Chemical Vapor Deposition Growth of 2D Transition Metal Dichalcogenides on 3D Substrates toward Electrocatalytic-Related Applications

Lijie Zhu, Pengfei Yang, Yahan Huan, Fan Zhou, and Yanfeng Zhang*

Recently, 2D transition metal dichalcogenides (TMDCs) have emerged as promising materials for energy-related applications, due to their fascinating properties such as abundant catalytic active sites, large specific surface area, and low cost. To promote these applications, the scalable preparation of 2D TMDCs is an essential issue. Chemical vapor deposition (CVD) has been proved to be a powerful method for the syntheses of TMDCs with designable morphologies, controllable layer thicknesses, tunable phases, etc. In the CVD growth process, the morphologies, structures, and compositions of substrates play crucial roles in modulating the geometric features and physical/chemical properties of the resultant TMDCs products. Comparing with commonly used lamellar substrates, 3D-architected substrates show great potentials for tailoring the morphologies and properties of TMDCs, due to their large specific surface areas, designable structures, and variable compositions, etc. In this topical review, the introduction of recent progresses in the CVD growth of TMDCs on 3D substrates, as well as their applications in electrochemical hydrogen evolution reaction (HER) is focused. The current challenges and future research directions in this research area are also discussed.

1. Introduction

Two-dimensional (2D) transition metal dichalcogenides (TMDCs) have garnered extensive attentions in recent years due to their unique physical and chemical properties, which are distinct from their bulk counterparts. They exhibit diverse properties determined by their compositions. For example, Mo- and W-based group-VIB TMDCs (e.g., MoS$_2$ and WS$_2$) are the typical 2D semiconducting TMDCs (s-TMDCs) with certain bandgaps, whereas the V-, Nb-, Ta-based group-VB TMDCs (e.g., VSe$_2$, NbS$_2$, and TaS$_2$) are representative metallic TMDCs (m-TMDCs) with excellent electrical conductivities. Particularly, the properties of TMDCs can be tailored according to the number and stacking order of layers. For example, by reducing the layer number from bulk to monolayer, the bandgap of semiconducting MoS$_2$ can be tuned from $\approx 1.2$ eV (indirect) to 1.9 eV (direct), along with enhanced optical responsivity and light--matter coupling. Most TMDCs have three structural phases, i.e., trigonal (1T), hexagonal (2H), and rhombohedral (3R) phases, in view of the different stacking orders of the composite layers. Also, phase transformation can occur under certain circumstances. For example, MoS$_2$ crystals can be converted from semiconducting 2H-phase into metastable metallic 1T-phase by lithium intercalation or strain engineering.

Recently, 2D TMDCs (e.g., MoS$_2$, WS$_2$) are regarded as promising alternatives to noble-metal (e.g., Pt) electrocatalysts for hydrogen evolution reaction (HER), due to their high electrocatalytic activity, high electrochemical stability and low cost, etc. To achieve high-performance electrocatalysts, large specific surface areas and abundant exposed active sites are highly desired. Specifically, large surface areas can afford abundant sites for electrostatic adsorption of ions, thus allowing adequate electrochemical reactions to occur. Moreover, the edge sites of 2D TMDCs are proved to be electrocatalytic active sites for HER. In this context, tremendous efforts have been devoted to preparing ultrathin TMDCs for maximizing the accessible surface areas and exposed edge sites. However, the flat TMDCs nanosheets tend to aggregate during the electrode assembling processes, due to the van der Waals (vdW) interactions between layers, thereby reducing their accessible surface areas and impairing their electrocatalytic performances. The assembly of 2D TMDCs nanosheets into 3D architectures thus appears to be an appealing strategy to tackle this issue, as the restacking of the adjacent layers can be dramatically suppressed. In addition, plenty of nanopores and nanochannels are generally involved.
in the 3D-architected TMDCs, which can effectively reduce the mass and ion transport distances, leading to facilitated electrochemical processes.

Currently, there are two synthetic routes for constructing 2D TMDCs with 3D architectures, including solution-based synthesis and chemical vapor deposition (CVD) methods. The solution-phase based methods, such as vacuum filtration, self-assembly, and hydrothermal reaction, are compatible with mass production. However, the products inevitably suffer from unsatisfactory crystallinity, abundant intrinsic/extrinsic defects, and poor thickness uniformity. Alternatively, CVD is a powerful strategy for growing TMDCs with designable morphologies and controllable layer numbers. The yield of CVD can be scaled up to the industrial level by enlarging the growth setup. However, TMDCs layers tend to grow horizontally on the flat surfaces, and it is relatively difficult to obtain 3D-structured TMDCs on conventional laminar substrates (e.g., SiO2/Si, mica, sapphire). Fortunately, 3D-structured materials (e.g., nanoporous gold [NPG], carbon cloth [CC]) have been developed as templates for directing the growth of 2D TMDCs with 3D architectures. For instance, 3D-mesoporous monolayer MoS2 films and vertically oriented TaS2 arrays have been successfully synthesized on NPG substrates, which were directly used as high-efficiency electrocatalysts for HER.

Herein, we provide a review of the recent progresses in the CVD growth of TMDCs on 3D substrates, as well as their applications in electrocatalytic-related fields. First, the geometric features, crystal quality, and potential applications of TMDCs synthesized on 3D substrates with different compositions are summarized. The internal growth mechanisms and specific parameter optimizations for the CVD growth (e.g., growth temperature, precursor supply route) are also extensively discussed. Second, the recent advances of the applications of 2D TMDCs in electrocatalysis for HER are also summarized. Finally, an outlook of the challenges and future opportunities for the CVD syntheses of 2D TMDCs with 3D architectures is provided from the viewpoints of electrocatalytic applications.

2. CVD Synthesis of 2D TMDCs on 3D-Structured Substrates

CVD growths on conventional laminar substrates (e.g., SiO2/Si, sapphire) are promising strategies for the syntheses of high-quality and large-area uniform 2D TMDCs films, which show great potential in the fabrication of next-generation electronic and optoelectronic devices. However, these laminar substrates are incompatible with the mass production of 2D TMDCs, due to the limited superficial areas. In contrast, the CVD synthesis on 3D-architected substrates enable the production of a large quantity of 2D TMDCs flakes or bicontinuous TMDC networks. Comparing with conventional laminar substrates, these 3D-architected substrates show greater advantages for the syntheses of 2D TMDCs toward energy-, environment-, and catalyst-related applications. In this part, we discuss the CVD growth of 2D TMDCs on 3D-structured substrates, as are divided into four groups according to their compositions, including nanoporous metals, carbon-based materials, 3D oxides, and salt powders.

2.1. TMDCs Nanosheets Grown on Nanoporous Metal Substrates

Comparing with lamellar metal foils, 3D-structured metal substrates, featured with large curved surface areas, are more compatible with the batch production of 2D TMDCs nanosheets or films, enabling their applications as electrodes in energy-related fields. For example, in 2014, Geng et al. realized the growth of vertically aligned MoS2 arrays on a graphene-coated 3D-Ni-foam-networks by thermalizing the tetrakis (diethylaminothiocarbomato) molybdate (IV) precursors at a relatively low temperature of \( \approx 400 \) °C. The as-grown products were then directly used as electrocatalysts for HER in alkaline solution. In this regard, the coating of graphene on most commonly used metals (e.g., Ni, Cu, etc.) is highly necessary, due to relatively high reactivity of metals with chalcogens. However, the growth temperature is much lower than usual, thus not suitable for growing high-quality TMDCs.

In 2007, the Au(111) substrate was first introduced for the growth of monolayer MoS2 nanocrystals. Later on, Au foils and NPG were successively developed as substrates for the CVD growth of TMDCs, due to their chemical inertness toward S or Se environments, as well as their compatibilities with direct electrocatalytic related applications. Hitherto, several TMDCs, including semiconducting TMDCs (e.g., MoS2, WSe2, WS2) and metallic TMDCs (e.g., TaS2, TaSe2), have been successfully synthesized on commercial Au foils. By virtue of the excellent conductivities and chemical stabilities of Au foils, such derived TMDCs were then directly used as electrocatalysts for HER, thus providing an ideal platform for examining the electrochemical properties of 2D TMDCs nanosheets. The electron coupling between TMDCs nanosheets and Au foils was confirmed to be beneficial for the interfacial charge transfer, thus facilitating their applications in energy conversion and storage related fields.

In contrast to laminar Au foil, 3D NPG foam has larger accessible surface area, shorter ion and mass transport distance, showing great potential in preparing 2D TMDCs toward electrocatalytic-related applications. Tremendous endeavors have been devoted to preparing 2D TMDCs nanosheets on NPG, aiming at achieving high-performance electrocatalytic HER. In 2014, Tan et al. first synthesized continuous MoS2 films on chemically dealloyed 3D NPG templates using MoO3 and S powders as precursors. After a typical CVD procedure at \( \approx 650 \) °C for 30 min, uniform and continuous MoS2 films were achieved at the curved internal surfaces of 3D NPG templates (as representatively shown in Figure 1a). The thickness of MoS2 was tunable from monolayer to few layers by optimizing the CVD growth time, and the distance between MoS2 precursor and NPG substrate. The annular bright-field scanning transmission electron microscopy (ABF-STEM) image on the flat regions of NPG revealed the 2H-phase structure of monolayer MoS2 (Figure 1b). The MoS2 films naturally inherited the 3D curvature of the NPG substrate, usually possessing obvious lattice distortions at the curved regions, due to large out-of-plane lattice strains. Notably, the strain effect can be applied to tune the electronic structure of MoS2 and enhance the electrocatalytic activity for HER, as evidenced by the small Tafel slope of \( \approx 46 \) mV dec\(^{-1}\) and low onset overpotential of \( \approx 118 \) mV. This growth strategy using the NPG
template contributes to a facile way for tailoring the catalytic activities of TMDCs, by naturally introducing strain effects using the highly corrugated NPG substrates.

More intriguingly, Huan et al. \[41\] demonstrated that, vertically oriented metallic 1T-TaS$_2$ nanosheets can also be grown on NPG substrates, using TaCl$_5$ and S powders as precursors via a facile atmospheric pressure CVD (APCVD) method (Figure 1c–f). The nanoporous structures of NPG can provide more nucleation sites comparing with the conventional flat substrates, promoting the rapid sulfurization of TaCl$_5$ during the CVD growth. As a result, large-area uniform, vertically oriented 1T-TaS$_2$ nanosheets arrays were obtained on the NPG substrate in only 5 min (at /C25600/C14C) (Figure 1d–e). The thickness of obtained 1T-TaS$_2$ shows a relatively narrow distribution of 18–24 nm. The high-angle annular dark-field STEM (HAADF-STEM) image showed perfect crystal lattices, indicating the relatively high crystalline quality of the CVD-derived 1T-TaS$_2$ nanosheets (Figure 1f). Notably, the lattice constant (\(\approx 3.21 \text{ Å}\)) is slightly smaller than that of the previous result (\(\approx 3.32 \text{ Å}\)), probably due to the compressive strain effect in the vertical 1T-TaS$_2$. The curved surface, abundant nucleation site, and optimized carrier gas ratio (Ar: H$_2$ ratio \(\approx 10:1\)) were proposed to determine the vertical orientation of TaS$_2$ nanosheet. Notably, the vertically oriented nanosheets have great advantages in electrocatalytic-related applications, for their capable of affording more abundant active sites and more efficient release of H$_2$ bubbles from electrode surfaces.

Recently, a surface-limited growth method for achieving various atomically thin TMDCs films was developed by Booth and coworkers,\[55\] through alloying transition metal M (e.g., Mo, W) films with Au, which has limited solubility of X elements (X = S, Se, etc.). A thin metal M layer (\(\approx 20 \text{ nm}\)) was first sputtered onto the sapphire (c-plane) substrate by physical vapor deposition (PVD), followed by the deposition of a thick layer of Au (\(\approx 500 \text{ nm}\)). Then, the Au–M layer was heated to \(\approx 850 ^\circ \text{C}\) to form an alloy with an Au {111} surface, which was subsequently exposed to vapor-phase precursor of X element. Due to the limited solubility of X element in Au, the buried M atoms in the Au–M alloys diffused out and reacted with X vapor at the alloy surface (at the solid–gas interface), resulting in the formation of few-atom thick layers of MX$_n$ compound on the Au surface. Notably, the role of Au herein is to promote the phase separation of metal M and X precursors, so that they can react only at the vapor–solid interface. Once the interface was passivated by the MX$_n$ layer, the growth was terminated, generating a surface-limited growth mode.

Interestingly, the surface-alloy-assisted synthetic strategy can also be used to construct 3D-structured TMDCs, by simply replacing 2D Au foils with 3D-structured NPG substrates. For example, Chen et al.\[42\] demonstrated that, a wide variety of 2D metal compounds with 3D bicontinuous nanoporous structures were synthesized on 3D NPG substrates, through the surface alloy strategy in a facile APCVD process (Figure 2). For a
typical example, a 3D-structured MoSSe film was synthesized by transporting the metal-organic precursor (Mo(CO)_6) on the NPG substrate, followed by a thermal annealing procedure at 300–400 °C to form the Au–Mo surface alloy, which was subsequently exposed to vapor-phase S and Se precursors at ≈700 °C to synthesize MoSSe films (Figure 2a). After 30–40 min growth, homogenous and continuous MoSSe films were obtained on NPG templates, featured with typical pore sizes of ≈50 nm (Figure 2b). The thickness of the CVD-derived MoSSe film was determined by the concentration of Mo in Au–Mo surface alloy, which was deliberately controlled ≤3 at% to obtain few-layer products. The MoSSe films were grown on the surfaces of dealloyed NPG, inheriting the nanoporous structures of NPG (containing both positive and negative curvatures). Moreover, the bicontinuous structure of the MoSSe film was well preserved after removing the NPG template (by a KI/I_2 aqueous solution), as shown in the transmission electron microscopy (TEM) image in Figure 2c. Moreover, a phase transition from 2H to 1T was also observed in the obtained MoSSe film, probably induced by the lattice strain introduced by the 3D-curved morphology.

In summary, metal-based 3D substrates, especially NPG, have presented great advantages in preparing 2D TMDCs nanosheets or films with 3D architectures using the facile CVD route. This is because most of the metals are vulnerable to S or Se atmospheres. Only limited metal (so far Au) is proved to be suitable for the preparation of high-quality TMDCs. Moreover, only limited types of microstructures of the 3D templates (e.g., NPG) are developed that can resist the relatively high growth temperature while maintaining their original morphologies. Therefore, from the viewpoints of promoting the CVD growth and energy-related application explorations of 2D TMDCs, it is essential to search novel conductive substrates with low cost, high thermal and chemical stabilities, as well as plentiful 3D microstructures.

2.2. Carbon-Based 3D Substrates

Up to now, many kinds of carbon-based materials (e.g., porous carbon [PC], graphite paper, graphene, and carbon nanotube) have been proved to be good substrates for preparing 2D TMDCs with 3D architectures toward energy-related applications, due to their high conductivities, high thermal and chemical stabilities, and large specific surface areas, which are beneficial for charge and ion transfer in the electrochemical processes. It has been reported that, carbon materials can help enhancing the electrochemical performance by ameliorating the electric conductivities of TMDCs nanosheets. Up to now, most of the TMDCs/carbon products are synthesized by hydrothermal or solution synthesis methods. The obtained TMDCs nanosheets usually present low-crystalline or amorphous structures with severe structural defects, resulting in unsatisfactory structural stabilities and degraded electrochemical performances. In view of this, the CVD method has been pursued for preparing high-quality TMDCs/carbon hybrids to enhance their performances. However, due to the complex nucleation environments on the highly corrugated carbon materials, it is difficult to accurately control the thicknesses of the CVD-grown TMDCs nanosheets.

To tackle this, Zhou et al. developed a space-confined growth method for synthesizing few-layer (<5 layers) MoS_2 nanosheets on 3D porous carbon nanosheets networks (PCNNs) (3DFL-MoS_2@PCNNs). As shown in Figure 3a, 3DFL-MoS_2@PCNNs were synthesized by annealing the mixture of CuH_2O_7, NH_2CSNH_2, and (NH_4)_2Mo_7O_24·4H_2O at ≈750 °C in a CVD system. Particularly, 3D self-assembled cubic NaCl particles were introduced in this growth system to direct the growth of 3DFL-MoS_2@PCNNs. They served as growth templates with 2D-confined space, for the growth of few-layer (1–3 layers) MoS_2 nanosheets on the surfaces of carbon nanosheets networks. To
achieve monolayer MoS$_2$ nanosheets, Huang et al.\cite{57} developed a self-limited CVD growth strategy on 3D PC substrate, using MoO$_3$ nanodots as precursor (Figure 3b–d). As shown in Figure 3c, well-dispersed MoO$_3$ nanodots (1–2 nm) were obtained by impregnating the PC supports in molybdate solution followed with a thermal annealing process. The MoS$_2$ nanolayers were then achieved by sulfuring the MoO$_3$ nanodots in S vapor (Figure 3d). Due to the limited Mo source in the whole CVD process, the onsite achieved MoS$_2$ nanosheets were mostly in the form of monolayer ($\approx85\%$), with an average lateral size of $\approx2.77 \pm 0.96$ nm. The achieved ultrasmall MoS$_2$ monolayers on the porous conductive substrates were then proved to be high-performance electrocatalysts for HER, with a low overpotential of $\approx126$ mV at 10 mA cm$^{-2}$. Notably, the TMDCs synthesized on 3D PC templates are often in the forms of powders. For electrochemical applications, additional binder materials (e.g., Nafton solution) with low electrical conductivity are generally needed to gather the catalysts onto test electrodes (e.g., glassy carbon [GC] electrode, CC), which may introduce extra interfacial resistance between catalyst and electrode. In addition, this process may induce the agglomeration of the obtained TMDCs products, leading to the degradation of their electrocatalytic performances.

In this case, free-standing binder-free carbon-based materials (e.g., graphite paper, CC) have been attractive substrates for the construction of 3D TMDCs architectures toward energy-related applications. In addition, some of these materials are flexible and bendable, which are suitable for the direct preparation of flexible electrodes. Wang et al.\cite{59} synthesized flexible WS$_2$/WO$_2.9$/C hybrid membranes, by dropping (NH$_4$)$_2$WS$_4$ and polyacrylonitrile (PAN) solutions on graphite papers, followed with two-step annealing processes at $500$ and $850^\circ$C, respectively (Figure 3e). To trigger the formation of tungsten oxide, trace amount of oxygen was also introduced in the CVD system during the cooling process. The achieved WS$_2$/WO$_2.9$/C product on graphite paper, featured with excellent mechanical flexibility (Figure 3f) and electrical conductivity, was directly utilized as the self-standing electrode for electrocatalytic HER, exempting any other binder materials. Moreover, the presence of strain and S vacancies was also observed in the flexible membranes, which were expected to enhance the HER activity of WS$_2$ nanosheets.

Figure 3. Syntheses of 2D TMDCs nanosheets on different carbon-based 3D substrates. a) Schematics of the space-confined synthesis of 3D FL-MoS$_2$@PCNNs. Reproduced with permission.\cite{56} Copyright 2015, American Chemical Society. b) SEM image of the PC support. HR-TEM image of c) MoO$_3$ nanodots and d) CVD-derived monolayer MoS$_2$. Reproduced with permission.\cite{57} Copyright 2018, Wiley-VCH GmbH. e) Schematic illustration of the synthesis process of flexible WS$_2$/WO$_2.9$/C hybrid membrane. f) Photograph of WS$_2$/WO$_2.9$ grown on a graphite paper (50 μm thick) with the formation of a flexible membrane. Reproduced with permission.\cite{59} Copyright 2016, Wiley-VCH GmbH. g,h) Different-magnification SEM images of vertically oriented 3D MoS$_{21-4}$Se$_{2x}$ nanosheets on CC. Inset in (g) shows a photograph of a CC after the growth of MoS$_{21-4}$Se$_{2x}$ alloy nanosheets. Reproduced with permission.\cite{60} Copyright 2016, The Royal Society of Chemistry. i) Distribution density of VSe$_2$ nanosheets grown on CC without VG (left highlighted panel) and with VG (right highlighted panel) nanowalls films. Reproduced with permission.\cite{61} Copyright 2020, American Chemical Society.
CC, woven from conductive carbon fibers, is another kind of popular flexible substrate for the growth of 2D TMDCs nanosheets. The abundant curved and corrugated surfaces of carbon fibers can provide sufficient nucleation sites for TMDCs. Hitherto, several 3D-architected TMDCs materials, including semiconducting TMDCs (e.g., MoSe$_2$, WS$_2$, ReS$_2$), metallic TMDCs (e.g., 1T' MoTe$_2$, VS$_2$, MoS$_2$), and their alloys (e.g., MoS$_{2x-1-y}$Se$_{2x}$), have been successfully synthesized on CCs using CVD techniques. Chen et al.$^{[60]}$ demonstrated the controllable growth of vertically oriented 3D MoS$_{2x-1-y}$Se$_{2x}$ alloy nanosheets on CC substrates, using MoO$_3$ as metal precursor, S and Se powers as chalcogen precursors. Several pieces of CC substrates were placed at the downstream with a distance of $\approx$4 cm away from the MoO$_3$ precursor in the high temperature zone (650–850 °C), and different contents of S and Se precursors were located in the low temperature zone (150–350 °C) at the upstream. After a typical CVD process, the surface of the CC was completely covered with vertically oriented MoS$_{2x-1-y}$Se$_{2x}$ nanosheets with relatively high uniformity (Figure 3g–h), showing typical thickness and lateral dimensions of $\approx$20 nm and $\approx$1.3 μm, respectively. The vertically oriented growth behavior was proposed to be mediated by the appropriate saturated vapor pressure of precursors, according to growth-time-dependent experimental results. Notably, due to the limited contact area, the interactions between vertically aligned TMDCs nanosheets and CC were usually very weak, resulting in large contact resistance. Recently, Ci et al.$^{[61]}$ found that, the contact resistance of VSe$_2$ nanosheets and CC can be decreased by introducing vertically oriented graphene (VG) as a buffer layer, as evidenced by the enhanced reaction kinetics of VSe$_2$-VG@CC electrodes compared with those of VSe$_2$@CC electrodes in Li–S cells. In addition, the nucleation density of VSe$_2$ was remarkably increased (about fourfold under the same growth condition) after the deposition of VG nanowalls (Figure 3i). Herein, the introduced VG layer, featured with abundant edge sites, is proposed to serve as nucleation platforms to boost the growth of VSe$_2$ nanosheets.

Briefly, carbon-based materials are promising 3D substrates due to their high conductivity, designable structure and high surface area, and some of them are even flexible and tenable, which is highly desirable for practical electrochemical-related applications (Table 1). Most of these materials are low-cost, light-weight, and environmentally friendly, and is compatible with mass production. However, due to the complex nucleation environment, delicate controls of the layer thicknesses and sizes of 2D TMDCs nanosheets on carbon-based 3D materials are still challenging. In addition, due to the weak binding forces between TMDCs and carbon-based materials, binders are usually indispensable in electrode fabrication processes, usually leading to increased charge transfer resistances and degraded electrochemical performances.

### 2.3. 3D Oxide Substrates

In addition to the aforementioned conductive substrates, some high-melting-point inorganic oxide materials (e.g., TiO$_2$, $^{[21-24]}$ SiO$_2$, $^{[77]}$ and MgO$^{[66,79]}$) have also been used as templates for the synthesis of 2D TMDCs for specific purposes. Several researches demonstrated that, the optical and electrical properties of 2D TMDCs nanosheets could be tailored by incorporating them on suitable oxides (e.g., TiO$_2$ and SiO$_2$), rendering more versatile applications in optoelectronics related fields (e.g., photodetector, sensor, and photocatalyst). For instance, Zhang et al.$^{[71]}$ reported that, high-efficiency photocatalysis for hydrogen production ($\approx$1.6 mmol h$^{-1}$ g$^{-1}$) at MoS$_2$ loading of $\approx$50 wt% was realized by integrating MoS$_2$ nanosheets onto TiO$_2$ substrates to form MoS$_2$/TiO$_2$ heterostructures. They proposed that, the 2D MoS$_2$ nanosheet served as a light harvester, and the MoS$_2$/TiO$_2$ heterostructure-induced efficient charge separation to suppress the electro-hole recombination, thus synergistically leading to high photocatalytic activity. In addition, Paul et al.$^{[73]}$ reported that, the photoluminescence (PL) intensity of monolayer MoS$_2$ was greatly enhanced (by $\approx$30-fold as deposited on 3D TiO$_2$ nanoflowers, comparing with that of MoS$_2$/sapphire), which induced the migration of excess electrons from MoS$_2$ to TiO$_2$. Particularly, this PL enhancement enabled the fabrication of high-performance photodetector, affording a high responsivity and detectivity of $\approx$35.9 A W$^{-1}$ and $\approx$1.98 Jones (in the UV region).

Mi et al.$^{[75]}$ demonstrated that, the excitonic properties of monolayer MoS$_2$ nanosheets was tunable on 3D SiO$_2$ microsphere resonators. Specifically, monolayer MoS$_2$ nanosheets were directly synthesized on SiO$_2$ microsphere arrays (diameter

### Table 1. A summary of the CVD growth of 2D TMDCs on carbon-based materials.

| Substrate | Material | Precursor | Growth temperature | Crystal size | Ref. |
|-----------|----------|-----------|--------------------|--------------|-----|
| PC        | MoS$_2$  | (NH$_4$)$_4$Mo$_8$O$_{24}$·4H$_2$O, NH$_4$CSNH$_2$ | 750 °C | 2–5 layers | $^{[56]}$ |
|           | MoS$_2$  | MoO$_3$ nanodots (1–2 nm) | 500 °C | 85% monolayer lateral size of (2.77 ± 0.96 nm) | $^{[57]}$ |
| Graphite paper | WS$_2$/WO$_3$ | (NH$_4$)$_2$WS$_4$ | 500/800 °C | | $^{[59]}$ |
| CC        | MoS$_{2x-1-y}$Se$_{2x}$ | MoO$_3$, S, Se powders | 650–850 °C | Thickness (20 nm) | $^{[60]}$ |
|           | VSe$_2$  | VCl$_2$, Se powders | 600 °C | Thickness (17.5 μm) | $^{[61]}$ |
|           | MoTe$_2$ | MoTe$_3$, Te powders | 700 °C | | $^{[63]}$ |
|           | MoSe$_2$ | MoO$_3$, Se powders | 600–900 °C | | $^{[69]}$ |
| 3D graphene foam | Re$_2$S$_3$ | ReO$_2$, S powders | 450–850 °C | Lateral size (200 nm–several micrometers) | $^{[65]}$ |
|           | MoS$_2$  | (NH$_4$)$_4$Mo$_8$S$_4$ | 400 °C | Less than 100 nm | $^{[66]}$ |
| Carbon nanotube | VS$_2$ | VCl$_2$, S powders | 700 °C | Lateral size (1 μm) | $^{[67]}$ |
ranging from ≈4 to 10 μm) using a facile CVD method with MoO₃ and sulfur powders serving as Mo and S precursors, respectively. The morphology of the obtained product is schematically shown in Figure 4a,b, showing the uniform growth of triangular-shaped monolayer MoS₂ nanoflakes all-around the surfaces of close-pack arranged SiO₂ microspheres. Further optical investigations suggested that, the SiO₂ microspheres can serve as optical microcavities for tailoring the excitonic property of MoS₂. The room-temperature PL spectra of monolayer MoS₂/SiO₂ exhibited evident oscillation peaks, which was ascribed to whispering gallery mode (WGM) cavity modes. In addition, due to the Purcell effect of microcavity, the radiative recombination lifetime of monolayer MoS₂ is shortened by a factor of ≈1.65. A refractive index sensing established by this monolayer MoS₂/SiO₂ microcavity presented a high sensitivity up to 150 nm per refractive index unit (RIU), demonstrating its great application potential in optoelectronic devices and sensors.

Beyond serving as functional substrates for tailoring the optical and electronic properties, 3D oxides can also be utilized as templates for engineering the morphologies of TMDCs. As an example, Tang et al. [76] realized the construction of 3D mesoporous vdW heterostructure of nitrogen-doped MoS₂/graphene (G@N-MoS₂), using Mg(OH)₂-derived mesoporous MgO as template (Figure 4c). A thin layer of graphene was first deposited on MgO template using CH₄ as carbon source at ≈950 °C, followed with in situ deposition of ultrathin nitrogen-doped MoS₂ (N-MoS₂) using MoCl₅, sulfur, and NH₃ as precursors at ≈800 °C. The N-MoS₂ nanosheets (lateral size <20 nm, thickness <3 layers) were locally curved and intimately merged with previously deposited graphene to form a vertical G@N-MoS₂ vdW heterostructure with 3D mesoporous structure. The mesoporous morphology of G@N-MoS₂ was well preserved after the removal of MgO template by HCl etching. Such 3D mesoporous G@N-MoS₂ was then used as efficient electrocatalyst for HER, showing relatively low overpotential of ≈243 mV (at 10 mA cm⁻²) and Tafel slope of ≈82.5 mV dec⁻¹.

In summary, 3D oxides (e.g., TiO₂, SiO₂, MgO) can serve as ideal platforms for exploring the optical and electronic properties, and more importantly, function as hierarchical templates for engineering the morphologies of TMDCs. Their high melting points and excellent stabilities in S and Se atmospheres enable the fabrications of various TMDCs materials. In addition, they are low-cost and naturally abundant, and compatible with batch production. However, the poor electrical conductivity and the complex substrate removal process obviously restrict their direct applications as electrocatalysts in HER. In this regard, more TMDCs materials featured with high conductivities and catalytic activities (e.g., metallic TaS₂, NbS₂) can be grown on oxides through CVD methods for engineering more versatile applications in energy-related fields. Alternatively, searching for easily removable 3D templates (such as salt) should be another promising strategy, and deserves more attention.

2.4. Salt Powders

To promote the practical applications, the batch production of high-quality TMDCs nanosheets is of crucial importance. Previous reports demonstrated that, the batch production of high-quality graphene can be realized via the CVD method, using natural ubiquitous powder-like 3D substrates (e.g., diatomites [78] and SiO particles [79]) as templates. However, the removal of such templates usually involves a wet-chemical etching process, which inevitably impairs the quality of graphene. Directly depositing 2D TMDCs nanosheets on naturally abundant 3D substrates should be a promising strategy, especially when the templates can be removed by an environmentally friendly process.

Huan et al. [80] realized the batch production of metallic TMDCs nanosheets powders (including TaS₂, VSe₂, and NbS₂) using microcrystalline NaCl crystals as templates via facile APCVD methods (Figure 5a–d). The NaCl powder was chosen as substrate due to its high thermal stability (melting point ≈801 °C) and high solubility in water. In addition, it is a naturally

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**Figure 4.** Syntheses of 2D TMDCs nanosheets on oxides substrates with 3D structures. a,b) Schematic of the SiO₂ microspheres covered by triangular-shaped MoS₂ nanoflakes. Reproduced with permission [75] Copyright 2017, Wiley-VCH GmbH. c) Schematic illustration of the syntheses of 3D mesoporous G@N-MoS₂ heterostructures on porous MgO templates. Reproduced with permission [76] Copyright 2017, Wiley-VCH GmbH.
abundant crystal powder with low cost, which is compatible with the batch production of 2D TMDCs powders. The synthesis process of TaS$_2$ nanoflakes, and the stereoscopic structure of TaS$_2$/NaCl are schematically shown in Figure 5a. After a CVD growth process, TaS$_2$ nanosheets were grown vertically on the surfaces of NaCl crystals. The thicknesses and domain sizes of the obtained TaS$_2$ nanosheets were distributed in a very narrow range of 38 ± 5 nm and 1 ± 0.5 μm, respectively (Figure 5b). According to the SEM images (Figure 5c), 2D TaS$_2$ nanosheets tend to nucleate and grow at the edges and corners of micrometer-sized NaCl crystals, which was attributed to the high surface energies of the highly curved surfaces. In addition, by virtue of the water-soluble nature of NaCl, a purified product was achieved by simply dissolving the CVD product in deionized water and filtering the solution through a filter membrane. Moreover, thus-produced nanosheets showed excellent dispersibility in several solvents (e.g., deionized water, ethanol, and N-methyl-2-pyrrolidone (NMP)), which was beneficial for the preparation of homogenous TMDCs inks for specific applications (e.g., large-area printing electronics). Figure 5d shows the ethanol dispersions of TaS$_2$ nanosheets with various concentrations from 0.05 to 0.2 mg mL$^{-1}$, whose homogeneity is evidenced by the existence of Tyndall effect. Briefly, this work develops a practical way for the batch production of high-quality metallic TMDCs powders, which should propel their applications in energy-related fields, such as electrocatalytic HER, supercapacitors, etc.

To enhance the scalability of 3D-substrate-assisted CVD growth systems, it is essential to guarantee the homogenous and sufficient supply of precursors, especially for the metal precursor. Taking the growth of MoS$_2$ as an example, the ultralow melting point of MoCl$_5$ (≈194 °C) often leads to a high sublimation rate, resulting in excessive nucleation sites and thicker domains. On the contrary, the melting point of MoO$_3$ (≈795 °C) is relatively high, which usually induces insufficient release and nonuniform distribution of Mo precursor along the gas-flow direction. In this regard, novel precursor feeding strategy (e.g., mixing metal oxides with alkali halides) should be introduced for engineering the batch production of 2D TMDCs nanosheets powders.

Very recently, Zhu et al.$^{[81]}$ demonstrated the controllable syntheses of 2D MoS$_2$ nanosheets powders on NaCl (and KCl) crystals via a facile CVD strategy (Figure 5e). To guarantee the sufficient release of the precursor, a low-pressure CVD apparatus was adapted in the growth process. In addition, trace amount of NaCl was added in the MoO$_3$ precursor to promote the volatilization of Mo precursor. The gas-phase intermediate compound

Figure 5. Syntheses of 2D TMDCs nanosheets on oxides substrates with 3D structures. a) Schematic illustration of the growth of 2D 1T-TaS$_2$ nanosheets on micrometer-sized NaCl crystals. b) AFM image and corresponding height profile of dispersed 1T-TaS$_2$ nanosheets on SiO$_2$/Si. c) SEM image of as-grown 1T-TaS$_2$ nanosheets on NaCl crystals. Reproduced with permission.$^{[80]}$ Copyright 2019, American Chemical Society. d) Photographs of the uniformly dispersed 1T-TaS$_2$ nanosheets in ethanol at different concentrations. e) Schematic illustration of the salt-template directed CVD growth of 2D MoS$_2$ nanosheets on NaCl crystals. f,g) SEM images of NaCl@MoS$_2$ crystals. Reproduced with permission.$^{[81]}$ Copyright 2020, Springer Nature.
(Mo_2CIO_2) was proved to be the main metal precursor in this system. The scalability of the growth system and the uniformity of derived products were remarkably improved through this metal precursor feeding strategy. The SEM images in Figure S1–g show that, triangular-shaped MoS_2 nanosheets are grown horizontally on the surfaces of NaCl crystals with excellent uniformities. In addition, the average thicknesses of the nanosheets were tunable from ~1.93 to 2.62 nm by adjusting the growth temperatures from ~500 to 650 °C. The high-resolution TEM images of the purified MoS_2 nanosheets presented perfect hexagonally arranged lattices, indicating the high crystalline quality of the CVD-derived products.

In summary, the salt-template-assisted growth strategy is an effective route toward the mass production of high-quality TMDCs nanosheets powders with uniform thicknesses and domain sizes. More intriguingly, this synthetic strategy is compatible with the “green” transfer process, since the salt template can be removed facilely using pure water as purification media. The high-quality TMDCs powders or their dispersions can be easily obtained, thus shedding light on their practical applications in energy related fields.

3. TMDCs Catalysts for HER

Developing high-efficiency catalysts for electrocatalytic HER is of essential significance for clean and renewable energy applications. Thus far, platinum (Pt), iridium (Ir), and their compounds are known as the best electrocatalysts for HER, whereas the scarcity and expensive price limited their large-scale applications. Recently, 2D TMDCs nanosheets have been considered as promising alternatives to noble-metal electrocatalysts, due to their natural abundance, low cost, abundant accessible active sites, tunable electronic properties and relatively high chemical stability, etc. Although significant progresses have been achieved in the past decades, the HER performance is still far less than that of noblemetal (e.g., Pt). To promote their practical applications, searching effective strategies to boost their HER performance is of great significance. This section hereby focuses on the introduction of recent advances about the applications of 2D TMDCs nanosheets in electrocatalytic HER.

3.1. Applications of s-TMDCs in Electrocatalytic HER

As a typical category of s-TMDCs, ultrathin 2H-MoS_2 nanosheets have attracted extensive attentions due to their high chemical stabilities and excellent catalytic performances. However, the catalytic activity of 2H-MoS_2 domain mainly originates from its edge sites, while its basal plane is catalytically inert. To optimize the catalytic activity of MoS_2 in HER, several strategies have been proposed, mainly aiming at increasing the number of catalytically active edge sites, or activating the inert basal planes, etc.

For the first time, Chorkendorff et al. demonstrated that, the electrocatalytic activity of triangular-shaped monolayer MoS_2 on Au (111) single crystal was linearly correlated with the density of edge site. In this regard, engineering monolayer or few-layer MoS_2 nanostructures with more active edge sites is an effective way. To explore new candidate substrate with low cost (with regard to that of Au single crystal) is also crucial to carry out in-depth explorations. Shi et al. synthesized high-density monolayer nanosized MoS_2 triangular domains (edge length of ~200 nm) on a new-type substrate of Au foils (Figure 6a). The as-grown MoS_2/Au presented enhanced HER performance by increasing the coverage of monolayer MoS_2 (Figure 6b). The 80%-coverage monolayer MoS_2/Au exhibited a lowest Tafel slope of ~61 mV dec^−1 and a highest exchange current density of ~38.1 μA cm^−2. In addition to the abundant active edges in nanosized MoS_2 crystals, the strong electron coupling between monolayer MoS_2 and Au foil also contributed to its extraordinary HER property. Meanwhile, dendritic monolayer MoS_2 flakes with abundant edges were also directly synthesized by Zhang et al. on a special SrTiO_3(001) substrate via an APCVD method. After transferred onto Au foil electrodes, the fractal monolayer MoS_2 flakes presented much lower overpotential (~−270 mV at current density of 10 mA cm^−2) and higher exchanged current density (~24.5 μA cm^−2) than those of compact triangular-shaped MoS_2/Au sample. Furthermore, Xie et al. reported that, rich defects in monolayer MoS_2 nanosheets resulted in partial cracking of electrocatalytically inert basal planes, leading to the exposure of additional active edge sites. Enhanced HER activity was achieved with a small onset overpotential of ~120 mV and a Tafel slope of ~50 mV dec^−1. Engineering the morphology of monolayer semiconducting TMDCs (s-TMDCs) to expose more active edge sites can indeed enhance the HER performance. Notably, most of the achieved 2H-MoS_2 catalysts show negligible degeneration even after 1000 cyclic voltammetry (CV) circles, indicating the excellent electrocatalytic durability of MoS_2 catalysts in HER processes.

Beyond this, activating the inert basal plane by introducing catalytically active sites (e.g., vacancies) is also a powerful strategy toward promoting the HER activities of monolayer s-TMDCs. As theoretically calculated by Li et al., the hydrogen adsorption free energy (ΔG_H^ads) value of basal plane decreased from ~2 to 0.18 eV, when ~3.12% S-vacancies were introduced in monolayer 2H-MoS_2. Experimentally, the S-vacancies with a concentration of ~12.5% were introduced in CVD-grown monolayer 2H-MoS_2 nanosheets using plasma treatments. The introduced S-vacancies served as new active sites for HER, as evidenced by the drop of Tafel slope from ~98 to 82 mV dec^−1. In addition, the Tafel slope was further reduced to ~60 mV dec^−1 by applying suitable in-plane strains around the S-vacancies. According to theoretical calculation results, S-vacancies can introduce additional in-plane states that is favorable for H adsorption, while straining the S-vacancies can shift the gap states closer to the Fermi level and induce optimal ΔG_H^ads ~ 0 eV, thus improving the HER activity of monolayer MoS_2.

Apart from edges and S-vacancies, grain boundaries (GBs), which are rich in lattice defects, dislocations and distortions, have also proved to be effective catalytically active sites for HER. Recently, Zhu et al. revealed that, MoS_2 monolayer with rich 2 H–2 H domain boundaries presented better HER performance than that without domain boundaries, as evidenced by the decrease in overpotential from ~375 to 325 mV (at current density of 10 mA cm^−2) and the Tafel slope from ~110 to 95 mV dec^−1 (Figure 6c,d). To further increase the density of...
GBs, He et al. developed an Au-quantumdots (Au-QDs)-assisted vapor-phase growth method to achieve monolayer MoS$_2$ films with grain sizes typically <10 nm. Specifically, the Au-QDs (Figure 6e) were utilized to facilitate the nucleation of monolayer MoS$_2$ and confine the domain size below 10 nm, thus affording ultrahigh density of domain boundaries up to $\approx 10^{12}$ cm$^{-2}$. The nanograin film demonstrated excellent HER performance in micro-electrochemical measurements, with an onset potential of $\approx 25$ mV and a Tafel slope of $\approx 54$ mV dec$^{-1}$ (Figure 6f), suggesting the intrinsically high electrocatalytic activities of the monolayer MoS$_2$ GBs.

Except for introducing defects in s-TMDCs, the phase engineering is an effective strategy to enhance their intrinsic catalytic performance. Both theoretical calculation and experiment revealed that, metallic monolayer 1T' phase (i.e., distorted octahedral coordinated phase) MoS$_2$ exhibited better HER performance compared with that of semiconducting 2H phase MoS$_2$, due to their higher catalytic activities on the basal plane and better charge transport abilities. Recently, Liu et al. developed a potassium (K)-assisted CVD route to synthesize 1T' phase monolayer MoS$_2$ with $\approx 100\%$ phase purity. K$_2$MoS$_4$ was utilized as precursor for lowing the formation energy of 1T' phase MoS$_2$. The 1T' MoS$_2$ presented lower overpotential and Tafel slope ($\approx 205$ mV and $51$ mV dec$^{-1}$, respectively) than those of 2H phase MoS$_2$ ($\approx -286$ mV and $\approx 70$ mV dec$^{-1}$, respectively). However, due to the metastable feature of 1T' phase MoS$_2$, it can be easily converted to 2H phase even under mild annealing process, followed with degradation of the catalytic activity.

In brief, 2D s-TMDCs (especially 2H-MoS$_2$) have emerged as potential alternatives for noble metals in electrocatalytic HER. To promote their HER performances, several strategies have been proposed, including engineering the morphologies to achieve denser active sites, activating the inert planes by introducing S-vacancies, defects, or lattice strains. Although great efforts have been made, more effective routes should be explored for developing more efficient electrocatalysts: 1) introducing dopant atoms; 2) hybridizing s-TMDCs with other functional materials; and 3) developing novel materials with high conductivities and catalytic activities (e.g., TaS$_2$, NbS$_2$).

### 3.2. Applications of 2D m-TMDCs in Electrocatalytic HER

Despite various advantages of s-TMDCs have been revealed in electrocatalytic-related applications, the limited catalytically active sites (mainly located at the edges), and low conductivities...
strongly limit their practical applications. As a substitute, various 2D metallic TMDCs (m-TMDCs) (e.g., 1T-VS$_2$, 2H-TaS$_2$, 1T-TaS$_2$, 2H-NbS$_2$) have been predicted as robust electrocatalysts. Density functional theory (DFT) calculations reveal that, both the basal planes and edges of m-TMDCs are catalytic active sites, which is different from that of s-TMDCs where only the metallic edges are catalytically active. Particularly, the electron transports from electrodes to catalytically active sites can be facilitated by virtue of the high conductivities of m-TMDCs.

In 2015, Yuan et al. reported that, the CVD-synthesized 1T phase (i.e., octahedral coordinated phase) VS$_2$ nanosheets exhibited excellent electrocatalytic performance in HER, affording an overpotential of $\approx 68$ mV and a Tafel slope of $\approx 34$ mV dec$^{-1}$ (Figure 7b). As calculated by Shi et al., the $\Delta G_{\text{H}^*}$ of Ta-edge, S-edge, and basal planes of 2H phase TaS$_2$ were $-0.04$, $-0.10$, and $-0.15$ eV, respectively, which are all comparable with that of the monolayer MoS$_2$ edge ($0.08$ eV) but obviously lower than that of the MoS$_2$ basal plane ($\approx 2$ eV; Figure 7c). These results indicated that, both the edges and basal planes of 2H-TaS$_2$ were catalytic active sites for HER. Experimentally, they realized the thickness-tunable syntheses of 2D 2H-TaS$_2$ nanosheets on Au foils via an APCVD route (Figure 7e). The as-grown 2H-phase TaS$_2$ with different thicknesses (from $\approx 20$ to $350$ nm) showed superior HER performance with a relatively low overpotential ($\approx 65$ mV at 10 mA cm$^{-2}$), and dramatically improved kinetics of electrochemical reactions (Tafel slopes of 33–42 mV dec$^{-1}$; Figure 7d). Intriguingly, the 2 H-TaS$_2$ nanosheets showed much better HER performance after 5000 CV cycles, with regard to that at the initial stage. This is possibly because the metallic 2H-TaS$_2$ nanosheets are vulnerable to ambient conditions, and the surfaces are easily oxidized into oxides (with worse catalytic activity). The surface oxides are peeled off by hydrogen bubbles in the following cycling processes. The intrinsic electrocatalytic activities of 2H-TaS$_2$ nanosheets are thus presented.

In addition to aforementioned VS$_2$ and TaS$_2$, other m-TMDCs materials were also utilized as highly efficient catalysts in HER. Yang et al. reported the synthesis of metallic 2H-phase of niobium disulfide with additional niobium (2H Nb$_{1-x}$S$_2$, where $x$ is $\approx 0.35$) via the CVD method. The phase state of NbS$_2$ depended on the thickness of the material, where 2H phase Nb$_{1-x}$S$_2$ was mainly observed in the thinner crystals with thickness less than 20 nm, and 3R phase for thicker samples. The metallic 2H Nb$_{1-x}$S$_2$ sample manifested a high current density of over 5000 mA cm$^{-2}$ at $\approx 420$ mV, which was suitable for practical electrocatalytic applications. Theoretical calculations revealed that, the $\Delta G_{\text{H}^*}$ value of 2H Nb$_{1-x}$S$_2$ with Nb-terminated surface was close to thermoneutral, thus dramatically facilitating HER process.

Despite great advancements, most of the CVD-grown 2D m-TMDCs are vulnerable to ambient conditions, which inevitably limits their practical applications. In this regard, metallic electrocatalysts with excellent environmental stabilities, and high catalytic activities are highly desirable. Recently, Shi et al. synthesized metallic 2D 1T-NiTe$_2$ nanosheets on GC substrates via a facile CVD method (Figure 7f). Thanks to the high crystalline quality, the 2D 1T-NiTe$_2$ presented robust environmental stability for more than 1 year, even after a variety of harsh treatments. More interestingly, the NiTe$_2$ flakes exhibited excellent electrocatalytic performances of metallic TMDCs (m-TMDCs) nanosheets in HER. a) SEM images of VS$_2$ nanosheets. b) Tafel slope of VS$_2$ in HER. Reproduced with permission. Copyright 2015, Wiley-VCH GmbH. c) $\Delta G_{\text{H}^*}$ of different H adsorption states of TaS$_2$. d) Tafel slopes of 2H-TaS$_2$ with different thicknesses. e) Schematic illustration of the thickness-controllable growth of 2H-TaS$_2$ nanosheets on Au foils. Reproduced with permission. Copyright 2017, Nature Publishing. f) Optical microscopy (OM) image of CVD-grown 1T-NiTe$_2$ nanosheets on GC electrodes. g) Tafel slopes of CVD-grown 1T-NiTe$_2$ nanosheets with different coverages. Reproduced with permission. Copyright 2020, American Chemical Society.
electrocatalytic activities in pH-universal HER (Tafel slope: 33–41 and 62–82 mV dec⁻¹ for pH = 0 and 14, respectively) (Figure 7g). This was attributed to the ultrahigh conductivity (≈1.15 × 10⁶ S m⁻¹) of the material that can facilitate the charge transfer in the electrocatalytic reactions. Furthermore, Shi et al. also synthesized the 2D 1T-VTe₂ nanosheet with ultrahigh conductivity, i.e., average sheet resistance of ≈350 Ω sq⁻¹, comparable with that of few-layer graphene (≈280 Ω sq⁻¹). Superior electrocatalytic property for HER was also achieved, as evidenced by rather low Tafel slope of 38–46 mV dec⁻¹.

In summary, m-TMDCs (e.g., TaS₂, NbS₂) can serve as effective electrocatalysts for HER, by virtue of the abundant catalytically active sites and intrinsically high conductivities. However, comparing with noble metal catalysts (e.g., Pt, Ir), 2D m-TMDCs still face some challenges to serve as catalysts for practical applications, such as relatively high onset potential and low exchange current density. In addition, most of the m-TMDCs are achieved on 2D lamellar substrates, suffering from limited catalytically active sites. More effective strategies should be developed for realizing highly efficient HER applications, such as developing 2D m-TMDCs heterostructures with synergistic catalytic effects, or designing 3D structures to increase the densities of catalytically active sites.

3.3. Applications of 3D-Structured TMDCs in Electrocatalytic HER

Considering the limited catalytically active sites of 2D structures, it is reasonable to assemble 2D TMDCs into 3D structures to increase the densities of active sites. Kibsgaard et al. reported the syntheses of highly ordered double-gyroid MoS₂ bicontinuous networks with nanosized pores. The high surface curvature of this mesostructured catalyst allowed the exposure of a large portion of edge sites, offering an excellent HER activity with a Tafel slope of ≈50 mV dec⁻¹. To further expose the edge sites, Kong et al. obtained MoS₂ (MoSe₂) films with vertically aligned geometries, through sulfurizing (selenizing) the deposited Mo films. Such edge-terminated films indeed promoted the HER activity of MoS₂, leading to a large exchange current density of ≈2 μA cm⁻², along with a low Tafel slope of ≈44 mV dec⁻¹.

Developing 3D-structured TMDCs with both porous structures and vertically aligned layers should be a more promising route. Deng et al. synthesized 3D mesoporous MoS₂ foams (mPF-MoS₂), using colloidal SiO₂ nanospheres as templates. In the resultant architecture, homogeneous mesopores (≈30 nm) were connected with each other, around which MoS₂ flakes were arranged vertically. This mesoporous structure facilitated the transport of H₂O and H₂, and enlarged the accessible surface areas of MoS₂ concurrently. Furthermore, the vertically aligned nanosheets around the mesopores induced increased densities of active edge sites. As a result, the overpotential of mPF-MoS₂ was reduced by ≈195 mV (to ≈210 mV) at the current density of 10 mA cm⁻², comparing with that of random-oriented MoS₂ (rNS-MoS₂) nanosheets (≈405 mV) prepared without SiO₂ templates (Figure 8a). Meanwhile, 3D hierarchical MoSe₂ nanoarchitectures, constructed with few-layer vertically oriented nanosheets, were also achieved on SiO₂/Si by Zheng et al. using a CVD route. Comparing with conventional horizontally oriented MoSe₂ flakes (C₄l ≈ 35.9 μF cm⁻², Tafel slope≈123.8 mV dec⁻¹), the 3D MoSe₂ architectures presented larger effective electrochemically active area (≈438.8 μF cm⁻²), and lower Tafel slope ≈47.3 mV dec⁻¹. This was attributed to the denser active edge sites exposed by the vertically aligned layers, with regard to those of the horizontally aligned 2D flakes.

Although great achievements have been made, most of the achieved 3D TMDCs still need to be transferred onto electrode materials (e.g., GC) for electrochemical measurements, which inevitably damages the structure and degrades the catalytic performances. The direct growth of 3D TMDCs on electrode materials should be a feasible route for further improving their catalytic performances. Huan et al. obtained vertically aligned metallic 1T-TaS₂ on 3D NPG substrates (Figure 8b–e). Especially, the as-grown 1T-TaS₂ nanosheets were directly used as catalysts. The underlying NPG templates were served as electrodes, considering their high conductivities and chemical stabilities. Thanks to the abundant exposed edge sites, as well as excellent electrical transport property, such vertical 1T-TaS₂ nanosheets presented excellent HER activity, offering low Tafel slopes of 67–82 mV dec⁻¹ and a high exchange current density of ≈67.6 μA cm⁻² (Figure 8d,e).

Directly depositing TMDCs on 3D structures can induce the formation of lattice strains, leading to the changes in electronic structures and HER activities.[40,42,102] For example, Tan et al. found that, massive “out-of-plane” strains occurred on the curved regions of monolayer MoS₂ films (Figure 1b), which were synthesized conformally on the internal surfaces of NPG substrates. Intriguingly, the strain, which was mediated by the high curvature of NPG surface, can change the band gap and activate the basal plane of the “edge-free” monolayer MoS₂ film, resulting in remarkably high HER activity (with an overpotential of ≈226 mV at the current density of 10 mA cm⁻²) and a Tafel slope of ≈46 mV dec⁻¹ (Figure 8f,g). Further investigations demonstrate that, the “out-of-plane” strain can also trigger the 2H-to-1T phase transition of s-TMDCs (e.g., MoS₂, WS₂, MoSe₂) films, and promotes the formation of distorted 1T-phase with metallic features, as revealed by the HAADF-STEM image in Figure 8h.[42] According to previous reports, this phase transition can improve the electrocatalytic performance of the s-TMDCs catalyst.

In brief, assembling 2D TMDCs into 3D structures can dramatically improve the HER performances of the related electrocatalysts. The 3D structure can effectively inhibit the agglomeration of the TMDCs nanosheets, with more active sites exposed in the electrolytes. In addition, the presence of large number of holes and channels in the 3D structures can shorten the ion and mass transport distances, thus facilitating the electrochemical processes. Moreover, S-vacancies and lattice strains are generally introduced in 3D TMDCs, which further contribute to the high HER performances. Nevertheless, the preparation of 3D TMDCs with high structural stability is still challenging, as most of the 3D TMDCs tend to collapse after the removal of substrate. To avoid this problem, more efforts should be devoted to exploring novel 3D substrates, with low-cost, high conductivity, and ease of removal characteristics, etc.

To sum up, semiconducting TMDCs (e.g., MoS₂, MoSe₂) are promising electrocatalysts for HER, due to the high catalytic activities of edge sites. However, the relatively low electrical conductivities and the limited edge sites greatly restrict their catalytic
performances. Current strategies for improving their HER activities include: 1) engineering the morphologies to achieve high densities of active edge sites; 2) activating the inert basal planes by introducing defects, strains, etc. In addition, metallic TMDCs (e.g., VS\textsubscript{2}, NbS\textsubscript{2}, and TaS\textsubscript{2}) have also been proved to be potential electrocatalysts for HER, due to their high conductivities and intensive active sites on both edges and basal planes. Assembling 2D TMDCs into 3D structures should be a promising way to achieve high-performance catalysts, due to the highly exposed edge sites, and the facilitated ion transfer process. Moreover, the internal mechanisms still deserve to be better understood from both experimental and theoretical points of view, for better guiding the designs and syntheses of more effective HER catalysts.

4. Conclusion

In summary, 3D-architected substrates have attracted considerable attentions in producing 2D TMDCs nanosheets or films on 3D substrates. For example, the rational design and delicate controls over the morphologies of TMDCs are still challenging. Albeit several 3D-architected substrates have been developed, it is still difficult for TMDCs to completely replicate the morphologies of 3D substrate through the CVD process. In addition, due to complex nucleation environments of 3D substrates, it is challenging to delicately control the lateral sizes and thicknesses of the single crystal domains. Up to now, continuous monolayer TMDCs films are still difficult to be obtained on 3D substrates. In addition, the gradient distributions of precursor concentration and temperature along the axial and radial directions in the CVD system greatly affect the uniformity of conductive 3D substrates, such as nanoporous metals and carbon-based materials, can serve as templates for engineering the morphologies of TMDCs, and function as effective electrodes to enhance the electrochemical performances. For batch production, some naturally abundant and low-cost materials (e.g., salt powders) can be used as 3D templates to achieve high-quality 2D TMDCs nanosheets powders, which can serve as effective electrocatalysts for HER. To promote the activities of TMDCs, several advanced strategies have been proposed, including engineering the morphologies to expose more active edge sites, introducing S-vacancies to activate the inert basal planes of semiconducting TMDCs (e.g., MoS\textsubscript{2}, W\textsubscript{S}\textsubscript{2}), as well as tailoring the phases by strain engineering. Particularly, the advantages of 3D-substrate-derived TMDCs catalysts in the applications of electrocatalytic HER are highlighted in this Review.
TMDCs synthesized on 3D substrates, thus impeding its scalability toward uniform crystal quality, thickness, and domain size, etc. In a further step, to facilitate the practical applications of 3D-airchitectured TMDCs nanosheets in energy-related applications, to develop more intriguing 3D substrates with high conductivities, low-cost as well as designable structures should be essential issues in the related fields. Furthermore, more efforts should be devoted in improving the morphology uniformities of the CVD-grown 2D TMDCs. Developing more advanced precursor feeding strategies (e.g., coating metal precursor on the substrate, designing face-to-face precursor feeding route), or optimizing the CVD setups (e.g., designing vertical gas-flow CVD furnace) should be helpful to achieve this goal.

Although 2D TMDCs show great potentials as electrocatalysts for HER, challenges stills exist for practical applications comparing with noble metal catalysts (e.g., Pt, Ir), such as relatively high onset potential, low exchange current density and inferior long-term electrocatalytic stability. Nevertheless, breakthroughs will be made in the near future. The following strategies may be the possible directions: 1) synthesizing multicomponent catalysts by hybridizing TMDCs with other functional materials (e.g., N-doped graphene); 2) introducing more catalytic active sites by vacancy, doping or strain engineering (e.g., single-atom N-doped graphene); 3) exploring new-type catalysts possessing both high catalytic activity and chemical stability (e.g., 2D TMDCs alloys).

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Conflict of Interest

The authors declare no conflict of interest.

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Lijie Zhu received her B.S. degree in University of Science & Technology Beijing, in 2018. She is currently a Ph.D. candidate under the tutelage of Professor Yanfeng Zhang at Peking University of China. Her research interests center on controllable synthesis and applications of 2D materials.

Pengfei Yang received her B.S. degree in Shandong University, in 2016. She is currently a Ph.D. candidate under the tutelage of Professor Yanfeng Zhang at Peking University of China. Her research interests center on controllable synthesis and applications of 2D materials.

Yahuan Huan received her B.S. degree in Nanjing University of Science and Technology. After obtaining her Ph.D. from University of Science & Technology Beijing, she currently works as a postdoctoral fellow in the Peking University. Her research interests focus on controllable synthesis and applications of 2D materials.

Fan Zhou received her B.S. degree in Shandong University, in 2018. He is currently a Ph.D. candidate under the tutelage of Professor Yanfeng Zhang at Peking University of China. His research interests center on controllable synthesis and applications of 2D materials.
Yanfeng Zhang received her Ph.D. from the Institute of Physics in the Chinese Academy of Sciences, in 2005. In 2010, she joined the Center for Nanochemistry of Peking University and Department of Materials Science and Engineering, College of Engineering in Peking University. Now she is a full professor at the School of Materials Science and Engineering of Peking University. Her research interests relate to the controlled growth, accurate characterization, and novel property exploration of 2D atomic layer thin materials, such as graphene, h-BN–graphene heterostructures, and TMDCs, and their novel physical and chemical property explorations.