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Two-Dimensional Transition Metal Dichalcogenides for Electrocatalytic Energy Conversion Applications

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<http://dx.doi.org/10.5772/63947>

Abstract

Electrocatalytic energy conversion using renewable power sources is one of the most promising ways for energy storage and energy utilization in the new century. Specific catalysts are needed to improve the electrocatalytic reactions. Two-dimensional transition metal dichalcogenides (2D TMDs) have attracted considerable interest as alternatives to noble metal catalysts due to their unique electronic structure and high catalytic activity. Over the past years, a great number of 2D TMD-based catalysts have been explored for various electrocatalytic reactions, such as the hydrogen evolution reaction (HER) as a half reaction of water splitting and CO₂ reduction reaction as part of artificial photosynthesis. This chapter provides an overview of recent progress on TMD-based electrocatalysts, including mechanism understanding of the advantages of 2D materials, especially 2D TMDs and the up-to-date synthesizing approaches of TMDs, and state-of-the-art applications of TMDs in electrocatalytic reactions, and finally outlines the current challenges and future opportunities.

Keywords: 2D materials, transition metal dichalcogenide, electrocatalysis, water splitting, hydrogen evolution reaction, CO₂ reduction reaction, artificial photosynthesis

1. Introduction

Owing to the rapid development of modern society, the enormous demand for energy has become one of the most important issues affecting human life since twentieth century. However, the excessive reliance on the combustion of nonrenewable fossil fuels, such as coal, petroleum, and natural gas, brings not only ecological and environmental problems but also harsh ongoing impacts on the global economy and society [1]. Hence, it has become one of the

crucial challenges faced with our society to develop reliable and “green” approaches for energy conversion and storage.

Electrocatalytic energy conversion utilizing renewable power sources (e.g. solar and wind energy) is regarded as one of the most efficient and cleanest energy conversion pathways [2–5]. Furthermore, the converted energy is easy to store and use as clean energy or chemical stock. Specifically, the involvement of the electrocatalytic hydrogen evolution reaction (HER) in the cathode and the oxygen evolution reaction (OER) in the anode can efficiently drive water splitting and finally convert the electrical energy into chemical form, that is, hydrogen energy [6–8]. When CO_2 is reduced in the cathode while OER happens in the anode, which is the scheme of so-called artificial photosynthesis, it converts the electrical energy into chemical forms stocked in CO or hydrocarbons [9–11]. Hence, in such context, it is urgently required in both academic and industrial fields to build our power-supply systems based on electrocatalysis, amongst which developing efficient electrocatalysts for the aforementioned reactions is the most fundamental but vital task in this endeavour.

Two-dimensional (2D) materials have been widely studied for their important physical and chemical properties over the last several decades [12]. Since the recent discovery of graphene [13], 2D materials have gained extensive attention since they exhibit novel and unique physical, chemical, mechanical, and electronic properties [3, 14–19]. In the abundant family of 2D materials, transition metal dichalcogenides (TMDs) have attracted significant interest and become the focus of fundamental research and technological applications due to their unique crystal structures, a wide range of chemical compositions, and a variety of material properties [5, 14, 20–24]. Recently, TMDs have emerged as one kind of efficient electrocatalysts for energy-related reactions, such as the HER and CO_2 reduction reaction [15, 21, 25–29].

2. Properties of 2D TMDs and advantages for electrocatalysis

2D TMDs are usually denoted as MX_2 , where M is a transition metal of groups 4–10 (e.g. Ti, V, Co, Ni, Nb, Mo, Hf, Ta, and W) and X is a chalcogen (S, Se, and Te). MX_2 constructs layered structures by the formation of X-M-X, three layers of atoms with the chalcogen atoms in two hexagonal planes separated by a plane of metal atoms, and the valence states of metal (M) and chalcogen (X) atoms are +4 and -2, respectively (**Figure 1a**) [30–32]. There are two combination modes of metal and chalcogen elements in MX_2 , trigonal prismatic or octahedral phases, which are referred to as monolayer 2H and 1T- MX_2 , respectively (**Figure 1b–d**). Transition metals in different groups have different numbers of *d*-electrons, which fill up the non-bonding *d* bands to different levels, resulting in varied electronic properties ranging from insulators such as HfS_2 , semiconductors such as MoS_2 and WS_2 , semimetals such as WTe_2 and TiSe_2 , to true metals such as NbS_2 and VSe_2 . A few bulk TMDs such as NbSe_2 and TaS_2 exhibit low-temperature phenomena including superconductivity, charge density wave (CDW), and Mott transition [14]. When these materials are exfoliated into mono- or few layers, their properties largely preserve and also present additional characteristics due to confinement effects [14, 15, 27, 33]. The mono- or few-layer TMDs have thickness at the atomic level or significantly lower than their edge lengths and thus appear like sheets (namely, nanosheets). The atomic-thin nature

endows them with many distinctive properties with respect to their bulk counterparts, such as high specific surface area owing to planar structures, abundant uncoordinated surface atoms, excellent solution dispersity, and mechanical flexibility. These features make the 2D TMDs ideal candidates (or component parts for hybrid structures) with improved electrocatalytic performance to substitute their parent materials.

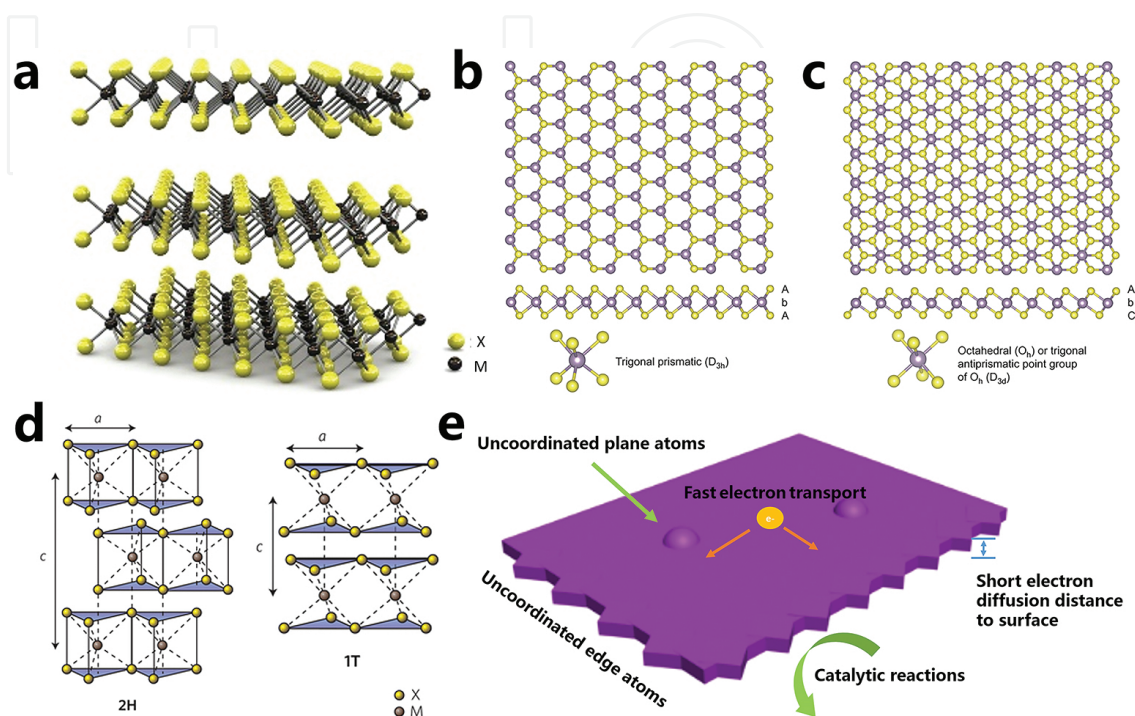


Figure 1. Structures of TMDs and schematic illustration for the advantages of TMDs as the electrocatalyst. (a) Structure of TMDs. Reproduced with permission from Radisavljevic et al. [32]; copyright 2011 Nature Publishing Group. Schematic representations of a typical TMD structure with trigonal prismatic (b) and octahedral (c) coordinations from *c*-axis (upper) and section view (middle). Reproduced with permission from Chhowalla et al. [14]; copyright 2013 Nature Publishing Group. (d) side view of the structure. Reproduced with permission from Wang et al. [33]; copyright 2012 Nature Publishing Group and (e) schematic illustration for the advantages of 2D TMDs as the electrocatalyst.

To advance the catalysis, especially electrocatalysis research, it is imperative to deepen the understanding on the underlying mechanisms involved in catalytic processes. As heterogeneous electrocatalysis essentially occurs at the interface of electrode (including catalyst) and bulk solution, the surface of catalysts should play a key role in determining species adsorption and electron transfer and, in turn, hold promise to tailoring reaction activity and selectivity in catalysis. In this regard, the 2D TMDs hold the advantages to catalyse the electrochemical reactions for the following reasons, except their unique intrinsic properties (**Figure 1e**).

(1) High surface areas. Since the electrocatalytic reactions occur on the surface of catalysts via electron transfer, species adsorption, and activation, it is the surface atom that mainly participates in the reactions. For this reason, boosting the surface-to-volume ratio would expose more atoms to the reaction species and thus help increase the probability of “active sites” to interact with reaction species. In comparison with conventional nanocatalysts, 2D materials possess significantly higher ratio of surface atom number to total atom number, thereby

promoting their catalytic activities. This ratio increases with the reduction in the number of atomic layers and hypothetically reaches its maximum value in monolayer.

(2) Abundant uncoordinated surface atoms. During a catalytic process, the reaction substrates are absorbed onto the surface atoms of the catalyst and then dissociated into highly reactive intermediates, which makes these surface atoms catalytically active sites. Certainly not all the surface atoms can efficiently participate in catalytic reactions. As a matter of fact, the adsorption and dissociation often take place on the coordinately unsaturated sites that are thermodynamically instable [16]. In the 2D materials, there are much more uncoordinatedly unsaturated atoms on the surface, which enhances their activities in catalysis. It is worth noting that the basal surfaces of catalysts might be catalytically inert in some certain reactions [14, 16]. Nevertheless, this feature does not diminish the advantage of 2D materials since catalytic activity can still arise from the active sites located along the edges of the nanosheets. For example, MoS_2 is a typical and efficient electrocatalyst for HER with higher activity at the edge compared to the basal part. The research indicates that atoms at the edges have lower coordination number than those on the surface, thereby providing reaction sites with higher catalytic activity [34, 35].

(3) Planar structure with atomic thickness. In general, the electrocatalytic performances of a catalyst are not only governed by the intrinsic nature and the number of active sites but also determined by the electron transfer between the active site and the supporting electrode [36]. From this point of view, the unique planar structure with atomic thickness of 2D materials is a decisive advantage for catalysis. The density of states should be significantly increased due to surface distortion of 2D materials, which favours the electron transport along the 2D conducting channels with high mobility as well as between its interface with other components or media, facilitating the electron diffusion between the catalytically active sites and the supporting electrode [37]. Furthermore, the unique planar structure of 2D materials also makes them ideal loading substrates for the assembly or growth of various novel hybrid catalysts. Other building blocks can be readily loaded on the flat surface or stacked layer by layer for various catalytic applications [38].

(4) Excellent solution dispersity. 2D materials often show excellent dispersity in certain solution whose type depends on their synthetic method. Thus far, exfoliation in aqueous solution is the most widespread method to produce 2D materials [39]. Most of the resulted materials are thus dispersible in water to facilitate further processing and applications towards green chemistry. In general, their superior dispersity to other counterparts is enabled by high surface area as well as large portion of uncoordinated surface atoms. The high specific surface area keeps nanosheets from precipitation, while electrostatic repulsion between the nanosheets further prevents their agglomeration.

(5) Highly tunable properties. One major difference between 2D TMDs and other 2D materials, such as graphene, is their high anisotropy and unique crystal structure. For this reason, the material properties of 2D TMDs can be effectively tuned in a wide range through different methodologies including reducing dimensions, intercalation, heterostructure, alloying, gating, pressure, lighting, and so forth [27, 40–44]. For example, through the intercalation of guest ions, the carrier densities of 2D TMDs can be tuned by multiple orders of magnitude,

which will affect the electron transfer rate in the electrocatalytic reactions [45]. 2D TMDs provide a great platform of tuning material properties towards desired activity and selectivity of a specific electrochemical reaction.

3. Preparation methods for 2D TMDs

2D TMDs provide excellent model systems to fundamentally establish structure-property relationship in electrocatalysis given their unique structural characteristics. Certainly the synthesis and fabrication of related materials are the central part of this research and both physical and chemical approaches have been utilized effectively for the synthesis of TMDs.

3.1. Exfoliation

Exfoliation is a top-down assembly method, in which physical and chemical driving forces are used to achieve separation of bulk materials. In the exfoliation of 2D materials, the precursors are usually their bulk counterparts. During the exfoliation, external or internal driving force is needed to weaken and eventually overcome the van der Waals force between adjacent layers. It can use mechanical force, such as friction or shear forces, or chemical force, in which the free energy or externally added electrochemical energy provides the driving force. Exfoliated sheets must typically be stabilized to prevent aggregation and re-stacking using surfactants, polymers, solvents, or liquid-liquid interfaces that trap and stabilize the exfoliated sheets [39, 46, 47].

It is the successful isolation of graphene from graphite using scotch tape that sparks the tremendous interest in exfoliating 2D TMD materials [13]. This mechanical exfoliation possesses the advantages of being highly reproducible and is quite suitable to fabricate single devices for research purposes and build devices based on all-layered materials [12, 48]. Nevertheless, mechanical exfoliation is not suitable for large-scale production due to the absence of layer number and lateral size control capability and it also suffers from low yield and contaminates monolayer surfaces with the adhesive polymer [32]. The limitations on throughput can be overcome by exfoliation in the liquid phases [46, 47, 49]. In general, direct sonication of a layered host is carried out in a solvent chosen to stabilize the exfoliated sheets and sometimes selected based on matching surface tension to solid surface energies. Although this method can partially exfoliate TMDs into few-layer materials, only a very low yield of monolayer TMDs can be produced.

In addition to the direct dry or liquid-phase exfoliation, a two-step process, ion intercalation followed by exfoliation, is able to produce TMDs with a higher yield. Lithium, sodium, or potassium ions are intercalated into the interlayer space and form ion-intercalated compounds, which can be further sonicated in water or organic solvents to form TMD dispersions [50]. Exfoliation of the bulk TMD crystals can also be achieved using organolithium compounds. For example, the *n*-BuLi reacts chemically with TMDs, forming Li-intercalated compounds [51]. The compounds are further exfoliated by the reaction of Li with water. A variety of TMD sheets, including MoS₂, TiS₂, TaS₂, and WS₂, can be produced by this method with the lateral size up to few microns (**Figure 2a**).

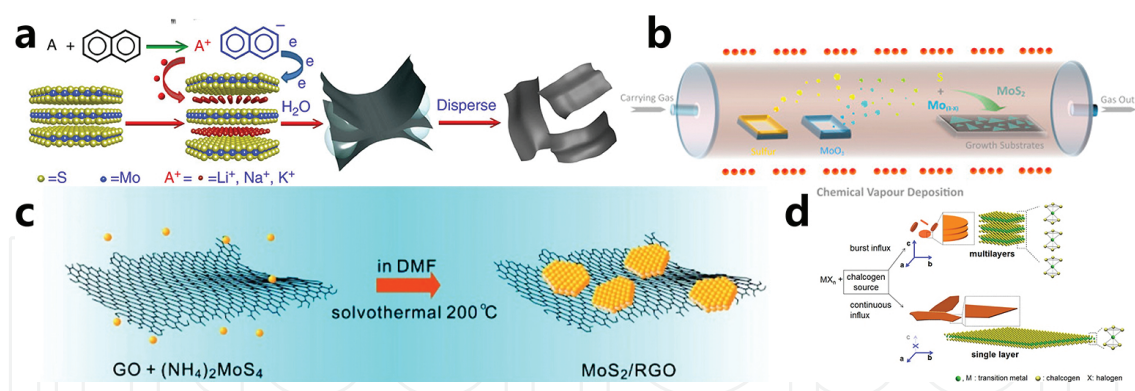
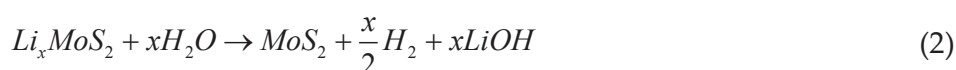


Figure 2. Preparation methods for TMDs. (a) Chemical exfoliation process of TMDs. Reproduced with permission from Zheng et al. [50]; copyright 2014 Nature Publishing Group, (b) CVD growth of TMDs. Reproduced with permission from Shi et al. [59]; copyright 2014 Royal Society of Chemistry, (c) hydrothermal growth of MoS₂ on reduced graphene oxide. Reproduced with permission from Li et al. [83]; copyright 2011 American Chemical Society, and (d) colloidal synthesis of TMDs. Reproduced with permission from Yoo et al. [85]; copyright 2014 American Chemical Society.

Electrochemical exfoliation has been used for several decades for exfoliation and restacking of layered materials to generate novel compounds [14]. It proceeds through the electrochemical insertion of an ion (such as Li⁺) into the host crystal. This destabilizes the crystal while inducing a phase change at the same time (Eq. (1)).



Placing the intercalated material in polar solvents forces hydrolysis of the lithiated species and formation of single-sheet colloidal suspensions (Eq. (2)) [52, 53]. The yield of this method is nearly 100% but requires long reaction times and careful exfoliation to prevent destruction. This method may be one of the most promising for large-scale fabrication of true monolayer materials [14, 52, 54, 55].

3.2. Chemical vapour deposition

Chemical vapour deposition (CVD) is an important and widely used technique for growing inorganic materials, which yields large, high-quality single crystals of oxide and chalcogenide materials with morphologies ranging from nanoribbons, plates, to monolayers [56–58]. In a typical CVD process, source powder(s) or molecular precursor in solution is heated. A carrier gas (e.g. argon, nitrogen, or forming gas) transports the vapour-phase precursors downstream to substrates that are placed in a region of appropriate temperature for nucleation of TMDs (Figure 2b). Optimization of substrate choice, molecular precursors, and reaction geometry can facilitate growth of monolayers [59]. Compared with chemical exfoliation, the CVD

method is more efficient in growing TMD monolayer films on substrates (SiO_2/Si [60] or Au [61]), with high quality and controllable thickness [46, 62].

Several CVD synthesis methods for TMDs have been studied, such as sulphurization of a transition metal or metal oxide thin film, thermal decomposition of thio-salts, and vapour-phase transport method [63–70]. Furthermore, Li and co-workers developed a growth method of TMDs via vapour-phase chemical reaction of transition metal oxide and chalcogen, which can control the thickness and crystallinity of TMDs [71, 72]. Specifically, metal oxide MoO_3 is used as transition metal source and it undergoes a two-step reaction. The suboxide MoO_{3-x} is firstly produced during the reaction, which further serves as an intermediate to react with chalcogen vapour (sulphur) and forms the monolayer TMDs with a triangular shape.

Further studies show that the formation of TMDs is controlled by the surface energy of substrate. The aromatic molecules can significantly enhance the wetting between precursors and the substrate surfaces and thus promote the nucleation and lateral growth of TMDs [73]. TMDs' single-crystal domain with lateral size up to several hundred micrometres can be produced by optimising the vapour-phase reaction conditions [74]. The direct vapour-phase reaction of transition metal oxide and sulphur/selenium has been widely adopted to produce TMDs including MoS_2 , WS_2 , MoSe_2 , and WSe_2 [62, 75–77].

3.3. Wet chemical approaches

Wet chemical approaches are bottom-up methods which offer a potentially powerful alternative to exfoliation and CVD. It can be used to synthesize TMDs with thicknesses ranging from the monolayer to hundreds of layers [78, 79]. Compared with CVD method, the reaction temperatures are much lower, and the produced materials are exceptional uniform and with low defect density. Thanks to diverse wet-chemical methods, the materials can be doped by adding other reagents during growth and one can also use ligand chemistry to cap the material's surface in order to modify or protect the surface [80–82]. Moreover, wet-chemical methods are often easily translated into larger-scale manufacturing processes, which may facilitate the commercialization of TMD materials. By selection of environmentally precursors and solvents, solution-based methods can be adapted to adhere to principles of green chemistry and manufacturing [80].

A traditional wet-chemical approach to chalcogenides involves hydrothermal or solvothermal growth (**Figure 2c**) [83]. Taking the synthesis of MoS_2 nanoflakes as an example, in a typical procedure, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ and thiourea have been utilized as the precursors for the Mo and S elements in hydrothermal reactions [84]. After reaction in a Teflon-lined stainless steel autoclave, the low-quality MoS_2 flakes with abundant active sites are obtained.

Colloidal synthesis is a well-established technique for synthesizing TMDs [80]. In a typical process, similar to other colloidal synthetic routes, a cold solution of precursor chemicals is injected into a hot solvent or a one-pot route can also be adopted where precursors are mixed together and then heated (up to 320°C). Recently, it was reported that monolayer TMDs such as TiS_2 , HfS_2 , and ZrS_2 could be synthesized by a novel colloidal referred to as “diluted chalcogen continuous influx” [85]. In this method, the delivery rate of a chalcogen source (such

as H_2S or CS_2) to a transition metal halide precursor in solution was controlled to be slow enough to favour the lateral (2D) growth over 3D growth (**Figure 2d**).

Although the wet-chemical approaches may unavoidably alter the lattice structure of thin TMDs and introduce extrinsic defects during exfoliation process, these defects may be helpful in electrocatalytic reactions [14, 16, 22].

4. Applications of 2D TMDs for electrocatalytic energy conversion

4.1. Hydrogen evolution reaction

H_2 is considered as one of the most promising energy carriers owing to its high energy density and environmentally benign character. Nevertheless, it is still a great challenge to produce H_2 efficiently [7, 9]. Amongst various H_2 production pathways, the electrocatalytic hydrogen evolution reaction is attracting tremendous attention due to its high energy-converting efficiency and the abundant raw material, namely, water. As is well known, hydrogen molecules can be generated from a process named water splitting, which can be divided into two independent half-reactions, HER to generate hydrogen in the cathode and OER to produce oxygen in the anode. However, the large electrolytic window of water means that appropriate electrocatalysts are required to lower the overpotential for water splitting.

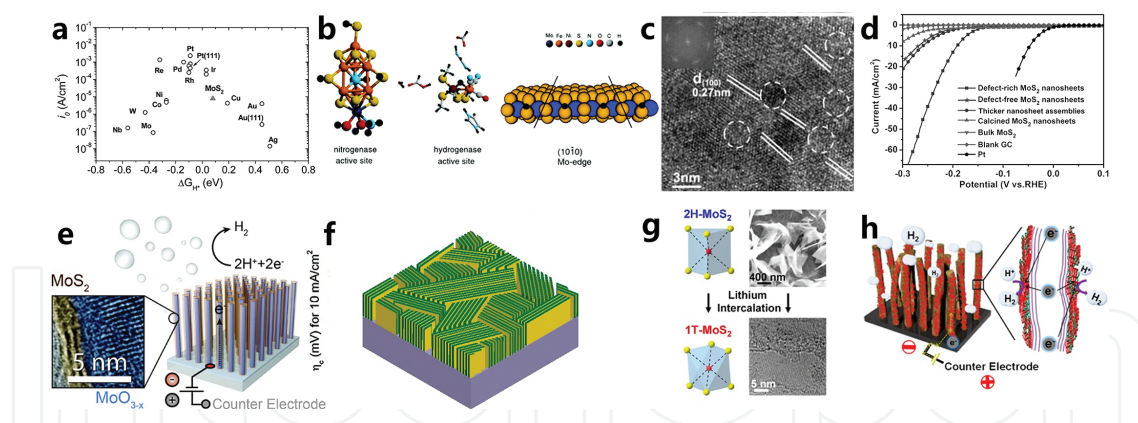


Figure 3. TMDs as electrocatalyst for HER. (a) Plot of exchange current density as a function of DFT-calculated Gibbs free energy of adsorbed atomic hydrogen for MoS₂ and pure metals. Reproduced with permission from Jaramillo et al. [34]; copyright 2007, American Association for the Advancement of Science, (b) nitrogenase (left) and hydrogenase (middle) inorganic compounds designed to mimic the edge sites of MoS₂ (right). Reproduced with permission from Hinnemann et al. [29]; copyright 2005 American Chemical Society, (c) HRTEM image and the Fourier transform pattern (inset) of the defect-rich MoS₂ ultrathin nanosheets, (d) polarization curves of various MoS₂-based samples as indicated. Reproduced with permission from Xie et al. [87]; copyright 2013 Wiley, (e) schematics of MoO₃-MoS₂ core-shell nanowires as catalysts for HER. Reproduced with permission from Chen et al. [90]; copyright 2011 American Chemical Society, (f) scheme for the vertically aligned MoS₂ layers. Reproduced with permission from Kong et al. [43]; copyright 2013 American Chemical Society, (g) exfoliation of 2H MoS₂ to 1T MoS₂ by lithium intercalation. Reproduced with permission from Lukowski et al. [91]; copyright 2013 American Chemical Society, and (h) scheme for the MoS₂/NCNT forest hybrid catalyst. Reproduced with permission from Li et al. [94]; copyright 2014 American Chemical Society.

Pt is currently the most efficient electroactive and electrochemically stable catalyst for HER, but its high cost and rare existence limit its wide application. Hence, exploring other earth abundant materials with high catalytic activities has attracted intensive interest. The experimental explorations of TMDs as the electrocatalyst for HER were motivated by theoretical calculations on MoS₂ materials, which demonstrated that the hydrogen-binding energy of MoS₂ was close to that of metals such as Pt, Rh, Re, and Ir (**Figure 3a**) [29, 34, 86]. The density functional theory (DFT) calculations showed that metallic edges of trigonal prismatic (2H) MoS₂ clusters were highly active compared to the basal plane of the chalcogenide, where it remained inert from the electrochemical point of view [14]. The surface-active sites of MoS₂ was also probed by biomimicry of Mo(IV)-disulphide inorganic and organic (**Figure 3b**) [29, 35].

The activities of TMDs are usually limited by the proportion of active edge sites [16]. To tackle this problem, Lou and co-workers fabricated the defect-rich MoS₂ ultrathin nanosheets by adding excess thiourea in the precursors (**Figure 3c and d**) [87]. The excess thiourea played a key role in the formation of defect-rich MoS₂, which not only worked as a reductant to reduce ^{VI}Mo to ^{IV}Mo but also worked as a capping agent to stabilize the morphology of MoS₂ nanosheets. The resultant defect-rich MoS₂ showed outstanding electrocatalytic activity towards HER. It held a low overpotential of 120 mV, a large current density, and a small Tafel slope of 50 mV decade⁻¹. They attributed the superior performance to the additional active edge sites exposed on defect-rich MoS₂ ultrathin nanosheets. To increase the active surface of MoS₂, Kibsgaard et al. fabricated a 3D MoS₂ porous network [88]. Chen et al. synthesized vertically oriented MoO₃-MoS₂ core-shell nanowires, in which the MoS₂ shell contributes to the outstanding catalytic response as well as to protection against corrosion (**Figure 3e**) [89, 90]. Cui's group synthesized MoS₂ films with vertically aligned layers [43]. The structure predominantly exposes the edges on the film surface maximally (**Figure 3f**). The edge-terminated surface is obtained by overcoming the free energy barrier kinetically through rapid sulphurization.

Besides the active sites, the electric conductivity of MoS₂ is another crucial factor to affect its electrocatalytic activity. Jin and co-workers reported metallic 1T-MoS₂ nanosheets, which were prepared by chemical exfoliation via lithium intercalation to from semiconducting 2H-MoS₂ nanostructures (**Figure 3g**) [91]. This catalyst exhibited metallic conductivity and achieved a current density of 10 mA cm⁻² at an overpotential of -187 mV vs. RHE. Additionally, a small Tafel slope of 43 mV decade⁻¹ was reported for this catalyst. Xie's group studied the influence of active sites and conductivity of MoS₂ on the electrocatalytic activity and achieved the balance between them by controlling disorder engineering and oxygen incorporation in MoS₂ ultrathin nanosheets. This oxygen-doped MoS₂ with synergistically structural and electronic modulations achieved high-efficient HER activity [84].

In order to further improve the catalytic efficiency and stability of TMD-based electrocatalysts, enormous research efforts have been devoted to the incorporation of TMDs with other materials, such as noble metals and carbon materials (**Figure 3h**) [92–96]. Zhang and co-workers demonstrated the wet-chemical synthesis of noble metal nanostructures epitaxially grown on TMD nanosheets. The noble metal-TMD composites exhibit good electrocatalytic activity in hydrogen evolution reaction [97, 98].

4.2. CO₂ reduction reaction

Despite the tremendous efforts being made to implement renewable energy sources, there remains a need in the longer term to be able to sustainably generate liquid fuels for applications including aviation and mining [9, 11]. Electrochemical CO₂ reduction, recycling CO₂ back to fuels, and commodity chemicals utilizing renewable energy as a power source could potentially provide a solution to this problem [99]. However, CO₂ is very stable under environmental conditions and HER often prevails over CO₂ reduction in aqueous electrolytes under cathodic polarization [100, 101], making it essential to find a suitable catalyst to achieve cost-effective CO₂ reduction with high efficiency and selectivity. Metals and especially nanostructured metals derived from metal oxide have been widely studied as electrocatalysts for CO₂ reduction [100, 102–106]; however, these systems generally show low activities and/or selectivity for a solo product (such as CO, formate, methanol, methane, ethylene, and ethanol) or need nonaqueous solvents which may limit practical application.

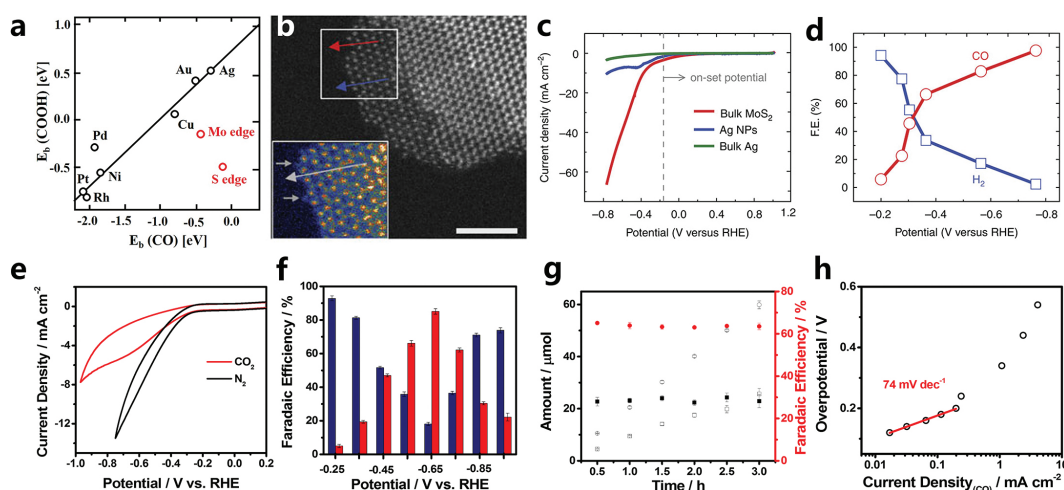


Figure 4. TMDs as electrocatalysts for electrochemical reduction of CO₂. (a) Binding energies $E_b(\text{COOH})$ vs. $E_b(\text{CO})$ for transition metals and Mo and S edges of MoS₂. Reproduced with permission from Shi et al. [108]; copyright 2014 Royal Society of Chemistry, (b) raw greyscale HAADF and false-colour low-angle annular dark-field (LAADF) image (inset) of MoS₂ edges (scale bar, 5 nm), (c) cyclic voltammetric (CV) curves for bulk MoS₂, Ag nanoparticles (Ag NPs), and bulk Ag in CO₂ environment. The electrolyte is a mixture of 96 mol% water and 4 mol% EMIM-BF₄, (d) CO and H₂ Faradaic efficiency (FE) at different applied potentials. Reproduced with permission from Asadi et al. [109]; copyright 2014 Nature Publishing Group, (e) CVs of rGO-PEI-MoS₂-modified GCE in N₂-saturated (black curve) and CO₂-saturated (red curve) 0.5 M aqueous NaHCO₃ solution. Scan rate was 50 mV s⁻¹, (f) Faradaic efficiency for CO (red bars) and H₂ (blue bars) as a function of potential, (g) amount and Faradaic efficiency of H₂ (circles) and CO (squares). Potentiostatic electrolysis at -0.4 V in CO₂-saturated 0.5 M aqueous NaHCO₃ solution and (h) Tafel plot of CO production partial current density vs. overpotential on rGO-PEI-MoS₂. Reproduced with permission from Li et al. [110]; copyright 2016 Royal Society of Chemistry.

Recently, Nørskov et al. demonstrated theoretically that MoS₂ or MoSe₂ could possibly be electrocatalysts for CO₂ reduction by DFT calculation [107, 108]. Their results indicate the edge site of MoS₂ or MoSe₂ is active for electrochemical CO₂ reduction due to the different scaling relationships of adsorption energies between key reaction intermediates (*CO and *COOH) on the edges of MoS₂ or MoSe₂ compared to transition metals (**Figure 4a**). Experimental results of MoS₂ as electrocatalyst for CO₂ reduction were firstly reported by Asadi et al. [109]

(Figure 4b–d). They uncovered that MoS₂ showed superior CO₂ reduction performance compared with the noble metals with a high current density and low overpotential (54 mV) in an ionic liquid. They also utilized DFT calculations to reveal the catalytic activity mainly arises from the molybdenum-terminated edges of MoS₂ due to their metallic character and a high *d*-electron density. The experimental result that vertically aligned MoS₂ showed an enhanced performance compared to bulk MoS₂ crystal supported their calculations.

Li and co-workers reported amorphous MoS₂ on a polyethylenimine-modified reduced graphene oxide substrate as an effective catalyst for electrocatalytic CO₂ reduction (Figure 4e–h) [110]. The catalyst is capable of producing CO at an overpotential as low as 140 mV and reaches a maximum Faradaic efficiency (FE) of 85.1% at an overpotential of 540 mV. Another interesting point is that at an overpotential of 290 mV with respect to the formation of CO, it catalyses the formation of syngas with high stability, which could be readily utilized in the current Fischer-Tropsch process and produce liquid fuels, such as ethanol and methanol. Their detailed mechanism investigation indicated that the efficiency and selectivity towards CO₂ reduction rather than hydrogen evolution at the optimal applied potential were attributed to the synergetic effect of MoS₂ and PEI: (1) the intrinsic properties of MoS₂ that it can selectively bind the intermediate during the CO₂ reduction reaction path is the principal factor contributing the CO₂ reduction and (2) PEI, an amine containing polymer with outstanding CO₂ adsorption capacity, can stabilize the intermediate and thus lower the energy barrier by hydrogen bond interaction.

5. Summary and outlook

Energy issue is one of the most urgent and critical topics in our modern society. Recently, there is increasing demand for cost-effective, efficient, and environmental-friendly energy conversion and storage devices to reduce the excessive reliance on nonrenewable fossil fuels. Due to the unique physicochemical properties of 2D TMDs, they have shown enormous potential for wide-ranging and diversified fundamental and technological applications, which include intensive research on electrocatalytic energy conversion applications, especially hydrogen evolution reaction and CO₂ reduction reaction. In these electrocatalytic reactions, the maximization of active edges and the conductivity are identified as the core issues for further development of TMD-based catalysts. A large number of synthetic strategies have been focused on maximizing the exposure of edge sites; phase structure tuning has also been as a potential tool for enhancing the electrical transport properties of TMDs.

Overall, the rich chemistry of TMDs builds an extensive platform for the study of fundamental and practical scientific phenomena in the development of real electrocatalysts for energy conversion applications. There is still much room to further improve the electrocatalytic performance of TMDs. Specifically, the fine tune of band structure and Fermi level could provide as powerful tools. Hence, a combination of theoretical, fundamental, and electrocatalysis-based applications should be explored in order to make a guidance to the developing directions. Furthermore, the mass-productive synthesis of high-quality TMDs should emerge as an urgent issue to adapt to the widely application of them in an industry level.

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