. Solid State Electrochem.* **2009**, 13, 537.
- [35] A. J. Appleby, J. H. Zagal, *J. Solid State Electrochem.* **2011**, 15, 1811.
- [36] J. Bonde, P. G. Moses, T. F. Jaramillo, J. K. Nørskov, Ib Chorkendorff, *Faraday Discuss.* **2009**, 140, 219.
- [37] T. Wang, D. Gao, J. Zhou, Z. Zhu, P. Papakonstantinou, Y. Li, M. Li, *Chem-Eur. J.* **2013**, 19, 11939.

- [38] H. Vrubel, D. Merki, X. Hu, *Energy Environ. Sci.* **2012**, 5, 6136.
- [39] D. Merki, S. Fierro, H. Vrubel, X. Hu, *Chem. Sci.* **2011**, 2, 1262.
- [40] X. Ge, L. Chen, L. Zhang, Y. Wen, A. Hirata, M. Chen, *Adv. Mater.* **2014**, 26, 3100.
- [41] T. Wang, J. Zhuo, K. Du, B. Chen, Z. Zhu, Y. Shao, M. Li, *Adv. Mater.* **2014**, 26, 3761.
- [42] S. Cho, S. J. Kim, Y. Lee, J.-S. Kim, W.-B. Jung, H.-W. Yoo, H. Kim, H.-T. Jung, *ACS Nano* **2015**, 9, 9314.
- [43] G. Deokar, P. Vancsó, R. Arenal, F. Ravoux, J. Casanova-Cháfer, E. Llober, A. Makarova, D. Vyalikh, C. Struzzi, P. Lambin, M. Jouiad, J. F. Colomer, *Adv. Mater. Interfaces* **2017**, 4, 1700801.
- [44] C. Ma, X. Qi, B. Chen, S. Bao, Z. Yin, X. Wu, Z. Luo, J. Wei, H. Zhang, H. Zhang, *Nanoscale* **2014**, 6, 5624.
- [45] J. Wang, D. Chao, J. Liu, L. Li, L. Lai, J. Lin, Z. Shen, *Nano Energy* **2014**, 7, 151-160.
- [46] H. Bian, Y. Ju, J. Yan, P. Li, Y. Li, S. Liu, *Small* **2018**, 14, 1703003.
- [47] K. Zhang, Y.-C. Lin, J. A. Robinson, *Semiconductors and Semimetals* **2016**, 95, 189.
- [48] D. Kong, H. Wang, J. J. Cha, M. Pasta, K. J. Koski, J. Yao, Y. Cui, *Nano Lett.* **2013**, 13, 1341.
- [49] S. Shin, Z. Jin, D. H. Kwon, R. Bose, Y.-S. Min, *Langmuir* **2015**, 31, 1196.
- [50] H. Wang, D. Kong, P. Johanes, J. J. Cha, G. Zheng, K. Yan, N. Niu, Y. Cui, *Nano. Lett.* **2013**, 13, 3426.
- [51] H. Wang, Z. Lu, S. Xu, D. Kong, J. J. Cha, G. Zheng, P.-C. Hsu, K. Yan, D. Bradshaw, F. B. Prinz, Y. Cui, *Proc. Natl. Acad. Sci. U. S. A.* **2013**, 110, 19701.
- [52] J. Kibsgaard, Z. Chen, B. N. Reinecke, T. F. Jaramillo, *Nat. Mater.* **2012**, 11, 963.
- [53] L. Zhang, H. Wu, Y. Yan, X. Wang, X. Lou, *Energy Environ. Sci.* **2014**, 7, 3302.
- [54] Y. Tan, P. Liu, L. Chen, W. Cong, Y. Ito, J. Han, X. Guo, Z. Tang, T. Fujita, A. Hirata, M. W. Chen, *Adv. Mater.* **2014**, 26, 8023.
- [55] J. Ding, Y. Zhou, Y. Li, S. Guo, X. Huang, *Chem. Mater.* **2016**, 28, 2074.

- [56] S. H. Choi, Y. N. Ko, J. Lee, Y. C. Kang, *Adv. Funct. Mater.* **2015**, 25, 1780.
- [57] L. Zhang, T. Wang, L. Sun, Y. Sun, T. Hu, K. Xu, F. Ma, *J. Mater. Chem. A* **2017**, 5, 19752.
- [58] Y. Liu, L. Ren, Z. Zhang, X. Qi, H. Li, J. Zhong, *Sci. Rep.* **2015**, 6, 22516.
- [59] M. Zou, J. Zhang, H. Zhu, M. Du, Q. Wang, M. Zhang, X. Zhang, *J. Mater. Chem. A* **2015**, 3, 12149.
- [60] D. Voiry, H. Yamaguchi, J. Li, R. Silva, D. C. B. Alves, T. Fujita, M. Chen, T. Asefa, V. B. Shenoy, G. Eda, M. Chhowalla, *Nat. Mater.* **2013**, 12, 850.
- [61] Y. Zhang, J. Shi, G. Han, M. Li, Q. Ji, D. Ma, Y. Zhang, C. Li, X. Lang, Y. Zhang, Z. Liu, *Nano Res.* **2015**, 8, 2881.
- [62] J. Shi, D. Ma, G.-F. Han, Y. Zhang, Q. Ji, T. Gao, J. Sun, X. Song, C. Li, Y. Zhang, X.-Y. Lang, Y. Zhang, Z. Liu, *ACS Nano* **2014**, 8, 10196.
- [63] D. Voiry, M. Salehi, R. Silva, T. Fujita, M. Chen, T. Asefa, V. B. Shenoy, G. Eda, M. Chhowalla, *Nano Lett.* **2013**, 13, 6222.
- [64] Y. Li, L. Wang, S. Zhang, X. Dong, Y. Song, T. Cai, Y. Liu, *Catal. Sci. Technol.* **2017**, 7, 718.
- [65] J. Xie, H. Zhang, S. Li, R. Wang, X. Sun, M. Zhou, J. Zhou, X. W. D. Lou, Y. Xie, *Adv. Mater.* **2013**, 25, 5807.
- [66] Y. Li, K. Yin, L. Wang, X. Lu, Y. Zhang, Y. Liu, D. Yan, Y. Song, S. Luo, *Appl. Catal. B-Environ.* **2018**, 239, 537.
- [67] K. Chang, X. Hai, H. Pang, H. Zhang, L. Shi, G. Liu, H. Liu, G. Zhao, M. Li, J. Ye, *Adv. Mater.* **2016**, 28, 10033.
- [68] Q. He, L. Wang, K. Yin, S. Luo, *Nanoscale Res. Lett.* **2018**, 13, 167.
- [69] C. Tan, Z. Luo, A. Chaturvedi, Y. Cai, Y. Du, Y. Gong, Y. Huang, Z. Lai, X. Zhang, L. Zheng, X. Qi, M. H. Goh, J. Wang, S. Han, X.-J. Wu, L. Gu, C. Kloc, H. Zhang, *Adv. Mater.* **2018**, 30, 1705509.

- [70] L. Lin, The Preparation and characterisation of graphene and its analogues, University of Sheffield, **2013**.
- [71] L. Lin, N. Miao, J. Huang, S. Zhang, Y. Zhu, D. D. Horsell, P. Ghosez, Z. Sun, D. A. Allwood, *Nano Energy* **2017**, 38, 544.
- [72] G. Ye, Y. Gong, J. Lin, B. Li, Y. He, S. T. Pantelides, W. Zhou, R. Vajtai, P. M. Ajayan, *Nano Lett.* **2016**, 16, 1097.
- [73] H. Li, Y. Tan, P. Liu, C. Guo, M. Luo, J. Han, T. Lin, F. Huang, M. Chen, *Adv. Mater.* **2016**, 28, 8945.
- [74] J. N. Coleman, M. Lotya, A. O'Neill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, R. J. Smith, I. V Shvets, S. K. Arora, G. Stanton, H.-Y. Kim, K. Lee, G. T. Kim, G. S. Duesberg, T. Hallam, J. J. Boland, J. J. Wang, J. F. Donegan, J. C. Grunlan, G. Moriarty, A. Shmeliov, R. J. Nicholls, J. M. Perkins, E. M. Grieveson, K. Theuwissen, D. W. McComb, P. D. Nellist, V. Nicolosi, *Science* **2011**, 331, 568.
- [75] Z. Lei, S. Xu, P. Wu, *Phys. Chem. Chem. Phys.* **2016**, 18, 70.
- [76] L. Lin, Y. Xu, S. Zhang, I. M. Ross, A. C. M. Ong, D. A. Allwood, *ACS Nano* **2013**, 7, 8214.
- [77] S. Xu, D. Li, P. Wu, *Adv. Funct. Mater.* **2015**, 25, 1127.
- [78] H. Li, R. Y. Tay, S. H. Tsang, X. Zhen, E. H. T. Teo, *Small* **2015**, 11, 6491.
- [79] S. Jeong, D. Yoo, M. Ahn, P. Miró, T. Heine, J. Cheon, *Nat. Commun.* **2015**, 6, 5763.
- [80] Y. Ouyang, C. Ling, Q. Chen, Z. Wang, L. Shi, J. Wang, *Chem. Mater.* **2016**, 28, 4390.
- [81] J. Hong, Z. Hu, M. Probert, K. Li, D. Lv, X. Yang, L. Gu, N. Mao, Q. Feng, L. Xie, J. Zhang, D. Wu, Z. Zhang, C. Jin, W. Ji, X. Zhang, J. Yuan, Z. Zhang, *Nat. Commun.* **2015**, 6, 6293.
- [82] S. Najmaei, Z. Liu, W. Zhou, X. Zou, G. Shi, S. Lei, B. I. Yakobson, J.-C. Idrobo, P. M. Ajayan, J. Lou, *Nat. Mater.* **2013**, 12, 754.
- [83] Q. Ma, P. M. Odenthal, J. Mann, D. Le, C. S. Wang, Y. Zhu, T. Chen, D. Sun, K.

- Yamaguchi, T. Tran, M. Wurch, J. L. McKinley, J. Wyrick, K. Magnone, T. F. Heinz, T. S. Rahman, R. Kawakami, L. Bartels, *J. Phys. Condens. Matter* **2013**, 25, 252201.
- [84] H.-P. Komsa, J. Kotakoski, S. Kurasch, O. Lehtinen, U. Kaiser, A. V. Krashenninnikov, *Phys. Rev. Lett.* **2012**, 109, 035503.
- [85] D. Liu, Y. Guo, L. Fang, J. Robertson, *Appl. Phys. Lett.* **2013**, 103, 183113.
- [86] H. Li, C. Tsai, A. L. Koh, L. Cai, A. W. Contryman, A. H. Fragapane, J. Zhao, H. S. Han, H. C. Manoharan, F. Abild-Pedersen, J. K. Nørskov, X. Zheng, *Nat. Mater.* **2016**, 15, 48.
- [87] B. Yildiz, *MRS Bull.* **2014**, 39, 147.
- [88] W. Zhou, X. Zou, S. Najmaei, Z. Liu, Y. Shi, J. Kong, J. Lou, P. M. Ajayan, B. I. Yakobson, J.-C. Idrobo, *Nano Lett.* **2013**, 13, 2615.
- [89] A. W. Bott, *Curr. Sep.* **1998**, 17, 87.
- [90] A. Liu, L. Zhao, J. Zhang, L. Lin, H. Wu, *ACS Appl. Mater. Interfaces* **2016**, 8, 25210.
- [91] M. A. Lukowski, A. S. Daniel, F. Meng, A. Forticaux, L. Li, S. Jin, *J. Am. Chem. Soc.* **2013**, 135, 10274.
- [92] D. Merki, H. Vrubel, L. Rovelli, S. Fierro, X. Hu, *Chem. Sci.* **2012**, 3, 2515.
- [93] J. Deng, H. Li, J. Xiao, Y. Tu, D. Deng, H. Yang, H. Tian, J. Li, P. Ren, X. Bao, *Energy Environ. Sci.* **2015**, 8, 1594.
- [94] X. Dai, K. Du, Z. Li, M. Liu, Y. Ma, H. Sun, X. Zhang, Y. Yang, *ACS Appl. Mater. Interfaces* **2015**, 7, 27242.
- [95] X. Zhang, F. Meng, S. Mao, Q. Ding, M. J. Shearer, M. S. Faber, J. Chen, R. J. Hamers, S. Jin, *Energy Environ. Sci.* **2015**, 8, 862.
- [96] X.-J. Lv, G.-W. She, S.-X. Zhou, Y.-M. Li, *RSC Adv.* **2013**, 3, 21231.
- [97] X. Ren, Q. Ma, H. Fan, L. Pang, Y. Zhang, Y. Yao, X. Ren, S. (Frank) Liu, *Chem. Commun.* **2015**, 51, 15997.
- [98] C. Sun, J. Zhang, J. Ma, P. Liu, D. Gao, K. Tao, D. Xue, *J. Mater. Chem. A* **2016**, 4,

11234.

- [99] T. A. Shifa, F. Wang, K. Liu, Z. Cheng, K. Xu, Z. Wang, X. Zhan, C. Jiang, J. He, *Small* **2017**, *13*, 1603706.
- [100] A. Jiang, B. Zhang, Z. Li, G. Jin, J. Hao, *Chem. - An Asian J.* **2018**, *13*, 1438.
- [101] X. Ren, Q. Ma, P. Ren, Y. Wang, *Int. J. Hydrogen Energy* **2018**, *43*, 15275.
- [102] Y. Zhao, W. Wang, C. Li, L. He, *Sci. Rep.* **2017**, *7*, 17088.
- [103] G. Zhang, X. Zheng, Q. Xu, J. Zhang, W. Liu, J. Chen, *J. Mater. Chem. A* **2018**, *6*, 4793.
- [104] Y. Qu, H. Pan, C. T. Kwok, Z. Wang, *Nanoscale Res. Lett.* **2015**, *10*, 480.
- [105] J. Xie, J. Zhang, S. Li, F. Grote, X. Zhang, H. Zhang, R. Wang, Y. Lei, B. Pan, Y. Xie, *J. Am. Chem. Soc.* **2013**, *135*, 17881.
- [106] D. Voiry, A. Goswami, R. Kappera, C. de C. C. e Silva, D. Kaplan, T. Fujita, M. Chen, T. Asefa, M. Chhowalla, *Nat. Chem.* **2015**, *7*, 45.
- [107] Q. Tang, D. Jiang, *Chem. Mater.* **2015**, *27*, 3743.
- [108] X. Shi, M. Fields, J. Park, J. M. McEnaney, H. Yan, Y. Zhang, C. Tsai, T. F. Jaramillo, R. Sinclair, J. K. Nørskov, X. Zheng, *Energy Environ. Sci.* **2018**, *11*, 2270.
- [109] H. Wang, C. Tsai, D. Kong, K. Chan, F. Abild-Pedersen, J. K. Nørskov, Y. Cui, *Nano Res.* **2015**, *8*, 566.
- [110] P. Liu, J. Zhu, J. Zhang, P. Xi, K. Tao, D. Gao, D. Xue, *ACS Energy Lett.* **2017**, *2*, 745.
- [111] D. Gao, B. Xia, C. Zhu, Y. Du, P. Xi, D. Xue, J. Ding, J. Wang, *J. Mater. Chem. A* **2018**, *6*, 510.
- [112] T. Kou, T. Smart, B. Yao, I. Chen, D. Thota, Y. Ping, Y. Li, *Adv. Energy Mater.* **2018**, *8*, 1703538.
- [113] T. H. M. Lau, X. Lu, J. Kulhavý, S. Wu, L. Lu, T.-S. Wu, R. Kato, J. S. Foord, Y.-L. Soo, K. Suenaga, S. C. E. Tsang, *Chem. Sci.* **2018**, *9*, 4769.
- [114] X. Chen, Y. Qiu, G. Liu, W. Zheng, W. Feng, F. Gao, W. Cao, Y. Fu, W. Hu, P. Hu, J.

- Mater. Chem. A* **2017**, *5*, 11357.
- [115] R. Li, L. Yang, T. Xiong, Y. Wu, L. Cao, D. Yuan, W. Zhou, *J. Power Sources* **2017**, *356*, 133.
- [116] L. Bian, W. Gao, J. Sun, M. Han, F. Li, Z. Gao, L. Shu, N. Han, Z. Yang, A. Song, Y. Qu, J. C. Ho, *ChemCatChem* **2018**, *10*, 1571.
- [117] K. Guruprasad, T. Maiyalagan, S. Shanmugam, *ACS Appl. Energy Mater.* **2019**, *2*, 6184.
- [118] Q. Yang, Z. Wang, L. Dong, W. Zhao, Y. Jin, L. Fang, B. Hu, M. Dong, *J. Phys. Chem. C* **2019**, *123*, 10917.
- [119] F. Zhang, Y. Lu, D. S. Schulman, T. Zhang, K. Fujisawa, Z. Lin, Y. Lei, A. L. Elias, S. Das, S. B. Sinnott, M. Terrones, *Sci. Adv.* **2019**, *5*, eaav5003.
- [120] J. Zhang, S. Jia, I. Kholmanov, L. Dong, D. Er, W. Chen, H. Guo, Z. Jin, V. B. Shenoy, L. Shi, J. Lou, *ACS Nano* **2017**, *11*, 8192.
- [121] Y. Zhou, E. Song, J. Zhou, J. Lin, R. Ma, Y. Wang, W. Qiu, R. Shen, K. Suenaga, Q. Liu, J. Wang, Z. Liu, J. Liu, *ACS Nano* **2018**, *12*, 4486.
- [122] A.-Y. Lu, H. Zhu, J. Xiao, C.-P. Chuu, Y. Han, M.-H. Chiu, C.-C. Cheng, C.-W. Yang, K.-H. Wei, Y. Yang, Y. Wang, D. Sokaras, D. Nordlund, P. Yang, D. A. Muller, M.-Y. Chou, X. Zhang, L.-J. Li, *Nat. Nanotechnol.* **2017**, *12*, 744.
- [123] D. Er, H. Ye, N. C. Frey, H. Kumar, J. Lou, V. B. Shenoy, *Nano Lett.* **2018**, *18*, 3943.
- [124] Q. Xiong, J. Zhou, J. Zhang, T. Kitamura, Z. Li, *Phys. Chem. Chem. Phys.* **2018**, *20*, 20988.
- [125] Y. Guo, S. Zhou, Y. Bai, J. Zhao, *Appl. Phys. Lett.* **2017**, *110*, 163102.
- [126] W. Shi, Z. Wang, *J. Phys. Condens. Matter* **2018**, *30*, 215301.
- [127] Z. Zhao, F. Qin, S. Kasiraju, L. Xie, M. K. Alam, S. Chen, D. Wang, Z. Ren, Z. Wang, L. C. Grabow, J. Bao, *ACS Catal.* **2017**, *7*, 7312.
- [128] M. Shao, Y. Shao, S. Ding, R. Tong, X. Zhong, L. Yao, W. F. Ip, B. Xu, X.-Q. Shi, Y.-

- Y. Sun, X. Wang, H. Pan, *ACS Sustainable Chem. Eng.* **2019**, 7, 4220.
- [129] J. Jeon, Y. Park, S. Choi, J. Lee, S. S. Lim, B. H. Lee, Y. J. Song, J. H. Cho, Y. H. Jang, S. Lee, *ACS Nano* **2018**, 12, 338.
- [130] J. R. Kitchin, J. K. Nørskov, M. A. Barteau, J. G. Chen, *Catal. Today* **2005**, 105, 66.
- [131] D. J. Ham, J. S. Lee, *Energies* **2009**, 2, 873.
- [132] C. Liu, Y. Wen, L. Lin, H. Zhang, X. Li, S. Zhang, *Int. J. Hydrogen. Energ.* **2018**, 43, 15650.
- [133] K. Zhang, Y. Zhao, S. Zhang, H. Yu, Y. Chen, P. Gao, C. Zhu, *J. Mater. Chem. A* **2014**, 2, 18715.
- [134] Y. Li, X. Wu, H. Zhang, J. Zhang, *ACS Appl. Energy Mater.* **2018**, 1, 3377.
- [135] C. Tang, W. Wang, A. Sun, C. Qi, D. Zhang, Z. Wu, D. Wang, *ACS Catal.* **2015**, 5, 6956.
- [136] H. Ang, H. T. Tan, Z. M. Luo, Y. Zhang, Y. Y. Guo, G. Guo, H. Zhang, Q. Yan, *Small* **2015**, 16, 6278.
- [137] Y. Huang, H. Lu, H. Gu, J. Fu, S. Mo, C. Wei, Y.-E. Miao, T. Liu, *Nanoscale* **2015**, 7, 18595.
- [138] H. Tang, K. Dou, C.-C. Kaun, Q. Kuang, S. Yang, *J. Mater. Chem. A* **2014**, 2, 360.
- [139] S. Kamila, B. Mohanty, A. K. Samantara, P. Guha, A. Ghosh, B. Jena, P. V. Satyam, B. K. Mishra, B. Kumar, *Sci. Rep.* **2017**, 7, 8378.
- [140] K. Ojha, S. Saha, S. Banerjee, A. K. Ganguli, *ACS Appl. Mater. Interfaces* **2017**, 9, 19455.
- [141] S. Yang, Y. Zhang, S. Wang, J. Shi, X. Liu, L. Li, *J. Mater. Chem. A* **2019**, 7, 23886.
- [142] G. Solomon, R. Mazaaro, S. You, M. M. Natile, V. Morandi, I. Concina, A. Vomiero, *ACS Appl. Mater. Interfaces* **2019**, 11, 22380.
- [143] L. Yang, W. Zhou, D. Hou, K. Zhou, G. Li, Z. Tang, L. Li, S. Chen, *J. Mater. Chem. A* **2015**, 7, 5203.

- [144] M. Sarno, A. Garamella, C. Cirillo, P. Ciambelli, *Chem. Eng. Trans.* **2014**, *41*, 385.
- [145] S.-K. Park, D. Y. Chung, D. Ko, Y.-E. Sung, Y. Piao, *J. Mater. Chem. A* **2016**, *4*, 12720.
- [146] R. Subbaraman, D. Tripkovic, D. Strmcnik, K.-C. Chang, M. Uchimura, A. P. Paulikas, V. Stamenkovic, N. M. Markovic, *Science* **2011**, *334*, 1256.
- [147] L. Ledezma-Yanez, W. D. Z. Wallace, P. Sebastián-Pascual, V. Climent, J. M. Feliu, m. T. M. Koper, *Nat. Energy* **2017**, *2*, 17031.
- [148] J. Liu, Y. Zheng, D. Zhu, A. Vasileff, T. Ling, S.-Z. Qiao, *Nanoscale* **2017**, *9*, 16616.
- [149] J. Hu, C. Zhang, L. Jiang, H. Lin, Y. An, D. Zhou, M. K. H. Leung, S. Yang, *Joule* **2017**, *1*, 383.
- [150] Z. Wu, M. Song, X. Liu, *J. Electrochem. Soc.* **2018**, *165*, F976.
- [151] Y. Huang, Y. Sun, X. Zheng, T. Aoki, B. Pattengale, J. Huang, X. He, W. Bian, S. Younan, N. Williams, J. Hu, J. Ge, N. Pu, X. Yan, X. Pan, L. Zhang, Y. Wei, J. Gu, *Nat. Commun.* **2019**, *10*, 982.
- [152] Y. Zang, S. Niu, Y. Wu, X. Zheng, J. Cai, J. Ye, Y. Xie, Y. Liu, J. Zhou, J. Zhu, X. Liu, G. Wang, Y. Qian, *Nat. Commun.* **2019**, *10*, 1217.
- [153] X. Zhang, Y. Liang, *Adv. Sci.* **2018**, *5*, 1700644.
- [154] D. Voiry, R. Fullon, J. Yang, C. de Carvalho Castro e Silva, R. Kappera, I. Bozkurt, D. Kaplan, M. J. Lagos, P. E. Batson, G. Gupta, A. D. Mohite, L. Dong, D. Er, V. B. Shenoy, T. Asefa, M. Chhowalla, *Nat. Mater.* **2016**, *15*, 1003.
- [155] R. Kappera, D. Voiry, S. E. Yalcin, B. Branch, G. Gupta, A. D. Mohite, M. Chhowalla, *Nat. Mater.* **2014**, *13*, 1128.
- [156] R. Kappera, D. Voiry, S. E. Yalcin, W. Jen, M. Acerce, S. Torrel, B. Branch, S. Lei, W. Chen, S. Najmaei, J. Lou, P. M. Ajayan, G. Gupta, A. D. Mohite, M. Chhowalla, *APL Mater.* **2014**, *2*, 092516.
- [157] D. Vikraman, S. Hussain, K. Akbar, L. Truong, A. Kathalingam, S.-H. Chun, J. Jung,

- H. J. Park, H.-S. Kim, *ACS Sustain. Chem. Eng.* **2018**, *6*, 8400.
- [158] K. C. Kwon, S. Choi, K. Hong, C. W. Moon, Y.-S. Shim, D. H. Kim, T. Kim, W. Sohn, J.-M. Jeon, C.-H. Lee, K. T. Nam, S. Han, S. Y. Kim, H. W. Jang, *Energy Environ. Sci.* **2016**, *9*, 2240.
- [159] J. Greeley, T. F. Jaramillo, J. Bonde, Ib Chorkendorff, J. K. Nørskov, *Nat. Mat.* **2006**, *5*, 909.
- [160] M. Fang, W. Gao, G. Dong, Z. Xia, S. Yip, Y. Qin, Y. Qu, J. C. Ho, *Nano Energy* **2016**, *27*, 247.
- [161] J. F. Gallejas, C. G. Read, C. W. Roske, N. S. Lewis, R. Schaak, *Chem. Mater.* **2016**, *28*, 6017.
- [162] S. Saha, K. V. Ramanujachary, S. E. Lofland, A. K. Ganguli, *Mater. Res. Express* **2016**, *3*, 016501.
- [163] S. Ye, F. Luo, Q. Zhang, P. Zhang, T. Xu, Q. Wang, D. He, L. Guo, Y. Zhang, C. He, X. Ouyuan, M. Gu, J. Liu, X. Sun, *Energy Environ. Sci.* **2019**, *12*, 1000.
- [164] M. Li, Q. Ma, W. Zhi, X. Liu, X. Zhu, S. Liu, *Sci. Adv.* **2015**, *1*, e1400268.
- [165] J. Zhang, Y. Zhao, X. Guo, C. Chen, C.-L. Dong, R.-S. Liu, C.-P. Han, Y. Li, Y. Gogotsi, G. Wang, *Nat. Catal.* **2018**, *1*, 985.
- [166] A. Kumatani, C. Miura, H. Kuramochi, T. Ohto, M. Wakisaka, Y. Nagata, H. Ida, Y. Takahashi, K. Hu, S. Jeong, J.-i. Fujita, T. Matsue, *Adv. Sci.* **2019**, *6*, 1900119.
- [167] B. R. Sathe, X. X. Zou, T. Asefa, *Catal. Sci. Technol.* **2014**, *4*, 2023.
- [168] L. Yang, X. Wang, J. Wang, G. Cui, D. Liu, *Nanotechnology* **2018**, *29*, 345705.
- [169] B. Zhang, H.-H. Wang, H. Su, L.-B. Lv, T.-J. Zhao, J.-M. Ge, X. Wei, K.-X. Wang, X.-H. Li, J.-S. Chen, *Nano. Res.* **2016**, *9*, 2606.
- [170] Y. Zheng, Y. Jiao, L. H. Li, T. Xing, Y. Chen, M. Jaroniec, S. Z. Qiao, *ACS Nano* **2014**, *27*, 5290.
- [171] L. Lin, W. Lei, S. Zhang, Y. Liu, G. G. Wallace, J. Chen, *Energy Storage Mater.* **2019**,

- 19, 408.
- [172] J. Kibsgaard, C. Tsai, K. Chan, J. D. Benck, J. K. Nørskov, F. Abild-Pedersen, T. F. Jaramillo, *Energy Environ. Sci.* **2015**, 8, 3022.
- [173] A. B. Laursen, K. R. Patraju, M. K. Whitaker, M. Retuerto, T. Sarkar, N. Yao, K. V. Ramanujachary, M. Greenblatt, G. C. Dismukes, *Energy Environ. Sci.* **2015**, 8, 1027.
- [174] J. Tian, Q. Liu, Y. Liang, Z. Xing, A. M. Asiri, X. Sun, *ACS Appl. Mater. Interfaces* **2014**, 6, 20579.
- [175] J. F. Callejas, C. G. Read, C. W. Roske, N. S. Lewis, R. E. Schaak, *Chem. Mater.* **2016**, 28, 6017.
- [176] K. K. Dey, S. Jha, A. Kumar, G. Gupta, A. K. Srivastava, P. P. Ingole, *Electrochim. Acta* 2019, 312, 89.
- [177] M. S. Burke, L. J. Enman, A. S. Batchellor, S. Zou, S. W. Bottcher, *Chem. Mater.* **2015**, 27, 7549.
- [178] M. P. Browne, Z. Sofer, M. Pumera, *Energy Environ. Sci.* **2019**, 12, 41.
- [179] Z. Lu, H. Wang, D. Kong, K. Yan, P.-C. Hsu, G. Zheng, H. Yao, Z. Liang, X. Sun, Y. Cui, *Nat. Commun.* **2014**, 5, 4345.
- [180] Z. W. Seh, K. D. Fredrickson, B. Anasori, J. Kibsgaard, A. L. Strickler, M. R. Lukatskaya, Y. Gototsi, T. F. Jaramillo, A. Vojvodic, *ACS Energy Lett.* **2016**, 1, 589.
- [181] J. Peng, X. Chen, W.-J. Ong, X. Zhao, N. Li, *Chem* **2019**, 5, 18.
- [182] E. G. da Silveria Firmiano, A. C. Rabelo, C. J. Dalmaschio, A. N. Pinheiro, E. C. Pereria, W. H. Schreiner, E. R. Leite, *Adv. Energy Mater.* **2014**, 4, 1301380.
- [182] T. Wang, D. Gao, J. Zhuo, Z. Zhu, P. Papakonstantinou, Y. Li, M. Li, *Chem. - A Eur. J.* **2013**, 19, 11939.
- [183] L. Zhao, C. Hong, L. Lin, H. Wu, Y. Su, X. Zhang, A. Liu, *Carbon* **2017**, 116, 223.
- [184] X. Zheng, X. Xiong, J. Yang, D. Chen, R. Jian, L. Lin, *Chem. Eng. J.* **2018**, 333, 153.
- [185] X. Zheng, H. Cheng, J. Yang, D. Chen, R. Jian, L. Lin, *ACS Appl. Nano Mater.* **2018**, 1,

2754.

- [186] D. Mombrú, R. Faccio, Á. W. Mombrú, *Appl. Surf. Sci.* **2018**, 462, 409.
- [187] D. Chen, X. Zhang, J. Tang, H. Cui, Y. Li, *Appl. Phys. A* **2018**, 124, 194.
- [188] J. Zhang, J. Wu, H. Gao, W. Chen, J. Yuan, U. Martinez, G. Gupta, A. Mohite, P. M. Ajayan, J. Lou, *Adv. Mater.* **2017**, 29, 1701955.
- [189] E. Mitterreiter, Y. Liang, M. Golibrzuch, D. McLaughlin, C. Csoklich, J. D. Bartl, A. Holleitner, U. Wurstbauer, A. S. Bandarenka, *npj 2D Mater. Appl.* **2019**, 3, 25.
- [190] B. C. Bayer, R. Kainhard, M. Reza A. Monazam, T. Susi, J. Kotakoski, T. Gupta, D. Eder, W. Waldhauser, J. C. Meyer, *ACS Nano* **2018**, 12, 8758.
- [191] BT. Hartman, C. S. Wondergem, N. Kumar, A. van den Berg, B. M. Weckhusen, *J. Phys. Chem. Lett.* **2016**, 7, 1570.
- [192] X. Chen, A. R. McDonald, *Adv. Mater.* **2016**, 28, 5738.
- [193] D. Sarkar, X. Xie, J. Kang, H. Zhang, W. Liu, J. Navarrete, M. Moskovits, K. Banerjee, *Nano Lett.* **2015**, 15, 2852.
- [194] D.-H. Kang, S. R. Pae, J. Shim, G. Yoo, J. Jeon, J. W. Leem, J. S. Yu, S. Lee, B. Shin, J.-H. Park, *Adv. Mater.* **2016**, 28, 7799.
- [195] X. Huang, B. Zheng, Z. Liu, C. Tan, J. Liu, B. Chen, H. Li, J. Chen, X. Zhang, Z. Fan, W. Zhang, Z. Guo, F. Huo, Y. Yang, L.-H. Xie, W. Huang, H. Zhang, *ACS Nano* **2014**, 8, 8695.
- [196] M. I. Gonzalez, A. B. Turkiewicz, L. E. Darago, J. Oktawiec, K. Bustillo, F. Grandjean, G. J. Long, J. R. Long, *Nature* **2020**, 577, 64.
- [197] X. Zhang, Z. Zhang, D. Wu, X. Zhang, X. Zhao, Z. Zhou, *Small Methods* **2018**, 2, 1700359.
- [198] S. Seo, S. Kim, H. Choi, J. Lee, H. Yoon, G. Piao, J. Park, Y. Jung, J. Song, S. Y. Jeong, H. Park, S. Lee, *Adv. Sci.* **2019**, 6, 1900301.
- [199] F. M. Pesci, M. S. Sokolikova, C. Grotta, P. C. Sherrell, F. Reale, K. Sharda, N. Ni, P.

- Palczynski, C. Mattevi, *ACS Catal.* **2017**, 7, 4990.
- [200] P. C. Sherrell, P. Palczynski, M. S. Sokolikova, F. Reale, F. M. Pesci, M. Och, C. Mattevi, *ACS Appl. Energy Mater.* **2019**, 2, 5877.
- [201] S. Zhu, P. Pochet, H. T. Johnson, *ACS Nano* **2019**, 13, 6925.
- [202] G. Iannaccone, F. Bonaccorso, L. Colombo, G. Fiori, *Nat. Nanotechnol.* **2018**, 13, 183.
- [203] T. K. Patra, F. Zhang, D. S. Schulman, H. Chan, M. J. Cherukara, M. Terrones, S. Das, B. Narayanan, S. K. R. S. Sankaranarayanan, *ACS Nano* **2018**, 12, 8006.
- [204] S. H. Noh, J. Hwang, J. Kang, M. H. Seo, D. Choi, B. Han, *J. Mater. Chem. A* **2018**, 6, 20005.

TOC

Building on the fundamental understandings in the catalytic process and advancements in chemical, electronic, and structural tuning of transition metal chalcogenides, the key concepts for the electrochemical HER are provided and their potentials as the next-generation of HER catalysts are discussed, providing a clear pathway forward for viable hydrogen evolution.

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