



2D-Layered Non-Precious Electrocatalysts for Hydrogen Evolution Reaction: Fundamentals to Applications

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Abstract: The production of hydrogen via the water splitting process is one of the most promising technologies for future clean energy requirements, and one of the best related challenges is the choice of the most highly efficient and cost effective electrocatalyst. Conventional electrocatalysts based on precious metals are rare and very-expensive for large-scale production of hydrogen, demanding the exploration for low-cost earth abundant alternatives. In this context, extensive works from both theoretical and experimental investigations have shown that two-dimensional (2D) layered materials have gained considerable attention as highly effective electrocatalytic materials for electrical-driven hydrogen production because of their unique layered structure and exciting electrical properties. This review highlights recent advancements on 2D layered materials, including graphene, transitional metal dichalcogenides (TMDs), layered double hydroxides (LDHs), MXene, and graphitic carbon nitride (g-C₃N₄) as cost-effective and highly efficient electrocatalysts for hydrogen production. In addition, some fundamental aspects of the hydrogen evolution reaction (HER) process and a wide ranging overview on several strategies to design and synthesize 2D layered material as HER electrocatalysts for commercial applications are introduced. Finally, the conclusion and futuristic prospects and challenges of the advancement of 2D layered materials as non-precious HER electrocatalysts are briefly discussed.

Keywords: graphene; graphitic carbon nitride; hydrogen evolution reaction; layered double hydroxides; MXene; transitional metal dichalcogenides

1. Introduction

Over recent years, the energy crisis and environmental pollution have become global concerns. As the energy demand increases with the long-term growth of society, these issues are getting more and more serious due to the limited energy sources and the quick consumption of fossil-based energies. Over the previous century, the very high consumption of natural energy sources has created increasingly harmful impact on our ecosystem, such as air pollution, the greenhouse effect and global warming. The main reasons for all these problems are the harmful gasses and wastes that evolve from the energy producing process. For a green and sustainable future, there is an ongoing search for clean and renewable energy sources as substitutes for traditional fossil fuels. In some cases, national grids could deliver efficient electricity energy from renewable sources, such as sunlight, wind, hydropower and geothermal power. However, the excess amount of renewable energy



Citation: Sahoo, P.K.; Bisoi, S.R.; Huang, Y.-J.; Tsai, D.-S.; Lee, C.-P. 2D-Layered Non-Precious Electrocatalysts for Hydrogen Evolution Reaction: Fundamentals to Applications. *Catalysts* **2021**, *11*, 689. https://doi.org/10.3390/ catal11060689

Academic Editor: Tomasz Mikołajczyk

Received: 27 April 2021 Accepted: 27 May 2021 Published: 29 May 2021

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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). will be wasted due to the lack of large-scale and long-term storage systems. For example, the excess of solar energy in daytime needs to be stored for night-time use. There are also many methods for storing the energy sources, such as batteries, mechanical energy storage, capacitors or storage in the form of chemical products (such as hydrogen (H_2)) [1,2].

Among all chemical fuels, H₂ is considered as an efficient renewable and clean energy source with highest energy density (142 MJ/kg). Compared with rechargeable battery system, the hydrogen energy storage system shows several benefits, such as long-term storage, long lifetime and low carbon footprint. Therefore, H₂ is one of the most promising green energy sources. Up to date, many techniques for hydrogen production have been reported, such as the photocatalytic water splitting method [2–5], electrocatalytic water splitting [6–8], vapor reforming [9], natural gas oxidation [10], iodine-sulfur cycle [11] and biomass electrolysis [12,13]. The cleanest method of hydrogen production is the spitting of water, where the main products of reaction are hydrogen and oxygen. Compared with photocatalytic water splitting, the electrocatalytic water splitting for hydrogen evolution is one of the best ways to store electrical energy because there are no limitations of sunlight intensity depending on geographical locations, weather, time and seasons [14,15].

Commonly, platinum (Pt) and other precious metals have been considered as wellknown catalysts for HER due to their low overpotential and small Tafel slope [16,17]. However, the commercial implications of the precious metals for hydrogen production on a large scale limited by their high cost and low abundance nature. Enormous efforts have been performed to lessen their use and maintain the efficiency by modifying electronic structures and catalysts composition [18,19]. Recently, researchers are more focused on developing non-precious and highly active catalysts, which are cheaper, earth abundant, highly efficient, durable and possible to replace the high-priced precious metal catalysts [20–22]. Inspired by these multiple challenges, this review provides the recent advancements on designs of cost-effective and highly efficient non-precious electrocatalysts based on 2D layered materials for HER applications, including graphene, transitional metal dichalcogenides (TMDs), layered double hydroxides (LDHs), MXene, and graphitic carbon nitride (g- C_3N_4).

1.1. Fundamentals to Electrocatalytic Hydrogen Evolution Reaction

For converting electrical energy to hydrogen fuel, the splitting of water is the best method; where, the water is used as main source and the by-products are H_2 and O_2 . Generally, there are two half reactions in water splitting processes: (a) oxygen obtained at an anode, called an oxygen evolution reaction (OER); and (b) hydrogen obtained at a cathode, called a hydrogen evolution reaction (HER) [3]. There are many theoretical and experimental efforts that have focused on the HER mechanism in acidic and alkaline mediums, which utilize the Volmer–Heyrovsky or Volmer–Tafel pathways in both the acidic and alkaline mediums (Figure 1) [23].

For the 1st step in acidic HER: hydrogen is adsorbed on the electrode surface due to the reaction between the electron and proton, called electrochemical hydrogen adsorption. In the 2nd step, a desorption reaction occurs, i.e., molecular hydrogen is obtained by the reaction between the electron, proton and adsorbed hydrogen. In the 3rd step, H₂ is generated by a combination of two adsorbed hydrogens (H*) [5].

For acidic media,

$$H^+ + e^- \rightarrow H^*$$
 (Volmer step) (1)

$$H^* + H^+ + e^- \rightarrow H_2$$
 (Heyrovsky step) (2)

$$2H^* \rightarrow H_2 \text{ (Tafel step)}$$
 (3)

The HER in alkaline media begins with dissociating H_2O molecules to provide protons, involving both the Volmer step and the Heyrovsky step, while the Tafel step keeps no change compared with the acid solution [4].

$$H_2O + e^- \rightarrow H^* + OH^-$$
 (Volmer step) (4)

$$H^* + H_2O + e^- \rightarrow OH^- + H_2 \text{ (Heyrovsky step)}$$
(5)

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \text{ (Tafel step)} \tag{6}$$



Figure 1. Schematic illustration of the hydrogen evolution reaction mechanism in acidic and alkaline media [23].

1.2. Parameters Using in the Electrochemical Hydrogen Evolution Process

There are some important parameters that to be calculated to interpret the electrocatalytic process for HER. These parameters include overpotential/onset potential, faradic efficiency, Gibb's free energy, Tafel slope, turnover frequency, stability, and exchange current density. The valuable information about the activity of the catalyst is collected through the above parameters.

1.2.1. Overpotential

In the water electrolysis process, the accumulation of H_2 at the surface of electrode could hind the electrode reactions, leading to slow the reaction rate. To overcome this problem, some extra potential will be applied. The extra potential which is applied beyond the thermodynamic demand to run a water splitting at a specific rate is called overpotential (η) [24]. The electrolysis equation consists of three parts:

$$E_{\text{Electrolysis}} \rightarrow \Delta E_{\text{Irreversible}} + E_{\text{Reversible}} + \text{IR}$$
 (7)

where, $E_{Reversible}$ is the theoretical disintegration voltage, $\Delta E_{Irreversible}$ represents the overpotential and IR represents the dropped voltage (i.e., the product of electric current (I) and the resistance (R)) resulted by contact point, wires and electrolytes. According to many previous reports, the evaluation of the catalyst performance is usually performed by the overpotential at 10 mA cm⁻² current density (the vital reference). At higher current density those which can produce low overpotential are known as ideal electrocatalysts [24].

1.2.2. Tafel Plot

The Tafel plot signifies the dependance of steady-state current density on a variation of overpotentials (η), which can be acquired from the curves of linear sweep voltammetry (LSV). The LSV measurement, a voltametric method, is used to measure the current of a working electrode under a linearly sweeping potential between the working electrode and a reference electrode with time. By applying the Tafel plot for HER, the mechanism of the reaction and kinetics can be unveiled by the equation:

Tafel equation:
$$\eta = a + b \log j$$
 (8)

where, η = overpotential, a = log of exchange current (j₀), j = current density and b = Tafel slope. Tafel slope is used to study the kinetics of the electrochemical process in HER, representing possible reaction pathway and the rate-determining step as well as the basic electrocatalytic performance of the catalyst under equilibrium condition. When Volmer, Heyrovsky, or Tafel mechanisms are dominated the HER process, the corresponding value of 'b' (i.e., Tafel slopes) are 116, 38, and 29 mV dec⁻¹, respectively. Furthermore, the smaller 'b' values are associated with faster reaction kinetics. Generally, ideal electrocatalysts are those which have larger exchange current density and smaller Tafel slope [24]. If we consider the example of Ni₃FeN/r-GO-20, the smaller value of Tafel slope is 90 mV dec⁻¹. This material gives us the better performance towards electron transportation as compared other materials as shown in the Figure 2a [25]. Similarly, in case of Fe₃WC NRs/r-GO with the 'b' value of 50 mV dec⁻¹ gives better performance than others material as show in Figure 2b [26].

1.2.3. Faradic Efficiency

Faradaic efficiency represents the utilization efficiency of electrons transfer by an external circuit related to the electrochemical reaction. It can be calculated as the ratio of the experimental amount of H₂ produced to the theoretical value (Faradic efficiency = (experimental value of hydrogen)/(theoretical value of hydrogen)). Amount of H₂ produced was experimentally detected by water gas displacement or gas chromatography whereas theoretically calculated from potentiostatic or galvanostatic electrolysis by integration. In case of Mo₂N-Mo₂C/H-rGr in Figure 2c,d, the experimental amount and the theoretical amount of hydrogen generation as a function of time are almost same in both alkaline and acidic medium [27].



Figure 2. Tafel plots of (**a**) Ni₃FeN/r-GO-20, Ni₃Fe/r-GO-20, Ni₃N/r-GO-20, Fe₂N/r-GO-20, and Ni₃FeN [25]; (**b**) Pt/C, WC NRs/rGO, Fe₃W₃C NRs/rGO, and Pt/C [26]; The theoretical and experimental amount of H₂ vs. t (min) for Mo₂N-Mo₂C/H-rGr in (**c**) 0.5 M H₂SO₄ solution and (**d**) 1.0 M KOH solution for 60 min at -200 mV [28]; (**e**) TOF values of the as-synthesized Fe₂P, Fe₂P/Gr, and Fe₂P-ND/FGr at different overpotentials [29]; (**f**) turnover frequency (TOF) of MoS₂/N-rGO_{0.5}, MoS₂/rGO, MoS₂, and rGO-N at a scan rat of 50 mV s⁻¹ in a 0.5M H₂SO₄ solution [30]. (**g**) The ΔG_{H}^* value for HER based for various electrocatalysts [28]. (**h**) The calculated value of ΔG_{H}^* for Co, C, Co@C, N-C & Co@N-C, respectively [31].

1.2.4. Turnover Frequency (TOF)

With overpotential differentiation, the electrocatalytic performance can be easily evaluated at the similar current density (the amount of charge flow through a unit area of chosen cross-section per unit time, J = I/A, where "J" is the current density, "I" is the flowing current and "A" is the cross-sectional area). Various techniques are consistent with loading mass with so many dissimilarities, so to solve this type of difficulties, turnover frequency (TOF) is a significant parameter for evaluating better performance towards HER. The TOF quantifies the specific activity of catalytic center for a special reaction under defined reaction conditions by the number of molecular reactions or catalytic cycles occurring at the center per unit time (TOF = volumetric rate of reaction/number of centers per volume). The higher value of TOF indicates outstanding performance of electrocatalysts. As compared with Fe₂P/Gr and Fe₂P, Fe₂P-ND/F-Gr hybrid exhibits remarkable performance as shown in Figure 2e (TOF = 0.09 s⁻¹ at overpotential of 100 mV, 0.34 s⁻¹ at an overpotential 150 mV) [29]. As shown in Figure 2f, MoS₂/N-rGO_{0.5} (TOF = 0.89 s⁻¹) catalyst shows better HER catalytic efficiency at same over potential as compared to MoS₂/rGO (TOF = 0.51 s⁻¹) and MoS₂ (TOF = 0.29 s⁻¹) [30].

1.2.5. Gibbs Free Energy

According to the Sabatier principle [28,32], the electrical charges can transfer easily between the bonding of absorbed hydrogen and the electrocatalyst surface, leading to the formation of hydrogen gas easily. However, if the bonding between the electrocatalyst and adsorbed hydrogen is too strong, the limitation of desorption reaction (Heyrovsky/Tafel) will be occurred. Furthermore, if the bonding is too weak, there will be a bad impact on Volmer reaction. The hydrogen desorption or adsorption on the surface of electrocatalyst can be estimated by Gibbs free energy (ΔG_H^*). The kinetics of HER can be evaluated by the value of ΔG_{H}^{*} for adsorption of hydrogen. Therefore, ΔG_{H}^{*} is an important parameter for determining the electrocatalytic performance in HER. As compared to the ΔG_{H}^{*} value of single Mo₂N (-0.449 eV) and Mo₂C (-0.405 eV), the ΔG_{H}^* value of N-site (nitrogen site) is very small in case of N-Mo-C, i.e., 0.046 eV (Figure 2g) [28]. Figure 2h shows ΔG_{H}^* values for various electrocatalysts for HER. Compared with bare graphene, the hydrogen adsorption of bare Co is very strong. Therefore, the value of ΔG_{H}^{*} can be tuned up by synthesizing Co on graphene. The decrease in ΔG_{H}^{*} of N-doped graphene shows that the N-doping is favorable for HER. Furthermore, the $\Delta G_{\rm H}^*$ of a nanohybrid composite of Co cluster, N-doping, and graphene (Co@N-C) is close to zero, indicating good HER performance [31].

1.2.6. Electrochemical Active Surface Area

Electrochemical active surface area (ECSA) of an electrocatalyst particularly for porous substrate is a significant measuring parameter and exposure of active sites. A quite high value of ECSA indicates that catalysts have a higher level of unsaturated atoms coordination and higher exposing active sites, which signifies better performance of the catalyst. ECSA can be determined by using a double layer capacitance measurement. All the fluctuations in the non-Faradic overpotential zone (0.1 V window area near the open circuit voltage zone) are due to charge discharge operations of C_{dl} (double layer capacitance), according to an examination of CV polarization curve. Since the charging current (i_c) fluctuates with various scan rates, Equation (9) is usually used to compute the value of double layer capacitance; the approach is exact and practical because the slope of i_c -v curve equals to C_{dl} [33].

$$i_c = v C_{dl} \tag{9}$$

In which, i_c is the charging current, v is the scan rates and C_{dl} is the double layer capacitance.

$$ECSA = C_{dl}/C_s$$
(10)

In which C_{dl} is the double layer capacitance and C_s being the specific capacitance.

$$I = I_c + I_f \tag{11}$$

In which 'I' is the working electrode current, I_c is the double layer current and I_f is the faraday current.

$$I_{c} = dq/dt = d(C_{dl}\phi)/dt = C_{dl} (d\phi/dt) + \phi (dC_{dl}/dt) \approx C_{dl} (d\phi/dt) = C_{dl} v$$
(12)

In which, q is the potential, φ is the quantity of electric charge and ν is the scan rates. According to the Equation (10), ECSA is in proportion to the working electrode's electric double layer capacitance. I_c and I_f is the two parts of working electrode current (I). The total working electrode current is the sum of double layer current (I_c) and faraday current (I_f) (Equation (11)). Because no chemical reaction takes place on working electrode due to the low overall current density around zero and narrow potential sweep range (typically 0.1 V), If may be ignored and C_{dl} remains constant. The value of I_c can be represented by the Equation (12). The linear slope of resulting line is twice of C_{dl} when graphing the Δ J vs. the scan rates [34].

2. 2D Materials Used for Electrocatalytic HER

Two-dimensional (2D) material studies have been increasingly conducted toward understanding the principles and applications. Two-dimensional materials have attracted considerable attention in the last decades for their particular physical and chemical properties. Generally, 2D materials with a variety of possible structures (sheets, plates or flake-like shapes) that involve graphene and other monolayer materials, such as TMDs, LDHs, MXene, g-C₃N₄, diatomic hexagonal boron nitride and black phosphorus (BP or phosphorene). Because of their outstanding physical and chemical properties, 2D materials are highly interesting in comparison with their bulk counterparts. The atomically thin, single or few crystals provide strong interlayer covalent bonding and weak interlayer van-der Waals bonding, resulting in superior electrical and optical properties [35]. In addition, 2D materials exhibit remarkable high in-plane strength and stiffness, which is associated with their blending flexibility and atomic thickness in comparison with conventional 1D and 3D materials, as shown in Figure 3. In recent years, the 2D layered materials have given lots of interest because of their efficient applications towards different sectors, such as physics, chemistry, biology and energy [36,37]. According to the standard of a good catalyst for HER, 2D materials have massive recognition for acting as a favorable catalysts in electrochemical HER in comparison with other catalysts, due to their large surface area, abundant edge states, and tunable electronic properties as well as non-preciousness nature [38]. This review includes the recent advancements, remarks and future perspectives of the HER reactions based on non-precious electrocatalysts of 2D materials, such as graphene, TMDs, LDHs, MXene, and graphitic carbon nitride $(g-C_3N_4)$.

2.1. Synthesis Techniques for 2D Materials

In general, 2D family materials are categorized as layered and non-layered materials. The structures of materials depend upon the diverse synthesis techniques. There are two basic characterizations of synthetic techniques for synthesize the 2D materials:

(1) The top-down process which is used to synthesize 2D nanomaterials from their bulk materials by mechanical exfoliation method, scotch tape method, liquid exfoliation method, etc.

(2) The bottom-up process which assembles atomic ingredients to form 2D nanomaterials by physical vapor deposition (PVD), chemical vapor deposition (CVD), solution based chemical synthesis, etc. [39]. Several basic 2D material synthesis techniques are discussed below, which show some advantages and disadvantages depending upon their cost effectiveness, precursors, raw materials, processes, etc.



Figure 3. The summery of 2D materials including graphene, TMDs, LDHs, MXenes, and others [38].

2.1.1. Mechanical and Liquid Exfoliation Method

The exfoliation method is the most common approach to synthesize the single-layer or few-layer structure of 2D nanomaterials from bulk solids. This preparation method is also called a scotch tape method, which was used to create a monolayer of graphene for the first time. A piece of sticky tape is applied to the surface of 2D layered materials (bulk) so that the top 2D flakes (consisting of a small number of layers) of 2D materials (bulk) are attached to the tape, then the tape can be pressed onto the desired substrates to transfer the 2D flakes on it. Furthermore, the few-layer graphene could be prepared by chemical exfoliation in a binary-component solvent. For example, Liu et al. reported the synthesis process of graphene via a one-step chemical exfoliation method. In this synthesis method, two chemicals (sulfuric acid and peroxyacetic acid) are mixed with graphite. After about 4 h standing, the complete exfoliation of the graphene is achieved in the mixing [40].

Wei et al. explained the exfoliation method of bulk graphite for the mass production of a small graphene sheet, i.e., the scotch tape method (the easiest method) [41]. Yan et al. illustrated the solvothermal assisted liquid exfoliation and dispersion techniques of black phosphorus (BP) in acetonitrile solution, which is a conventional method for preparing large size and high-quality BP nanosheets. They gave the high-quality results in the preparation of 2D BP nanosheets with an average thickness of about 2 nm and the horizontal size at about 10 nm [42]. Shen et al. discussed in their work about the exfoliation of MoS₂ nanosheets via ultrasonication method. This exfoliation method in water involves the thinning and fractionation of 2D MoS₂ flakes, providing small lateral size and better stability of the materials [43]. Kuang et al. reported the synthesis of NiS₂/V-MXene hybrid composite by the two-step method (Figure 4a). First of all, Ni(OH)₂/V-MXene is synthesized by adding exfoliated V-MXene flakes into Ni(OH)₂ solution at 150 °C for 6 h [44]. Secondly, Ni(OH)₂/V-MXene and S powder (precursor) are undergone in situ CVD process (at 350 °C for 1 h under Ar atmosphere) to form NiS₂/V-MXene. Pacile et al. explained the preparation of very thin sheet of hexagonal boron nitride (h-BN), which was synthesized by facile micromechanical exfoliation method on the surface of the substrate, i.e., on SiO₂ or freely suspended. The obtained material has a very-small size of 10 μ m. This h-BN can be used catalyst in various applications such as energy storage, hydrogen evolution, etc. [45]. Liu et al. group prepared MoS₂-PVP (Molybdenum disulfide–polyvinylpyrrolidone) hybrid by a simple method of synthesis, i.e., the liquid exfoliation method. This hybrid material used as flexible memory device. At the transition, the current abruptly jumped from 1.4×10^{-5} to 1.6×10^{-4} and the on-off ratio was around 10^2 with a threshold voltage of 3.5 eV [46].



Figure 4. (a) Schematic illustration of the synthetic of NiS₂/V-MXene hybrid by using combination of HF etching, ultrasonic exfoliation, electrostatic adsorption, hydrothermal and in situ CVD processes [44]; (b) formation of V SACs@1T-WS₂ monolayers on the V₂O₃ film through a one-step CVD method by controlling the introduction of VCl₃ co-precursor [47]; (c) employment of fabrication equipment and the space-confined growth during the CVD synthesis of MoS₂ samples [48].

2.1.2. Chemical Vapor Deposition (CVD) Method

The CVD method is a class of bottom-up process for high quality and high performance solid materials. Generally, the gaseous reactants (which usually contains atomic ingredients of required films) are passed through the heated CVD furnace, where a thin layer of the required material will be synthesized after the chemical reactions in gaseous reactants or between the gaseous reactants and a substrate. Zhang et al. synthesized MoS₂ mono layer on SiO_2/Si substrates by CVD method. The correlation of growth conditions and morphologies of MoS_2 was observed during the CVD process [49]. Furthermore, Han et al. fabricated single-atom-V catalyst (V SACs) substitutions in 1T-WS₂ monolayers (V SACs@1T-WS₂) with 91% phase purity via controlling VCl₃ co-precursor during CVD process (at temperature 860 °C for 15 min) [47] (Figure 4b). Moreover, Chen et al. demonstrated a space-confined CVD method as shown in Figure 4c to grow 2D MoS₂ flakes with tunable dimensionality by controlling the experimental parameters such as the amount of S powder, growth temperature, and the distance between growth substrate/S powder and Mo foil [48]. Kim et al. focused on the preparation of monolayered (on Cu substrates) and multi-layered (on Fe substrates) h-BN films for real applications via CVD methods [50]. Chen et al. synthesized the high-quality mm size monolayer MoSe₂ by using CVD method. The monolayer crystal was developed on molten glass at an ambient pressure. The size of the monolayer crystal obtained is ~2.5 mm, which has a room temperature carrier mobility of up to \sim 95 cm²/V.s. This material can be used in different applications such as electrocatalytic HER, OER, etc., and other energy storage applications [51]. Liu et al. explained the synthesis of 2D layered hexagonal boron nitride (h-BN) via CVD method. This h-BN is an oxidation resistance coating, large scale, ultrathin and high-quality coating material. The material obtained in the synthetic process has a thickness of 3×3 cm. Next, 2D h-BN was synthesized and transferred after the synthesis process on to the SiO_2/Si substrate. It might be the thinnest covering ever demonstrated to resist such harsh conditions and has some potential applications such as chemically stable high-temperature coatings [52].

2.1.3. Hydrothermal Method

The hydrothermal method gives us different advantages as compared to the CVD method for the synthesis of 2D materials because of low cost, easy experimental setup and high amount of production. Basically, the powdery nanostructures could be obtained by the hydrothermal method which is the mixing of proper agents and precursors in water at high temperature and pressure. Peng et al. documented the integrating processes of MoS_2 nanosheets and SiC nanowires by the one-step hydrothermal method. As compared to naked MoS₂ materials, the electrocatalytic HER performance of MoS₂-SiC nanocomposite is improved further [53]. Furthermore, Liu et al. demonstrated the synthesis of CoFe LDH and Ce/CoFe LDHs with oxygen vacancies by hydrothermal method followed by plasma etching process (Figure 5a) [54]. Initially, CoFe LDH and Ce/CoFe LDHs are grown on the nickel foam by hydrothermal process. Subsequently, the as-synthesized CoFe LDH and Ce/CoFe LDHs are put on the quartz boat in a plasma reactor with different power densities (100, 200, 300, 400, and 500 W) of N₂ plasma. Moreover, Nguyen et al. successfully prepared WS₂ hollow nanospheres via hydrothermal method. The WS₂ hollow nanospheres (with the diameter from 300 nm to 2 μ m) show a good performance in electrocatalytic HER (Figure 5b) [55]. Besides, Liu et al. synthesized the nitrogen doped Mo₂C@C composites with different amount of cetyltrimethylammonium bromide (CTAB) via thermal method. Here, the CTAB is a carbon source and a structure guiding agent. The nitrogen doped Mo₂C@C composites could enhance electrocatalytic reactions because of their high conductivity and homogeneous dispersion of the nanocrystals (plentiful active sites). Accordingly, the CTAB assisted materials give the chance to synthesize the low cost and high-performance Mo based electrocatalyst for HER [56]. Wang et al. prepared MoS₂/r-GO via hydrothermal method of synthesis which is used as highly efficient catalyst for visible light pollutant degradation. All of the samples were heated for 3 h at 149 °C, followed by 5 h at 700 °C. The obtained composite gives excellent light adsorption and

great performance in photocatalytic activity than the pure MoS_2 [57]. Wang et al. used a speedy and simple hydrothermal synthetic approach to create TiO_2/Ti_3C_2TX composite. It is used as photocatalyst. Under identical experimental circumstances, the composite photocatalyst demonstrates considerably higher performance in case of solar hydrogen generation than pure TiO₂. Similarly, as compared to pure TiO₂ the composites exhibit 400% improvement in photocatalytic hydrogen evolution [58].



Figure 5. (a) Schematic illustration of synthesis of V-CoFe LDH and V-Ce/CoFe LDH through hydrothermal method followed by N_2 plasma itching [54]. (b) Synthesis of WS₂ hollow structure using a facile hydrothermal method [55]. (c) Schematic procedure of solvothermal synthesis of BP nanosheets for efficient HER and the inset image shows that the yield can be up to 2.1 g [59].

2.1.4. Solvothermal Method

As compared with hydrothermal method, organic solvent is used to replace water in solvothermal method. Furthermore, to increase the solubility of solvent and reaction rate, the reaction temperature is always higher than solvent's boiling point and all reactants are put in a sealed vessel (such as autoclave). Zhu et al. synthesized black phosphorus (BP) from red phosphorus under common laboratory condition via solvothermal method (Figure 5c). As compared with red phosphorus, the photocatalytic hydrogen production efficiency of the as-prepared BP nanosheets is higher (~40.6 times) and similar with the C_3N_4 nanosheets [59]. Furthermore, Govindaraju et al. reported the synthesis of Cu_3SnS_4 decorated r-GO by solvothermal method. The electrocatalytic activity for HER of the Cu_3SnS_4 -rGO is better than its native Cu_3SnS_4 [60]. Moreover, Chen et al. demonstrated

the preparation of MoS_2/r -GO by microwave assisted solvothermal process and clearly discussed the improved electrocatalytic HER behavior of the MoS_2/r -GO as compared with pure MoS_2 samples. The edge-rich and defects-rich MoS_2/r -GO can decrease the surface energy of MoS_2 , leading to the improvement in HER catalytic properties [61]. Cai et al. were applied a simple one-pot solvothermal process to prepare efficiently highly homogeneous composites of NiCo-LDH/r-GO (NiCo-layered double hydroxide and reduced graphene oxide). Synthesized NiCo-LDH/r-GO composite electrodes have outstanding super capacitive qualities, with a maximum specific capacitance of 1911.1 F g⁻¹ at a current density of 2.0 A g⁻¹. This composite is a perfect candidate for the application of energy conversion and energy storage device [62]. Feng et al. were effectively employing a unique mixed solvothermal technique based on the incorporation of organic solvent into the solution. The organic solvent used to synthesize the material is ethylene glycol. The average size of the material obtained is 90 mm. and the thickness was about 10–20 nm. The MoS₂ nanosheet can be used in different applications such as photocatalytic or electrolytic HER, supercapacitor, etc. [63].

2.1.5. Electrodeposition Method

The electrodeposition method is a simple, quick and inexpensive process for the synthesis of 2D materials, which is deposited on the surface of the conductive substrate. Electrodeposition has shown to be a cost effective and environmentally friendly method of fabricating 2D electrocatalysts since it uses an electrochemical pathway rather than hazardous reactants, high temperature, binder material, or an extra transfer step [64]. The basic electrodeposition cell consists of three electrodes—the reference, cathode and anode—which are linked by a power source and submerged in electrolyte that contains the ion of metals to be deposited as well as a supporting solution. Generally, the cathode is taken as substrate material on which electrodeposition takes place and at which the anode oxidation reaction takes place. This deposition process is excellent in controlling film composition, thickness, uniformity, and purity. Baber et al. synthesized an efficient two-dimensional NiFeCo LDH/NF electrocatalyst by a facile and low-cost electrodeposition method. This synthesized material is a highly effective electrocatalyst for the efficient hydrogen evolution and oxygen evolution in 1 M KOH. This composite requires overpotential of 210 mV and 108 mV for OER and HER, respectively, to achieve the current density of 10 mA cm^{-2} [65]. Furthermore, Li et al. have reported a one-step electrodeposition method for preparing Mo-W-S/CC (molybdenum-tungsten-sulfide on carbon cloth). As an electrocatalyst for HER, it has demonstrated very-good performance and excellent durability. A total of 0.5 M H₂SO₄ was utilized as the electrolytic solution for HER and for all the discussed material (Mo-W-S/CC_{OC}, Mo-S/CC and W-S/CC), Mo-W-S/CC_{OC} shows excellent overpotential of 198 mV at current density of 10 mA cm^{-2} [66]. Jia et al. have prepared MoSe₂ nanoparticles on the substrate of r-GO/PI (reduced graphene oxide/polyimide). The electrolytic performance can be examined in $0.5 \text{ M} \text{ H}_2\text{SO}_4$. In addition, in the hydrogen evolution (HER) process MoSe₂ thin film demonstrates better catalytic activity than MoSe₂ and MoS₂, i.e., the onset potential value for HER with high catalytic current density of 3.1 mAcm⁻² at -0.3 V [67].

2.2. Applications of 2D Materials on HER

Some applications of 2D materials on HER are discussed below.

2.2.1. Graphene

Recently, graphene-based materials have been used widely to improve the performance of HER due to their large surface area, high electrical conductivity and good chemical stability. As compared to precious metals such as Pt, graphene is consisted of carbon elements, which is low cost and plentifully available [68]. In addition, graphene is composed of sp² carbon atoms with three sigma (σ) bonds and its electronic characteristics and reaction kinetics could be tuned by chemical doping [69]. Yu et al. reported about the catalytic performance of the partially reduced graphene oxide/Molybdenum disulfide (MoS₂@pr-GO) which was synthesized by one-step hydrothermal method (Figure 6a-c) [70]. Owing to the N atoms (from the addition of triethanolamine), the high density of electron clouds is generated, leading to enhance the HER catalytic activity (the overpotential of 263 mV at current density of 10 mA cm⁻² and the Tafel slope of 60 mV dec⁻¹). Another very-important highly active catalyst, phosphorus-modified tungsten nitride/reduced graphene oxide (P-doped WN/r-GO), were synthesized by phosphorization processes using $H_3[PO_4(W_3O_9)_4]$ and Na₂H₂PO₂ [71]. The 4 nm sized tungsten nitride (WN) nanoparticles are distributed on the thin P-doped r-GO sheets, inducing a large number of active sites. The P-doped WN/r-GO shows the require overpotential of 85 mV at the current density of 10 mA cm^{-2} with good stability and low onset potential of 46 mV as well as Tafel slope of 54 mV dec⁻¹, indicating the good electrocatalytic properties. Furthermore, Jiao et al. synthesized a multicomponent catalyst of N-doped graphene coated with Co@Zn heterostructures on nickel foam (NG@Co@Zn@NF)) via hydrothermal method as shown in Figure 6d,e [72]. The multicomponent catalyst with 850 °C post-annealing (NG@Co@Zn@NF-850) shows the best HER electrocatalytic properties such as the lower overpotential of 34 mV dec $^{-1}$ for achieving 10 mA cm⁻² current density and the smaller Tafel slope of 36 mV dec⁻¹ [72]. In addition, NG@Co@Zn@NF-850 still had 50% catalytic activity after 90 h in alkaline medium and showed barely any difference in scanning electron microscopy (SEM) morphology after long-life test (Figure 6f). Li et al. developed core-shell 1D Ni₃S₂@NGCLs (i.e., Ni₃S₂ nanowires surrounded by N-doped graphene-like carbon layer) nanostructure on nickel foam (NF) in which Ni₃S₂ nanowire and NGCLs act as an active core and a conductive shell, respectively [73]. The lower magnification TEM image of Ni₃S₂@NGCLs nanowires in Figure 6g shows a well-defined nanowire with a diameter of about 60 nm wrapped with thin layer of graphene sheets. As compared with commercial RuO₂ and Pt/c catalysts, Ni₃S₂@NGCLs/NF shows the superior HER performance as shown in Figure 6h,i (a low overpotential of 134 mV at 10 mA cm⁻² in 1.0 M KOH aqueous electrolyte and a low Tafel slope of 84 mV dec $^{-1}$).

2.2.2. Transition Metal Dichalcogenides (TMDs)

TMDs are another family of 2D layer materials with the molecular formula MX₂, where M is the transition metal (Mo, W, etc.), which is sandwiched in between two chalcogenides X_2 (X-S, Se, Te, etc.) with thickness ≤ 1 nm. There are three crystal phases of TMDs monolayer and multilayer in the sense of thermodynamic stability, i.e., 1H for single layers (1H for most of group VI TMDs), 1T phase for octahedral (group IV, VII, and X) and finally 1T' phase for distorted lattice [74]. These are the most common crystal structures with different electronic properties (2H-Hexagonal, 1T-Octahedral and 1T'-Distorted octahedral). TMDs are acquiring much more attention in different research fields because of their unique characteristics such as large surface area, good hydrophilic nature, easier intercalation and modification, highly exposed active sites and their atomically thin structures. Hence, TMDs are considered as potential candidates for HER electrocatalysis applications [75]. If we consider the high chemical stability and wide range pH value, TMDs can perform well in comparison with other noble metal catalysts. Furthermore, the cost of TMDs is lower than noble metal catalysts. Until now, the related mechanisms of TMDs catalytically active sites, reaction limiting factor and structural control have been investigated over the years. Therefore, the layered TMDs can give superior HER activity via precise phase control, defect generation, size control and edge enrichment, chemical doping, and heterostructures [74,76]. For example, Chen et al. prepared the ultrathin and porous MoSe₂ nanosheets by modified liquid exfoliation method for HER (Figure 7a). The ultrathin and porous structures of MoSe2 give more active sites and effective electron transport, leading to a small onset potential of 75 mV dec⁻¹ and the Tafel slope of 80 mV dec⁻¹ as shown in the Figure 7b,c [77]. Furthermore, Han et al. had synthesized highly dispersed single vanadium atoms on the 1T-WS₂ monolayers (i.e., V SACs@1T-WS₂) by a one-step CVD process. The HER catalytic activity of V SACs@1T-WS₂ shows a low Tafel slope of 61 mVdec⁻¹ and high

turnover frequency (TOF) of $3.01 \,\mathrm{s}^{-1}$ at 100 mV, and an extraordinary long-term catalytic stability at current densities higher than 10 mA cm^{-2} in $0.5 \text{ M H}_2\text{SO}_4$ electrolyte for 100 h(Figure 7d-f) [47]. The V SACs@1T-WS₂ monolayers show outstanding HER activity as compared to their 2H counterparts and recently representative electrocatalysts owing to the highly active single-atom V sites. Moreover, Chen et al. demonstrated NiS@MoS₂ core-shell hierarchical microspheres through an interface engineering strategy for the HER in both acidic and alkaline conditions [78]. Under the optimized conditions, the as-synthesized NiS@MoS2 catalysts show low overpotential of 208 mV in 0.5 M H2SO4 and 146 mV in 1.0 M KOH at 10 mA cm^{-2} (Figure 7g). Under acidic conditions, the lower Tafel slope and charge transfer resistance (R_{ct}) of NiS@MoS₂-20 are 62.44 mV dec⁻¹ and 142.1 Ω , respectively, as compared to MoS₂ (131 mV dec⁻¹, 704.7 Ω), NiS@MoS₂-05 (106.98 mV dec⁻¹, 532.5 Ω), NiS@MoS₂-10 (65.39 mV dec⁻¹, 177.6 Ω), and NiS@MoS₂-40 (97.68 mV dec⁻¹, 355.8 Ω), indicating higher HER activity and fast charge transfer rate during HER processes (Figure 7h,i). Besides, Kumar et al. studied the HER catalytic behaviours of MoS₂ nanoparticles embedded over rGO (MoS₂/rGO) and GO (MoS₂/GO) nanosheets [79]. A low Tafel slope (~40 mV dec⁻¹) of MoS_2/GO indicates a promising electrocatalyst for HER in practical applications as compared to MoS_2/rGO (Tafel slope = 71.8 mV dec⁻¹). The difference in HER activity between MoS₂/GO and MoS₂/rGO is due to lower desorptive resistance of MoS₂/GO than MoS₂/rGO, confirmed by electrochemical impedance spectroscopy (EIS).



Figure 6. (a) Scheme of catalytic performance of partially reduced graphene oxide and molybdenum disulfide (MoS₂@pr-GO) composite, (b) polarization curves and (c) relevant Tafel slopes of bulk MoS₂, GO/MoS₂, bulk MoS₂/triethanolamine, GO/MoS₂/triethanolamine and MoS₂@prGO composites [70]; (d) The hydrogen evolution polarization curves and (e) Tafel plots of NG@Co@Zn@NF catalysts, (f) LSV curves of the NG@Co@Zn@NF-850 catalyst before and after 1000 CV cycles in the stability test [72]; (g) TEM image of as-synthesized Ni₃S₂@NGCLs/NF, (h) Polarization curves and (i) Tafel slopes of Ni₃S₂@GCNs/NF, Ni₃S₂@NGCLs/NF, Ni foam and Pt/C/NF, respectively [73].



Figure 7. (a) Synthesis description for the fabrication of porous $MoSe_2$ nanosheets; (b,c) polarization curves and Tafel plots of porous $MoSe_2$ nanosheets, respectively [77]; comparison (d) LSV and (e) Tafel plots of GC, 2H, 1T-400, $2H_{1T}$, Pt/C and V SACs@1T-WS₂ electrodes in 0.5 M H₂SO₄ with a scan rate of 5 mV s⁻¹; (f) TOF comparison with other representative electrocatalysts [47]; (g) polarization curves, (h) Tafel slopes, and (i) Nyquist plots of MoS_2 , NiS@MoS₂-05, NiS@MoS₂-10, NiS@MoS₂-20, NiS@MoS₂-40 and 20 wt% Pt/C in 0.5 M H₂SO₄ solution [78].

2.2.3. MXenes

MXenes are the new type of 2D materials with two categories such as transition metal carbides and nitrides obtained from exfoliated of MAX phase precursors $(M_{n+1}AX_n)$ (M = Mo, Ti, Zr, Cr; A = Al, Ga, Ge, Si; and X = C, N) [80]. Due to the abundant surface termination groups and the multi-layered structures, MXenes are the excellent materials for ion intercalation and electron transport in electrocatalytic HER. For example, Zhu et al. synthesized NiS_2/V -MXenes and NiS_2/Ti -MXenes composites by the exfoliation and hydrothermal methods for HER applications [44]. Because of the strong chemical and electronic interactions between V-MXene and NiS₂, electrons can move easily from V-MXene to NiS₂ (Figure 8a). Therefore, NiS₂/V-MXene displays much smaller overpotential of -179 mV at catalytic current density of -10 mA cm^{-2} than other counterparts such as NiS₂/Ti-MXene, NiS₂, V-MXene and Ti-MXene (Figure 8b). In addition, NiS₂/V-MXene exhibits smaller Tafel slope value of 85 mV dec⁻¹ as compared to their counterparts, indicating the outstanding reaction kinetics and catalytic performances of NiS₂/V-MXene as well as the HER process catalyzed through a Volmer–Heyrovsky mechanism. (Figure 8c). Moreover, Yoon et al. synthesized the nitride-titanium carbide MXene $(N-Ti_2CT_x)$ via high temperature nitridation of 2D titanium carbide MXene (Ti_2CT_x) using NaNH₂ [81]. As compared with pristine- Ti_2CT_x

(overpotential = -645 mV), the best N-Ti₂CT_x sample (11N-Ti₂CT_x) shows lower overpotential of -215 mV to achieve 10 mA cm⁻² current density in 0.5 M H₂SO₄, proving the excellent catalytic performances towards HER. In addition, after 24 h HER test, the LSV of 11N-Ti₂CT_x shows the overpotential required to attain 10 mA cm⁻² only increased by 5 mV, indicating excellent long-term stability of the 11N-Ti₂CT_x in acidic medium. Therefore, by surface modification, Ti_2CT_x can not only be enhanced the HER performance but also improved the durability. Furthermore, Wu et al. developed a carbon nanoplating strategy to fabricate the hierarchical MoS₂/Ti₃C₂-MXene@C (carbon coated few-layered MoS₂ nanoplates on carbon-stabilized Ti₃C₂ MXene) nanohybrids [82]. As shown in Figure 8d, MoS₂/Ti₃C₂-MXene@C electrocatalysts exhibits smaller value of onset potential of around -20 mV and overpotential of around -135 mV in 0.5 M H₂SO₄ solution as compared to $MoS_2/rGO@C$ (onset potential = -260 mV; overpotential = 352 mV) and $MoS_2/oxidized$ MXene (onset potential = -210 mV; overpotential = -332 mV) catalysts, suggesting superior HER activity. Furthermore, the smaller value of Tafel slope (45 mV dec⁻¹) of MoS₂/Ti₃C₂-MXene@C nanohybrids as compared to their counterparts indicates that Volmer-Heyrovsky mechanism involves in the HER catalysis process (Figure 8e). In addition, the long-term durability of MoS₂/Ti₃C₂-MXene@C nanohybrids in 0.5 M H₂SO₄ at a constant potential of -130 mV was exhibited by the stable current density over a period of 20 h (Figure 8f). According to the above results, the carbon nanoplating strategy can enhance further the reaction kinetics and the structural stability of MXene-based materials during the HER reaction. Besides, Liu et al. synthesized the MoS_2/TiC_2T_x nanoroll by quick freezing method. As shown in SEM image, the diameter and length of nanorolls are around 200 nm and several microns, respectively (Figure 8g) [83]. The high-resolution transmission electron microscopic (HRTEM) image reveals that the few-layered MoS₂ "bubble" such as structures are situated at the surface or/and in the channel of TiC_2T_x , which is helpful to the charge transfer and mass diffusion processes in the electrocatalysis reactions. As compared to pure MoS_2 and $Ti_3C_2T_x$ nanosheet, the MoS_2/TiC_2T_x hybrid gives a lower overpotential value of -152 mV to achieve the current density value of 10 mA cm⁻² (Figure 8h). MoS₂/TiC₂T_x hybrid exhibits the further lower Tafel slope of 70 mV dec⁻¹ as compared to pure MoS₂ and Ti₃C₂T_x nanosheet, indicating the Volmer–Heyrovsky mechanism in the HER catalysis process. The charge-transfer resistance of $MoS_2/Ti_3C_2T_x$ hybrid is much smaller than pure MoS₂, suggesting that electron transfer properties could be enhanced effectively by adding the conducting $Ti_3C_2T_x$ sheets (Figure 8i).

2.2.4. Layered Doubled Hydroxide (LDH)

LDH materials (previously called anionic clays) are 2D materials with brucite, such as lamellar crystal structures, which have attracted substantial attention. The general formula of an LDH is $M^{2+}_{1-x}M^{3+}_{x}(OH)_{2}$ $(A^{n-})_{x/n}$ ·yH₂O, where M^{2+} and M^{3+} represent divalent and trivalent cations such as Zn²⁺, Fe²⁺, Ni²⁺, Co²⁺ and Cr³⁺, Al³⁺, Fe³⁺ and Mn^{3+} respectively, and A^{n-} is the interlayer anion such as CO_3^{2-} , NO_3^{-} , SO_4^{2-} , and Cl⁻ for charge-compensation [84]. Recently, LDH has been in the spotlight for academic research and practical applications due to the unique 2D layered structures, a wide variety of material properties and tunable chemical compositions [84]. Yang et al. synthesized boron-doping-induced amorphization of crystalline NiCo LDH nanosheets supported on nickel foam (A-NiCo LDH/NF) through a simple and efficient strategy (Figure 9a) for the application on HER [85]. The A-NiCo LDH/NF shows a low overpotential of -151 mV to reach the current density of 100 mA cm⁻² as compared to NF (-406 mV), PA-NiCo LDH/NF (-266 mV), and crystalline NiCo LDH/NF (-269 mV), indicating higher HER activity (Figure 9b). Furthermore, it exhibits much lower Tafel slope (57 mV dec $^{-1}$) as compared to NiCo LDH/NF (70 mV dec⁻¹) and PA-NiCo LDH/NF (94 mV dec⁻¹), suggesting that HER catalytic mechanism follows the Volmer reaction path (Figure 9c). To confirm further the excellent long-term durability of the A-NiCo LDH/NF electrocatalysts, the current densities are kept at 500 mA cm⁻² and 1000 mA cm⁻² in 1 M KOH for 72 h.



Figure 8. (a) Schematic illustration for strong electron transfer takes place from V-MXene to NiS₂; (b) polarization curves and (c) Tafel slopes of NiS₂/V-MXene, NiS₂/Ti-MXene, NiS₂, V-MXene and Ti-MXene electrodes [44]; (d) polarization curves and (e) Tafel plots of MoS_2/Ti_3C_2 -MXene@C, $MoS_2/oxidized$ MXene, $MoS_2/rGO@C$, Ti_3C_2 MXene and Pt/C catalysts; (f) time-dependent current density curves for MoS_2/Ti_3C_2 -MXene@C catalyst at overpotential of -130 mV [82]; (g) SEM and TEM images of the "nanoroll" such as $MoS_2/Ti_3C_2T_x$ hybrid; (h) polarization curves of $MoS_2/Ti_3C_2T_x$ hybrid, $Ti_3C_2T_x$ nanosheets, and pure MoS_2 ; (i) EIS of $MoS_2/Ti_3C_2T_x$ hybrid, $Ti_3C_2T_x$ nanosheets, and pure MoS_2 at overpotential of -100 mV [83].

Ye et al. synthesized the nickel–chromium layered double hydroxide (NiCr-LDH) nanosheet arrays as a bifunctional catalyst by hydrothermal process [86]. By adjusting different Ni/Cr ratios in LDHs, Ni₂Cr₁-LDH (the samples with the optimized Ni/Cr ratio) exhibits very-low onset potential of -67 mV to reach current density of 10 mA cm⁻² compared to other counterparts such as Ni₃Cr₁-LDHs (82 mV at 10 mA cm⁻²) and Ni₁Cr₁-LDHs (-83 mV at 10 mA cm⁻²), confirming the extraordinary HER catalytic activity (Figure 9d). As compared with Ni₃Cr₁-LDH (62.2 mV dec⁻¹), Ni₄Cr₁-LDH (80.1 mV dec⁻¹), Ni₁Cr₁-LDH (72.2 mV dec⁻¹), and bare NF (136.9 mV dec⁻¹), the Tafel slope of the Ni₂Cr₁-LDH (61.5 mV dec⁻¹) is quite smaller (Figure 9e). In addition, Ni₂Cr₁-LDH shows outstanding durability by maintaining nearly constant current density over a period of 30 h at a constant potential of -0.07 V (Figure 9f).

Furthermore, Li et al. demonstrated a facile method for synthesis of the hierarchical hollow spheres assembled with ultrathin CoMn double hydroxide (DH) nanosheets as trifunctional electrocatalysts [87]. Among the tested catalysts (i.e., Co_1Mn_0 , Co_2Mn_1 , Co_4Mn_1 , Co_1Mn_3 , and Co_0Mn_1 spheres DH), the optimized sample (Co_2Mn_1 DHs) shows overpotential of -187 mV at a current density of 10 mA cm⁻² which is lower than Co_4Mn_1 DHs (-272 mV) and Co_1Mn_3 DHs (-337 mV) hollow spheres. In addition, Co_2Mn_1 DHs exhibits smaller Tafel slope (60 mV dec⁻¹) as compared with Co_0Mn_1 DHs (160 mV dec⁻¹), Co_1Mn_0 DHs (298 mV dec⁻¹), and Co_0Mn_1 DHs (106 mV dec⁻¹). The lower overpotential and Tafel slopes of Co_2Mn_1 DHs hollow spheres indicates higher HER activity and faster reaction kinetics. After the long-term HER process (for 23 h), 99.1% of the initial current density (10.2 mA cm⁻²) is retained, implying better catalytic stability of Co_2Mn_1 DH hollow spheres.

Liu et al. have studied the effect of oxygen vacancies and phase transformation engineering on HER activity by a model system (CoFe layered double hydroxide (LDH) grown on nickel foam) [54]. Plasma etched CoFe LDHs (the optimized sample) exhibits lower overpotential of -95 mV as compared to the pristine CoFe LDHs at the same current density (10 mA cm⁻²), indicating HER activity has been substantially improved after plasma etching (Figure 9g). After Ce doping into CoFe LDH followed by plasma treatment, the over potential of V-Ce/CoFe LDH could be decreased further to -73 mV. As compared with the pristine and doped CoFe LDHs, V-Ce/CoFe LDH also shows much lower Tafel slope (69 mV dec⁻¹), suggesting that performance of HER catalytic activity is dramatically improved due to more oxygen vacancies and beneficial phase transformations. At the same time, the V-Ce/CoFe LDH also shows smallest charge transfer resistance than un-itched and doped CoFe LDHs, indicating higher conducting and good reaction kinetics (Figure 9h). In addition, the better durability of V-Ce/CoFe LDH is revealed by showing slight change in polarization curve after 4000 cycles in the CV measurement and no significant change in the SEM image morphology (Figure 9i).



Figure 9. (a) Structure of boron-doping-induced amorphization of crystalline Ni-Co LDH nanosheets supported on nickel foam (denoted as A-Ni-Co LDH/NF); (b) LSV polarization curves and (c) Tafel plots of bare NF, Pt/C/NF, NiCo LDH/NF, PA-NiCo LDH/NF and A-NiCo LDH/NF for HER in 1 M KOH [85]; (d,e) graphical representation of polarization curves and the Tafel plots of different composites of LDHs, i.e., Ni₁Cr₁, Ni₂Cr₁, Ni₃Cr₁, Ni₄Cr₁ hybrid with LDH, foam of bare Ni and RuO₂; (f) curve of time dependence between electrode of reduced hydrogen of Ni₂Cr₁ composites with LDH and density of current below the potential value of -0.07 V [86]; (g) corrected polarization curves; (h) Tafel plots of CoFe LDH, V-CoFe LDH, Ce/CoFe LDH, and V-Ce/CoFe LDH in 1 M KOH electrolyte; (i) corrected polarization curves of V-Ce/CoFe LDH initially and after 4000 CV cycles [54].

2.2.5. Graphitic Carbon Nitride (g-C₃N₄)

Graphitic carbon nitride (g- C_3N_4), a low cost and non-metallic carbon-based material, has been used as an electrocatalyst for HER due to its layer structures and proper stability in acidic and alkaline solution. However, the electrocatalytic performance of the bulk g- C_3N_4 is still limited according to previous studies. To improve the electrocatalytic activity, many strategies have been developed such as construction of heterojunctions, element doping and creation of nanostructures (e.g., nanosheets) [88]. For example, Paul et al. synthesized $Cu_2O/g-C_3N_4$ nanocomposite for HER by using a simple hydrothermal route [89]. The as-synthesized $Cu_2O/g-C_3N_4$ nanocomposite shows lower Tafel slope (55 mV dec⁻¹), indicating that the HER pathway follows the Volmer–Heyrovsky mechanism. In addition, $Cu_2O/g-C_3N_4$ nanocomposite also exhibits smaller onset potential of 25 mV and lower charge transfer resistance of 3.42 Ω , indicating higher catalytic activity and higher fast electron transfer capability towards HER.

Furthermore, Li et al. synthesized g-C₃N₄/FeS₂/MoS₂ nanocomposites with different wt % of FeS₂ by hydrothermal method and demonstrated their HER electrocatalytic properties in 0.5 M H₂SO₄ solution [90]. Among all the as-prepared samples, g-C₃N₄/30% FeS₂/MoS₂ nanocomposite shows the smallest onset potential of -107 mV and overpotential of -193 mV at current density of -10 mA cm⁻², indicating the highest HER catalytic activity. Additionally, g-C₃N₄/30% FeS₂/MoS₂ nanocomposite exhibits the lowest Tafel slope (87.7 mV dec⁻¹) as compared to MoS₂ (90.4 mV dec⁻¹), g-C₃N₄ (155.4 mV dec⁻¹), g-C₃N₄/MoS₂ (121.1 mV dec⁻¹), g-C₃N₄/10% FeS₂/MoS₂ (95.5 mV dec⁻¹), and g-C₃N₄/50% FeS₂/MoS₂ (88.6 mV dec⁻¹), suggesting that the HER process obey the Volmer–Heyrovsky reaction mechanism. According to the EIS measurement, g-C₃N₄/30% FeS₂/MoS₂ exhibits smaller charge transfer resistance (R_{ct}) of 0.961 Ω with increasing electron transfer rate as compared with other as-prepared catalysts. Moreover, as-prepared g-C₃N₄/30% FeS₂/MoS₂ nanocomposite shows high HER catalytic durability by no obvious change of initial overpotential (-197 mV) after 3000 cycles.

Yousefzadeh et al. researched about the g-C₃N₄ nanosheet/quantum dot (NS/QD) with MoS₂ nanostructures for HER [88]. The two-step processes of exfoliation in a tip and bath sonication were used to synthesize g-C₃N₄ NS/QD. As compared with g-C₃N₄, the g-C₃N₄ (NS/QD) electrode shows a lower Tafel slope (88 mV dec⁻¹) and a lower overpotential (-0.28 V vs. RHEat current density -2 mA cm⁻²), and good HER stability after 1000 cycles and 100 days.

Table 1 summarizes the HER performance of various 2D-Layered Non-precious-based electrocatalysts in acidic and alkaline media. We can notice that some of these catalysts have similar or better performance than precious metal-based catalysts. This is possible due to adaptation of different design strategies and mechanisms of 2D-layered non-precious-based electrocatalysts towards HER performance.

Table 1. The FILL performance of 2D tayered non precious based electrocatarysis in acture and arrange in	HER performance of 2D-layered non-precious-based electrocatalysts in acidic and alkaline me	ned
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2D Materials	2D Materials-Based Catalysts	Electrolyte	Overpotential (mV) at 10 mA cm ⁻²	Tafel Slope (mV dec ⁻¹)	Ref
Graphene	MoS ₂ @pr-GO	0.5 M H ₂ SO ₄	263	60	[70]
	P-doped WN/r-GO	$0.5MH_2SO_4$	85	54	[71]
	NG@Co@Zn@NF-850	1.0 M KOH	34	36	[72]
	Ni ₃ S ₂ @NGCLs/NF	1.0 M KOH	134	84	[73]
TMDs	Porous MoSe ₂ Nanosheets	$0.5 \text{ M} \text{ H}_2\text{SO}_4$	150	80	[77]
	V SACs@ 1T-WS2	0.5 M H ₂ SO ₄	185	61	[47]
	NiS@ MoS ₂ -20	1.0 M KOH	146	67	[78]
	MoS ₂ /GO	0.5 M H ₂ SO ₄	13.1	40	[79]
MXenes	NiS ₂ /V-MXene	1.0M KOH	179	85	[44]
	11N-Ti ₂ CT _x	0.5 M H ₂ SO ₄	215	67	[81]
	MoS ₂ /Ti ₃ C ₂ -MXene@C	0.5 M H ₂ SO ₄	135	45	[82]
	MoS_2/TiC_2T_x hybrid	0.5 M H ₂ SO ₄	152	70	[83]
LDHs	A-NiCo LDH/NF	1 M KOH	151	57	[85]
	Ni ₂ Cr ₁ -LDH	1.0 M KOH	67	62	[86]
	Co ₂ Mn ₁ -DH	1 M KOH	187	60	[87]
	V-Ce/CoFe LDH	1 M KOH	73	69	[54]
g-C ₃ N ₄	g-C ₃ N ₄ /FeS ₂ /MoS ₂	0.5 M H ₂ SO ₄	193	88	[90]
	$g-C_3N_4$ NS/QD modified MoS ₂	0.5 M H ₂ SO ₄	280	88	[87]

3. Conclusions and Future Perspectives

The non-precious 2D layered electrocatalysts offer a variety of applications such as energy production and storage, fuel cells and production of bulk chemicals. One of the important electrochemical reaction is the HER, producing pure hydrogen for the fuel cell. Here, some advanced non-precious 2D layered catalysts (such as graphene, TMDs, LDHs, MXene, g-C₃N₄) are reported and a summarized their catalytic performance are provided to realize the development of cathode electrode in HER. In addition, some conventional synthesis techniques for improving the electrocatalytic performance in HER are also introduced. Thus, current studies may help to modify the fabrication processes of non-precious electrodes in order to decrease the cost and enhance the HER catalytic performance.

Apart from many achievements of non-precious 2D layered electrocatalysts for HER applications, there are still some important challenges to accomplish a wide range of commercial applications. Furthermore, the evolution of active sites and density of active sites, which are responsible for the electrocatalytic performance in HER need to be clarified more clearly in the non-precious 2D layered electrocatalysts. In other words, the basic mechanism on molecular levels of HER in the non-precious 2D layered electrocatalysts should be studied further. Therefore, advanced in situ techniques such as operando Raman spectroscopy, X-ray absorption near edge structure (XANES), extended X-ray absorption fine structure (EXAFS) and theoretical calculations such as DFT calculations are required in the near future to design and characterize high-active non-precious 2D layered electrocatalysts as well as understand the basic HER mechanisms on molecular levels. In addition, electrochemical surface area (ECSA) is a very crucial parameter of electrocatalysts, which depends largely on chemical properties and preparation method of electrode materials. Therefore, special attention should be paid to exploiting more ECSA at standardize current density. Likewise, other important parameters such as Tafel slopes, exchange current density (J_0) and turnover frequency (TOF) should be equally addressed. Again, defect, porosity and layered thickness of 2D materials significantly affect the activity of electrocatalysts. Therefore, the above requirements should not be ignored in order to prepare highly effective 2D layered electrocatalysts for HER. On the other hand, synthesis of 2D layered electrocatalysts through a greener approach and development of mixed 2D layered electrocatalysts are two key trends for designing next generation HER electrocatalysts. The above fundamental insights will be helpful to develop and optimize the non-precious electrocatalysts based on 2D materials for commercial applications.

Author Contributions: Conceptualization and organization, C.-P.L. and D.-S.T.; Writing—original draft, P.K.S., S.R.B. and Y.-J.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research received funding from Ministry of Science and Technology (MOST) of Taiwan.

Acknowledgments: This work was supported by the Ministry of Science and Technology (MOST) of Taiwan, under grant numbers 107-2113-M-845-001-MY3 and 109-2112-M-033-010-MY3.

Conflicts of Interest: The authors declare no conflict of interest.

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