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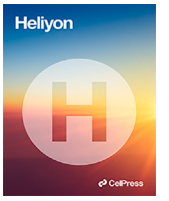

Review article

2D nanocomposite materials for HER electrocatalysts - a review

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ABSTRACT

Hydrogen energy has the potential to be a cost-effective and strong technology for brighter development. Hydrogen fuel production by water electrolyzers has attracted attention. 2D nanocomposites with distinctive properties have been extensively explored for various applications from hydrogen evolution reactions to improving the efficiency of water electrolyzer, which is the most eco-friendly, and high-performance for hydrogen production. Recently, typical 2D nanocomposites such as Metal-Free 2D, TMDs, Mxene, LDH, organic composites, and Heterostructure have recently been thoroughly researched for use in the HER. We discuss effective ways for increasing the HER efficiency of 2D catalysts in this paper, And the unique advantages and mechanisms for specific applications are highlighted. Several essential regulating strategies for developing 2D nanocomposite-based HER electrocatalysts are included such as interface engineering, defect engineering, heteroatom doping, strain & phase engineering, and hybridizing which improve HER kinetics, the electrical conductivity, accessibility to catalytic active sites, and reaction energy barrier can be optimized. Finally, the future prospects for 2D nanocomposites in HER are discussed, as well as a thorough overview of a variety of methodologies for designing 2D nanocomposites as HER electrocatalysts with excellent catalytic performance. We expect that this review will provide a thorough overview of 2D nanocatalysts for hydrogen production.

1. Introduction

Within the last decades, the changes in living standards and the global population growth have been subjected to enhance the worldwide amount of energy consumption. Global energy is mostly provided by fossil fuels, and there is an exceeding demand for energy, Worldwide. The restraining reserves of petroleum alongside the environmental and social glitches made by the fossil fuel needs (e.g. polluted water, local air quality worsening, universal warming) meltdown is a vital essential for the growth of new power plans with inadequate greenhouse gasses released [1,2]. To sustainably develop society, researchers have pursued clean and renewable energy sources, however, fossil fuels have become limited as the result of climate change, pollution, and energy security [3–6].

Nonetheless, it is indispensable to use extra cleaner, and renewable energy supplies like wind turbines, solar energy, geothermal power, and bio-materials Today Chemistry energy is for the sake of environmental gentleness. Therefore, countries have planned to diminish the used quantity of this restricted source and substitute it with alternate energies. Furthermore, such progress will depend

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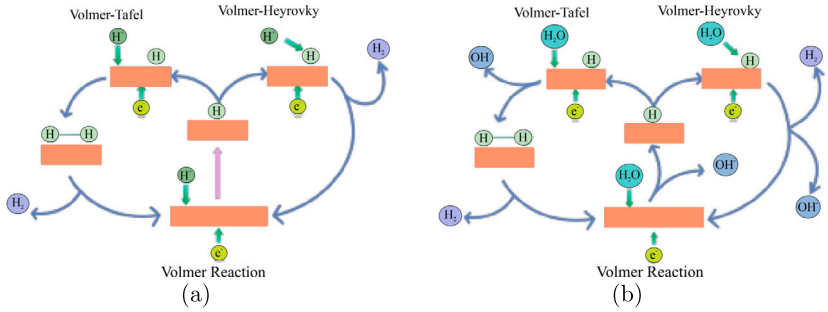

Fig. 1. Schematic molecular configurations of (a) acidic media, (b) alkaline media [29].

on renewable sources of energy (which are both plentiful and cleaner compared to fossil fuels) and chemical techniques for mock fuel synthesis [7–12]. Although this issue has been heeded, no specific development has been recognized in the use of alternative energies. Besides financial issues, the important problem with using restricted solar and wind sources is that they are able to function dependent on demand because their unprepared recurrent supply frequently diverges the network power needs. Accordingly, the growth and use of various systems for the effective and ease of storage of extra electrical power are involved [1]. From the several classifications of energy, hydrogen is regarded as an energy transporter and beneficial energy storage:

a. Water is the primary natural source of hydrogen [8,13],
b. Renewable or non-renewable sources best produce hydrogen. Moreover, both combustion engines and fuel cells (the first of which produces NOx simultaneously) consume hydrogen a lot [14],
c. Notably, the gravimetric energy density is high enough. It is almost three times more than liquid hydrocarbon-based fuels (nevertheless, its low volumetric energy density is noticeable. It is subject to safety concerns through its pressurized storage),
d. As water is the only product of its oxidation, it is not environmentally hazardous [1,11,12,14,15].

According to the aforementioned specifications, H_2 can be identified as an epitome and clean energy transporter. It is critical to access cost-effective and energy-efficient H_2 generation in order to finish the chemicals loop. As a result, H_2 is economically suitable. The fact is that it is not possible to find hydrogen as H_2. It exists as a constituent of substances, typically hydrocarbon material and water. The only choice is splitting water for H_2 generation remarking the finishing point of the chemicals loop as zero-emission. Hence, it has become a significant point to research [16].

Presently, the entire global production of hydrogen is roughly 500 billion cubic meters. Ammonia synthesis, oil refining, and metal refining are industries that utilized the mainstream [17]. It is noteworthy that water is the sole byproduct of combustion [16]. Hydrogen is a green energy source that is renewable, sustainable, and clean, as well as a viable energy transporter with the uppermost energy density of every chemical fuel ($142\,MJ\,kg^{-1}$). Hydrogen may be produced in a variety of ways. Among the ways of producing H_2 are photocatalytic water splitting, water electrolysis, steam reforming, natural gas oxidation, biomass electrolysis, and so on. In order to split water for hydrogen production, the freshest ways include Photocatalytic water splitting, electrolysis of water, biomass electrolysis, etc [18–21]. The proportion of hydrogen produced from various sources is around 48 percent from natural gas, 30 percent from oils, 18 percent from coal, and barely 4% from water electrolysis [22,23]. For the sake of high efficiency and eco-friendliness, since it is efficient enough and ecologically compatible and ecologically friendly, researchers have heeded this issue [24–26].

In acidic or alkaline media, electrochemical HER is identified as the cathodic process reaction for the electrolysis of water, in which three possible elementary steps are held. Fig. 1(a) divulges two serial steps through which the HER happened in acidic media. According to (Eq. (1)), the electrochemical adsorption of hydrogen (H_{ad}) on the electrode's surface is the commencement. The combining of free electrons with proton donor, such as (H_3O^+) in the acidic electrolyte is the origin of the halted hydrogen classes. After the desorption process is done, hydrogen can be produced, resulting in the addition of one additional free electron (Eq. (2)), and the reduction of another proton binding to H_{ad} (Eq. (3)) [26,27].

■ Volmer reaction

$$H_3O^+ + M + e^- \longrightarrow MH_{ad} + H_2O \tag{1}$$

■ Heyrovsky reaction

$$H^+ + MH_{ad} + e^- \longrightarrow H_2 + M \tag{2}$$

■ Tafel reaction

$$2\,MH_{ads} \longrightarrow H_2 + 2\,M \tag{3}$$

The creation and immobilization of H_{ad} (Eq. (4)) constitute the HER in alkaline media, similar to the reaction in acid medium, and sequestration of H_{ad} (Eq. (4)) is the Hydrogen evolution desorption method (Fig. 1(b)). Not like in acidic electrolyte the detachment of H_2O molecules provide, the proton givers in alkaline electrolyte. Both the Heyrovsky reaction (Eq. (5)) and the Tafel reaction (Eq. (6)) produces H_2, which helps to conduct the absorbed H_{ad} [28].

- Volmer reaction

$$2H_2O + M + e^- \longrightarrow 2MH_{ad} + 2OH^- \tag{4}$$

- Heyrovsky reaction

$$H_2O + 2MH_{ad} + e^- \longrightarrow H_2 + M + 2OH^- \tag{5}$$

- Tafel reaction

$$2MH_{ads} \longrightarrow H_2 + 2M \tag{6}$$

According to the aforementioned reaction, M is the electrode material, and H_{ad} in $M - H_{ad}$ is the adsorbed hydrogen atoms [29].

The energy performance of electrochemical water splitting is improved by the development of efficient and cost-effective electrocatalysts. This paves the way to obtain hydrogen generation on a large scale [30]. On one hand, the intrinsic activity of catalysts is significant, and on another hand, the construction of catalysts is also grave to obtaining impressive catalytic procedures in which the designing and synthesizing materials with long-term stability, exalting activity, and high selectivity are considered the main objective of electrocatalysis study. Because interfacial features have a direct influence on efficiency and selectivity, the interaction between catalyst structure and catalytic performance must be thoroughly investigated [31]. Totally, the following parameters can assess the accomplishment of HER electrocatalysts. These properties contain [32]:

1. the amount of catalytic active areas on the catalyst, which is characterized as the electrochemically active surface area (ECSA);
2. the voltage at each cathodic current which is known as the onset potential should be detected;
3. the extra potential vital to initiate a reaction in order to achieve a definite current density (j) that is called over potential (η);
4. The Tafel slope can be utilized to examine the rate-determining step because it is the slope between *eta* and $log|j|$;
5. the exchange current density (j_0), which is a critical criterion for determining catalytic efficiency;
6. the turnover frequency (TOF) that is defined as the number of the reacting molecules changed per active area per second;
7. the Faradic efficiency, which labels the efficiency of charge transmission in an electrochemical reaction; and
8. constancy, which is the main factor for assessing long-term catalyst performance.

[31])

Presently, noble metals and noble metal oxides are being extensively utilized as electrocatalysts because of their superior accomplishments in electrochemical reactions. Nevertheless, the usage is limited by restricted resources [31]. Despite the fact that Pt-based materials perform well in HER tests, their scarcity and enormous cost limit their usage on a broad scale [33,34]. Consequently, the HER should be involved in the expansion of catalysts that are cost-efficient, effective performance, and environmentally benign [35]. The HER should be scrutinized from the views of distinct transition-metal-based electrocatalysts, as well as carbides, sulfides, oxides, and nitrides [36–40]. Since nanomaterials have 2D unique structures and significant physical and electronic features, hotspot for nanocatalysts are the emergence of nanomaterials [29,41].

Currently, researchers are concentrating their efforts on modifying extremely active catalysts that are affordable, greatly efficient, earth-abundant, rough, and can replace expensive metal catalysts [36,42,43]. The advance of 2D electrocatalysts is subjected to the exploration of new 2D nanomaterials [44]. Remarking 2D materials for HER uses such as non-metal nanomaterials like graphene, graphitic carbon nitride (g-C_3N_4), black phosphorus, and transitional metal nanomaterials like dichalcogenides (TMDs), and other nanomaterials as heterostructure, MXene. Reducing the dimensionality of MXenes nanosheets leads to an expansion of active boundaries, while the creation of pore structures amplifies the active regions [251]. Mesoporous NiCo alloy nanoparticles of rGO (MNiCo/rGO) composites, for instance, may be synthesized by electroless deposition. A further example is how MoSSe/rGO has the least amount of overpotential and how a well-cyclic consistency characteristic was found for up to 1000 cycles. Graphitic carbon nitride (g-C_3N_4) composites with MoO_3 decorated Co_3O_4 nanorods (MoO_3/Co_3O_4/g-C_3N_4) are also produced by the hydrothermal process; these materials function as highly active and long-lasting electrocatalysts. Amorphous MoS_2/N-RGO nanocomposites were produced using a simple approach (plasma), and their exceptional HER activity suggests that they are very effective as catalysts for the enhancement of redox catalysis. Another case in point is 2D MoS_2, which shows promise as an active chemical for the HER because of its huge specific surface area and its resilience to abrasion. Mo_2CTx planes were catalytically active and showed HER activity modulation with a low overpotential [52,63,66,70,94]. The porous TM boride-Based is one of the emerging cost-effective and high-performance electrocatalysts for replacing precious Pt-based materials because porous TM B-Based possesses high surface area, electrical conductivity. For example a porous nanosheet catalyst, composed of Ni-substituted cobalt molybdenum boride (Ni-CMB), exhibited outstanding performance in the HER electrocatalyst within an alkaline environment, displaying a minimal overpotential of 69 mV at $10\,mA\,cm^{-2}$ [250,252].

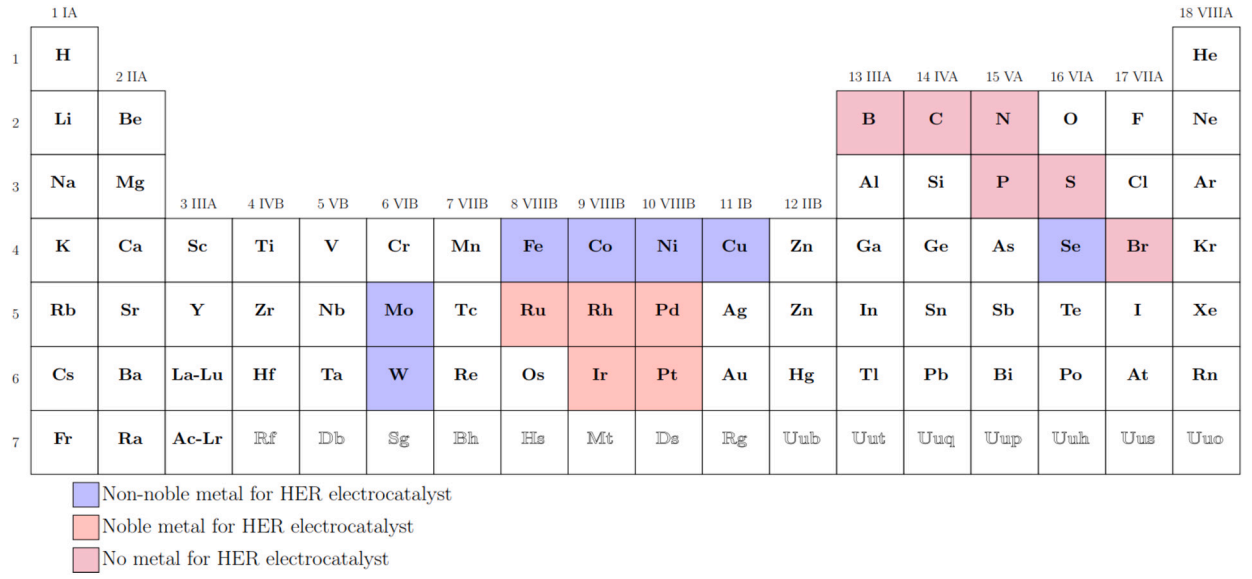

Fig. 2. Elements that are used for fabricating HER electrocatalysts.

The synthesis, characterization, functional processes, and HER performance of recent breakthroughs in 2D materials-based nanocomposites used in HER electrocatalysis are discussed in this review. And concentrate on effective strategies for enhancing HER electrocatalyst performance.

2. Nanocomposites of 2D materials for HER

The alterations in the physical and chemical features are donated to the atomic property, design, and structure of the 2D material [47]. In the meantime, the primary discovery of graphene, and 2D materials are extensively considered and applied in diverse fields. In recent years, it has been common practice to employ a large surface-to-volume ratio in few- or mono-layered structures of the 2D materials to store and convert energy [2]. 2D layered matters used as electrocatalysts in the water electrolysis for the creation of hydrogen have a far-reaching influence because of their enormous surface area, plentiful edge states, and variable electronic parameters [48–51]. Consequently, definite surface area, 2D structure, and electronic conductivity are the main points planned in terms of the attraction of 2D electrocatalysts. 2D matters hold the upmost surface to main part ratio. As a result, they retain numerous active areas for the adsorption of hydrogen. Moreover, the swift transfer of free electrons is assured by the atomically thin thickness. In addition, flaw engineering, composite construction, surface functionalization, and heteroatom doping can modify the open 2D planes. In fact, electrochemical HER enactment was enhanced by them [29] (Fig. 2).

In comparison to other nanomaterials, 2D nanomaterials hold a better consistently exposed crystal arrangement for electrocatalytic applications and obtain a larger concentration of unprotected electrocatalytically active areas with a definite electrocatalyst mass loading. Furthermore, the 2D nanomaterials' plain and well-organized molecular structure makes it easier to identify active areas from both theoretical and experimental outlooks. As 2D electrocatalysts are usually low-cost, they are highly regarded. Indeed, they are perfect substitutions for precious-metal-based electrocatalysts [6].

The current expansion of 2D materials in electrocatalytic research for HER is highlighted in this review. Fig. 4 illustrate that the insides comprise four parts [29,52]: 1. Metal-Free 2D Nanomaterials 2. TMDs, 3. Mxene, 4. Heterostructure.

2.1. *Metal-free* 2D *nanomaterials*

Significant strides have been made in creating 2D metal-free materials for efficient catalysis in several varieties of electrocatalytic methods. The sections below will provide valuable information about Graphene-based materials, graphitic carbon nitride, and black phosphorus.

2.1.1. *Graphene*

Novoselov (2004) used their well-known Scotch tape method and succeeded in their discovery. In consequence, graphene has become the utmost issue for researchers and it was remarkably heeded in several fields like electronics, electrocatalysis, and biomedical engineering [53]. Fig. 4(a) shows graphene, a two-dimensional carbon crystalline in which carbon atoms are organized in a hexagonal lattice that resembles a honeycomb. Because it is the most fundamental of carbon construction, graphene is acknowledged as the basic building block for other dimensional carbon substances, including 0D fullerenes, 1D CNTs, and 3D bulk graphite or different carbon structures [54]. Electrical conductivities ($106\,S\,cm^{-1}$) [55] and well thermal ($5000\,Wm^{-1}\,K^{-1}$) [56] and as well as exceptionally higher carrier mobility of $\backsim$ $15000\,cm^2\,V^{-1}\,s^{-1}$ and high modulus of elasticity (1.0 TPa) [57] at room temperature

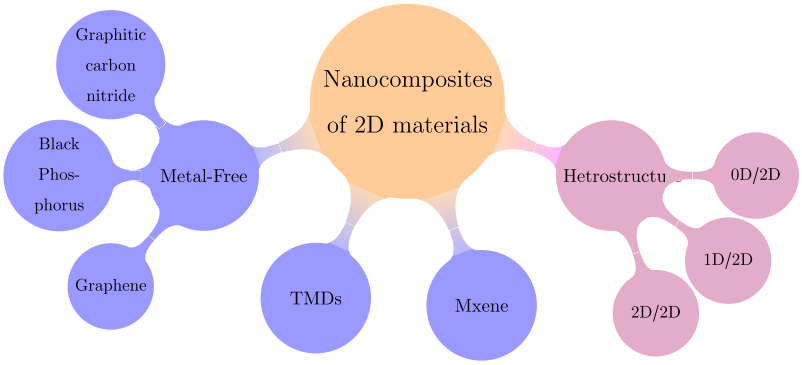

Fig. 3. Type of Nanocomposites of 2D materials for HER.

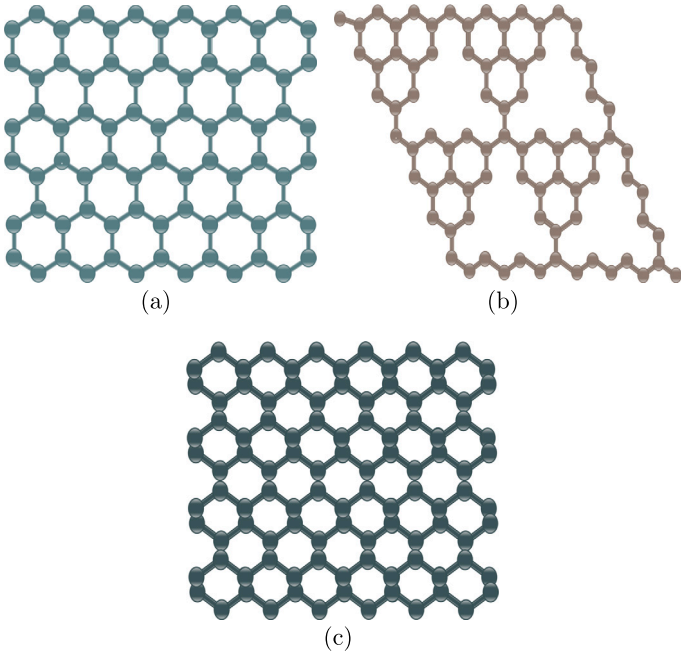

Fig. 4. (a) Graphene, (b) graphitic carbon nitride, and (c) black phosphorus molecular structures are shown schematically [6].

[58]. Theoretical surface area (2630 $m^2 g^{-1}$) [59], all have made researchers mull over graphene. Both challenges and opportunities are noticeable in graphene. Adsorption of chemical reaction intermediates is normally quite endothermic, assuming the delocalized *pi* bonding network of graphene. This subjects to poor inherent activity [60]. Subsequently, it is characterized by its distinctive specifications including an exclusive layered structure, unusual physical, chemical, and electronic features, in addition to a highly exposed active site. Hence, they are recognized as suitable to be applied in electrocatalytic uses [61,62].

A superficial and novel strategy was reported by Jing Dong et al. [63] They used an electroless deposition technique to synthesize mesoporous NiCo alloy nanoparticles of rGO (MNiCo/rGO) composites. Prominent HER electrocatalytic performances with an overpotential of 115 mV at 10 mA cm^{-2}, in addition to greater electrochemical constancy in alkaline solution were disclosed by the resultant ideal $MNi_{63}Co_{37}/rGO_5$ catalyst. In another example, Aruchamy Gowrisankar et al. [64] Studies on HER activity indicated that MoSSe/rGO displays the lowest overpotential of 285 mV at 10 mA cm^{-2}. Also, a well-cyclic constancy feature of up to 1000 cycles was detected. Graphene is an appealing stage for electrocatalytic utilization because of its huge specific surface area and strong electrical conductivity. Moreover, optimization engineering creation can simply alter graphene's electrical and surface properties [6,52].

2.1.2. Graphitic carbon nitride

According to the fact that a semiconductor, g-C_3N_4, has low electrical conductivity, it is not identified as a suitable candidate for HER [65]. Nevertheless, g-C_3N_4 marks worthy of thermal stability, appropriate electrical structure, and a reasonable cost. As a result, it has been identified as a maintainable material comprising "nitrogen pots" with many melon moieties. Henceforth, it is a

perfect potential site to modify molecular electronic structures [66–69]. Furthermore, g-C_3N_4 is sustained on a conductive substrate, allowing for the development of hybrid systems that are a prospective electrocatalyst for HER (Fig. 4(b)) [52].

For instance, Zheng et al. [66] combined it with doped graphene and discovered that loading of 33 wt% g-C_3N_4 outcome in the best HER activity, with a ∽ 240 mV overpotential [52]. Lee et al. [67] identified the similarities and the differences in the HER activity of graphene and g-C_3N_4 hybrids with P-doping and N-doping, respectively. The outcomes indicated that N-doping does not have the same good impact on HER performance as P-doping. Smith and colleagues [68] investigated numerous hybrids of g-C_3N_4@M-doped graphene (M = O, P, F, N, S, and B) using detailed DFT calculations. According to their findings, all graphene substrates had an increasing electron-withdrawing impact on the active layer of g-C_3N_4 by increasing the coverage of hydrogen atoms. As a result, the hydrogen atom intermediates, the probable effective treatment and the overpotential were constricted by the modulating. Mostly, such effects are improved by the p-doping of the substrate and subjected to better HER activity. Imtiaz Ahmed et al. [70] used a hydrothermal technique to create a g-C_3N_4 composites with MoO_3 adorned Co_3O_4 nanorods (MoO_3/Co_3O_4/g-C_3N_4), which works as an extremely active and durable electrocatalyst. This rod-shaped catalyst is extremely steady compared with its distinct component and produces the lowest overpotential of 125 mV at 10 mA cm^{-2} for HER in an acid condition.

2.1.3. Black phosphorus

Black phosphorus (BP) was created and its bulk state was the first time made in 1914 [71]. Black phosphorus is characterized by its semiconductor stacked with a crystalline construction; One phosphorus atom is covalently bonded with three others in Fig. 4(c), resulting in a wrinkled honeycomb structure in a layer. [72]. In fact, three electrons in the valance layer of P were engaged in three various bonds. Indeed, a band-gap is created, which may be regulated by varying the material thickness [73,74]. Lone pairs of electrons on the surface, sizable surface sites, and anisotropic electrical distinguish BP nanosheets as promising electrocatalysts [75,76]. The honeycomb structure of BP makes a significant contribution to exposing metal lone pair electrons. Because of the high activating impact of BP on metal atoms, HER activity can be improved [29].

Still, only a few studies have been done to mull over its application in electrocatalysis, which could be due to its weak electrical conductivity and low stability under electrocatalytic conditions [6]. Pumera and colleagues [75] initially confirmed that edge-plane BP presented a less start potential of (−0.35 V vs. SHE) than the basal-plane BP (−0.93 V vs. SHE), showing the edge-plane BP's likely catalytic activity. Even so, the electrochemical activity of other nonprecious electrocatalysts is much more than that of the black phosphorus edges. Phosphorene's HER activity can be boosted by doping or combining it with other active compounds. Metal-doped with phosphorene, such as BP(Mo), BP(Co), and BP(Ni), modifies the HER electrocatalyst, according to Yu et al. [77]. With an overpotential of 290 mV at 10 mA cm^{-2}, BP(Co) had the uppermost activity.

Lately, it was realized that when BP is combined with other materials in heterostructures; it has synergistic effects on the HER. In comparison to commercial Ni_2P, Luo and colleagues [78] developed a BP heterostructure and 0D-2D Ni_2P with a higher HER enactment in acidic conditions. The exceptional electrostatic enhancement of the mentioned hybrid was related to the BP gain surface area and the concentration of the adjusted charge transported between the BP interface and Ni_2P. To make the MoS_2-BP interfaces, Zeng and colleagues [79] placed MoS_2 flakes onto BP nanosheets together with phosphide. The value of overpotential (85 mV) at 10 mA cm^{-2} established the great HER activity resulted from transferring BP electron to MoS_2 and MoS_2-BP nanosheets. Another likely catalyst for HER is functionalizing phosphorene. Chen et al. [80] employed an exfoliation process that resulted in extremely thin BP nanosheets being formed. The subsequent NH_2-BP nanosheets demonstrated improved HER enactment with just an overpotential of 290 mV at 10 mA cm^{-2}. Wang et al. [81] used an optimum $\Delta G_H^{\star}$ of −0.02 eV, which is close to zero to link BP to Pt with This originates the solid Pt-P interface and noteworthy stability of Pt-P bonds. Ru metal was introduced to the BP-Pt catalyst by Li et al. [82] They found a considerable overpotential of 22 mV at 10 mA cm^{-2}, indicating considerably increased HER activity. In fact, it is considerably lower than the 77 mV of commercial Pt/C and the 64 mV of Pt NCs/BP. The hybrid interface holds the electrons. This causes an electron deficit in Ru. As a result, Ru atoms appear to be promising for electron-rich $H_2O^{\star}$ and $HO^{\star}$ classes.

2.2. TMDs(transition metal dichalcogenides)

TMDs, quickly developing material classes of layered 2D supercapacitor and water electrolyser electrode, quickly developing material classes of layered 2D supercapacitor and water electrolyser electrodes, which have been receiving a lot of interest in holding a good hydrophilic nature, high mechanical stability, and large specific surface area [83–85]. A graphene-like structure is detected in transition metal dichalcogenides (TMDs) [86–88]. From one hand, a strong chemical bonding of these layered materials makes them connect the in-plane atoms in each mono-layer. On the other hand, weak Van Der Waals (VDW) force stacked various layers. The final result is a type of bulk crystal [2,89]. While the overall crystal structure of a TMD monolayer has a sandwich-like form, bulk TMDs have monolayers that van der Waals forces stacked them. In this structure, one of the transition metal layer layers is located among chalcogen layers like a sandwich (X-M-X) with van der Waals exchanges. A strong ionic bond connects the M and the X [2,6,29,90]. TMDs need layer-dependent electronic structures, and appropriate feature ratio structures and there are several crystal-structured chemical phases of MX_2 TMDs. By utilizing various X-M-X layer stacking techniques, according to the crystal structures different phases of MX_2 TMDs can be recognized, including octahedral ($1T^0$), metallic octahedral (1T), and semiconducting (2H) phases.

1T, 1T', 2H, and 3R structures are numbers featuring out the stacking sequence of TMDs (Fig. 5). Specifically, the 3R (ABC sequence) or 2H (AB sequence) phase can be produced by stacking classification of 1H phase MX_2 [55]. In nature, the most thermodynamically steady one is the common semiconducting 2H phase MX_2. As an HER catalyst, MoS_2 has drawn a lot of interest. HER

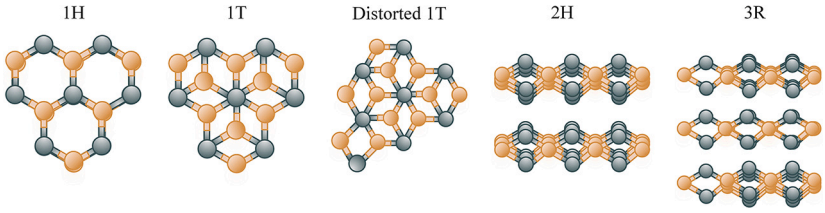

Fig. 5. Schematic of solvothermal MoS2/RGO heterostructure production.

can benefit from the Mo-edge of MoS_2 which has been reported. In contrast, specifications like higher electrical conductivity are the metallic features of the S-edge are sluggish, and electrocatalytic HER can take advantage of it [2,29,52,88,91,92].

Various crystal kinds and band gaps between the several TMDs provide different surface characteristics. Henceforth varied catalytic activities are diverse. The combination of both DFT calculations and experiments, the X sites at the layer margins have been identified for electrocatalytic applications as the catalytically active sites rather than the sites in the basal plane [6,45,46]. This finding led to the development of many techniques to find additional active edge spots. Indeed, with these methods, TMDs' electrocatalytic performance is improved [38,93,94]. Hence, materials can be easily changed into a small number of single layers, which have higher features to bulk materials in this size range. The lessening in the thickness of 2D-TMDs are usually subject to improved stability, conductivity and strength [49,95]. Having a thin layer for the 2D-TMDs enhances their several uses, such as gas sensors, solar cells, and transistors [88,96,97]. Furthermore, due to the electronic structure of transition metals, they have high sensitivity, and they are practiced in catalysts [86]. Many of the new investigations show that the indirect bandgap of 2D-TMDs can change to a direct bandgap as their thickness is reduced to a few atomic layers. It is subject to important improvement in optical specifications, therefore, photocatalysis takes advantage of them [98]. Additionally, the valance and conduction band of 2D-TMDs are coped with the decrease and water oxidation potential. Indeed, it shows that the water-splitting reaction can be catalyzed by them [88,99].

TMDs, particularly 2D layered transition metal dichalcogenides(2D-TMDs), have large surface areas, which allow for the creation of more exposed catalytically active sites due to their atomically thin structure. They have an easy preparation method and also can be done at a wide pH value for HER, which means having high chemical stability. From one hand, the raw materials are not costly. On the other hand, they are appropriate to be practiced for industrial uses in comparison with noble metal-based catalysts [86,100]. Moreover, layered TMDs can be advanced for creating a paved way to make heterostructures with higher HER activity. Although despite weak activities have weak activities, they are catalytically active toward HER even if no alteration is detected [52,101–103]. In comparison with graphene, TMDs have several gains regarding catalytic features. Initially, graphene is slow compared to TMDs' inherent activity for electrocatalytic processes. Then, TMDs have a variety of metallic or semiconducting phases, and they can display various types. Lastly, TMDs are maintained as more doping option in comparison with graphene because both nonmetal atoms and transition metal atoms can be doped into TMD lattices. Within the past few years, essential steps have been taken owing to these gains [31,51,104].

Their structure, such as 1T, 2H, 3R, and 1T' contribute to specifying the conductivity of 2D-TMDs. The low value and indirect bandgap contribute to measure and calculate the bandgap of TMDs. As a result, effective charge-carrier formation and recombination are challenging. Indeed, it was found that the bulk 2D-TMD materials can be considered as actual catalysts through which the hydrodesulfurization can be done [88,105–108]. As TMD nanosheets have exclusive features, like more active sites, large specific surface area, controllable 2H-to-1T phase transformation, and adaptable bandgap and band position, so much research has been focused on this issue. A number of studies have been conducted to consider the hybridization of TMDs with different functional nanomaterials (metal oxides, semiconductors, carbon materials, metals) so that the gains of TMDs for HERs can be efficiently put into practice. Nevertheless, structure engineering affects the development of the electrocatalytic activity of TMDs for HER. However, it cannot be compared to noble-metal catalysts, particularly the commencement overpotential and recent density as well as the noble metals. Outstanding noble metals, outstanding HER performance is expected to reveal only 2D stacked MX_2 materials with strong conductivity. It can also be identified by the other MX_2 nanostructures that have metallic borders [52,90].

The strong alterations in electronic structure led to different band gaps of monolayer and bulk MoS_2. Additionally, heteroatoms have the ability to activate either the M or X sites doped in the basal plane. Both metallic atom and non-metallic atom doping are effective for enhancing the electrocatalytic activity of TMDs in HER, according to DFT calculations and experiments [6,109,110]. In molybdenum chalcogenides, Mo is coordinated by six chalcogenide atoms in the shape of an octahedron or triangular prism. The tetragonal symmetry by 1T MoS_2, whereas 2H and 3R have hexagonal phases. The most well-known structure contains triangular prism coordination. The Mo in the 1T phase, the only metallic phase with high conductivity, is octahedrally synchronized. The 3R phase is quite similar to the 2H phase.

Although their bulk counterparts are not extremely active toward HER, semiconductor TMDs like 2H-MoS_2 have been proven to be. MoS_2 has been used for electrochemical hydrogen production since the 1970s. According to the studies, MoS_2 can be a potential replacement for commercial Pt/C as HER catalysts. The first studies on the structure of MoS_2 were started by Frindt and group (1966) for several years [31]. MoS_2 is a member of the 2D HER electrocatalyst group and also, the most typical example of TMD. Remarkably, several research has been carried out in this regard. The research has indicated that there are deficiencies in its edges, in the intrinsic activity of 2H-MoS_2. In case they are zig-zag, they are metallic. IJ.C. Bennett et al. (1977) considered the hydrogen evaluation reaction performance of bulk MoS_2, and it revealed a reduction of activity through a significant Tafel slope of 692 mV dec^{-1} and a high onset potential of nearly -0.09 V vs. RHE [46,111–113].

MoS_2 is identified as a usual semiconductor that its low conductivity is low. Consequently, pairing MoS_2 with a highly conductive support is grave so that its catalytic activity is improved. From the theoretical and experimental views, MoS_2 for HER catalysis has been confirmed. Since the bulk MoS_2 revealed meager activity, it has not been reflected as a likely HER catalyst. Furthermore, MoS_2 is less expensive and highly plentiful, and its light absorption less expensive, highly plentiful, its light absorption capacity is suitable. Finally, it can be simply coped with bandgap compared with graphene [45,90,114].

Hinnemann et al. (2005) discovered that the hydrogen coverage of the Mo edge of MoS_2 has a $\Delta GH^{\star}$ of very close to the ideal value. The Mo with a 50% sulfur content was determined to have the best edge surface [29,46,115,116]. Additionally, MoS_2/graphite nanoparticles were active toward the HER catalyst, according to Hinnemann et al., with an overpotential between 0.1 and 0.2 V. Additionally, using the DFT method, the free energy of the H adsorption is theoretically calculated. As a result of the DFT, the active sites for electrocatalysis include Mo-edge and S-edge. It has been proved that the edge sites of MoS_2 have metallic electronic states, whereas the basal plane is not like this. Additionally, experimental findings demonstrating that the activity is proportional to the number of edges rather than the surface area. Several chemical and, or physical plans were developed to uncover and, or spread their active edge sites when the active sites for MoS_2 materials were characterized [6,45,46,117,118].

Dai Zhang et al. [119] used a simple method (plasma) for as efficient and stable HER catalysts to amorphous MoS_2/N-RGO nanocomposites, indicating outstanding HER activity fabricated amorphous MoS_2/N-RGO nanocomposites. The synergistic consequence among the intrinsically high activity, plentiful active sites, and high conductivity are identified as the main sources of the improved HER performance. The present research paves a new direction design of several amorphous transition metal chalcogenide /G nanocomposites as stable, low-price, and efficient catalysts for electrochemical hydrogen generation.

Badiger et al. [120] have synthesized $MoS_2/MnMoO_4$ composite catalysts by a one-step hydrothermal procedure, utilizing different Mo:Mn ratios. The synthesized nanocomposite of $MoS_2/MnMoO_4$ with an optimized Mo:Mn ratio of 1:2.5 had a low overpotential of −153 mV vs. the RHE and the Tafel slope was measured to be 80 mV dec^{-1} at a current density of 10 mA.cm^{-2}. Furthermore, a remarkable level of stability, stability of 100 hours, was attained in a 0.5M H_2SO_4 H2SO4 electrolyte at the current density of 10mA.cm^{-2}.

Together with MoS_2, $MoSe_2$ also has a high inherent electrical conductivity, even more than $MoSe_2$, as a result of Se's more metallic characteristics. The Gibbs free energy for hydrogen adsorption onto the edges of $MoSe_2$ was also calculated theoretically to be lower than that of MoS_2, resulting in greater hydrogen adsorption coverage. Generally, their catalytic performance is remarkably affected by the phase of 2D TMDs. As aforementioned, the thermodynamically stable 2H-$MoSe_2$ does not disclose much higher reactivity as 1T-MoS_2 does [121]. $MoSe_2$ exhibits outstanding HER performance, similar to MoS_2. Because of its higher conductivity and significantly more predominant active area, 1T-$MoSe_2$ is superior to 2H-$MoSe_2$. In contrast to MoS_2 and $MoSe_2$, $MoTe_2$ has not yet drawn much interest from researchers. Most research to date has been on using bulk $MoTe_2$ single crystals or mechanically exfoliated nanosheets in HER. The low active sites and conductivity of $MoTe_2$ can be attributed to the HER, its activity of $MoTe_2$ is still poor (10 > 300 mv) [29,52,122–125].

Even though, the conductivity of semiconducting TMDs is not as good as that of metallic TMDs. It paves the way for faster electron transportation and electrode kinetics. Indeed, their potential is demonstrated as electrocatalysts. An actual way is through direct synthesis by means of simple methods so as to find metallic TMD-based electrocatalysts. Additionally, air and water affect metallic TMDs, and so, special their stability should be remarked. In general, metallic TMDs have been applied in electrocatalysis. Thus, they hold plentiful active sites on both edges. In order to achieve enhanced electrocatalytic performances, and basal planes need to develop more [31]. Metallic TMDs display a low charge-transfer resistance, which can help to improve the hydrogen evaluation reaction performance. WSe_2, $MoSe_2$, $MoS_2(1-x)Se_2x$, WS_2, VS_2, VSe_2, CoS_2, WTe_2, TaS_2, $PdTe_2$, and PtTe are among TMD materials that can be utilized as an active electrocatalyst for HER [2].

In the meantime, a significant number of articles have concentrated on the relationship between the catalytic activity and the modification of the electronic structure, like band structures and orbital structures. However, from the perspective of modulation techniques for TMDs, it still needs sorting and evaluation. To improve the catalytic performance of TMDs, great progress has been made to expose more active sites; nonetheless, these hard works are usually supplemented by losses in electrical conductivity and durability. Until now, several approaches like electronic inter-facial engineering, orbital directing, and structure modulation have been devoted and important processes have been attained in the past years. Gas management on the electrode, as well as the development of highly active catalysts, is essential for industrial applications to obtain high reaction rates at actual operating voltages [31,117,126].

2.3. Heterostructure

From the views of energy conversion and storage, researchers have focused on the design of heterostructures. Since heterostructure materials synergistically affect the interfaces among the multiple components. The electrochemical performance of the heterostructure materials is greater than that the single one [127]. The existence of interfaces is subject to enhance of electronic configuration by the interfacial electron transfer in the heterostructures. Hetero-structured electrocatalysts can reach the optimization of ΔG_H, development of electronic conductivity, and disclosure of more active sites, therefore resulting in the important improvement of HER catalytic activity [92,128,129]. The increased catalytic activity of electrocatalysts has been achieved by modifying the morphology and structure of the developed electrocatalysts. To increase the catalytic activity of electrocatalysts, zero-dimension (0D) such as nanoclusters and nanoparticles, one-dimensional (1D) such as nanorods, nanoribbons, nanotubes, nanowires, and nanofibers, and two dimensional (2D) such as nanoflakes, nanoplates, and nanosheets morphologies are the three divisions of such materials [130].

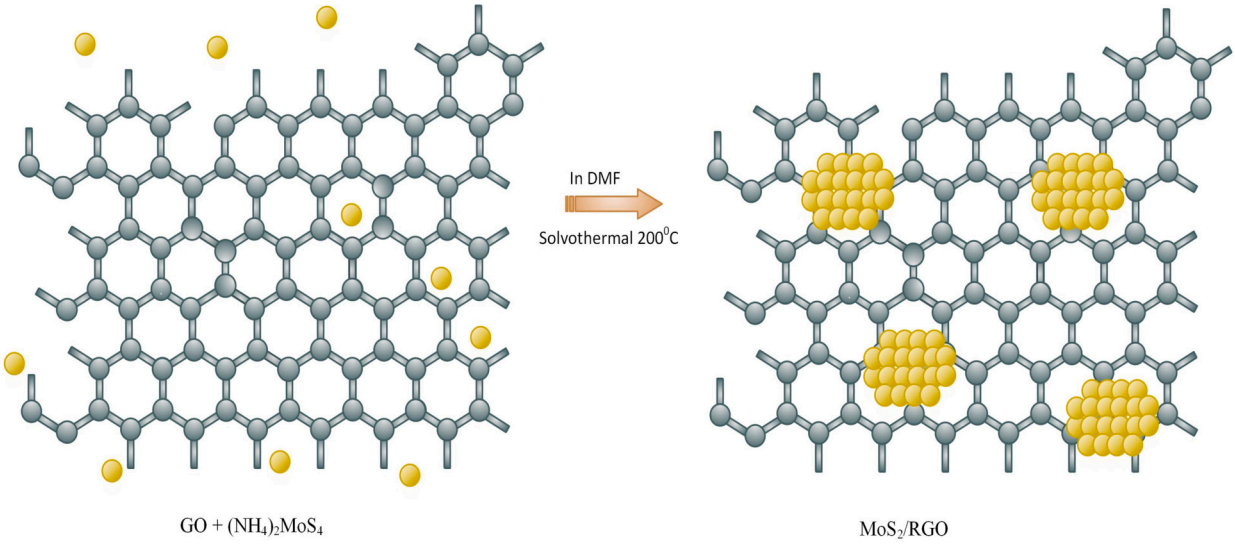

Fig. 6. Schematic of solvothermal MoS2/RGO heterostructure production.

On the whole, compared with the 0D, better electrochemical properties have resulted from 1D and 2D nanostructures. Active materials having 1D or 2D nanostructures are consequently drawn to with greater intent. They have received a great deal of attention as highly effective water splitting electrocatalysts [131].

The performance of 2D materials as catalysts is largely determined by interfacial structures like heterostructures, which can not only overcome the inherent drawbacks of each material but also develop novel features as a result of interfacial effects. Accordingly, the fabrication and design of heterostructures is a successful way to achieve excellent electrocatalytic performances since they are composed of 0D, 1D, and 2D materials. In order to develop high-performance electrocatalysts, there has been an increase in interest in the synthesis of 2D material-based heterostructures in recent years. Regarding 2D materials, including 0D/2D, 1D/2D, and 2D/2D heterostructures, heterostructures will be mulled over in the subsequent sections [31].

2.3.1. Heterostructure 0D/2D

Nanoparticles, clusters, Single atoms, and quantum dots are examples of 0D materials, which are substances with sizes in all three dimensions of less than 100 nm. As these materials are dealt with high active sites and catalytic activities, they are exceedingly used as catalysts. Nevertheless, 0D materials hold low electrical conductivities. Indeed, if they are merely used, they get inappropriate for electrocatalysis. Dispersing 0D materials on supports with high conductivity and large surface areas is an efficient way to overcome this problem. For instance, Li et al. [94] in situ grew MoS_2 nanoparticles onto RGO by a one-step solvothermal method. They reported that since 0D MoS_2 nanoparticles in comparison with 2D MoS_2 nanosheets have more plentiful S edge sites, their mixture with RGO can expressively endorse electrocatalytic activities. Additionally, using the in situ carbonization of MoS_2, Qiangmin Yu et al. synthesized a 0D/2D heterostructure electrocatalyst based on Mo_2C nanoparticles and MoS2 nanosheets (MoS_2/Mo_2C). Here, it was discovered that the resulting MoS_2/Mo_2C heterostructure had rough surfaces both at the micro- and nanoscale and showed suitable electrocatalytic activity (Fig. 6).

The enhanced interfacial mass transfer and the surface oxygen created on Mo_2C during HER were the reasons for the superior performance of this MoS_2/Mo_2C heterostructure. Now, the resulting heterostructure electrocatalyst was figured out to possess highly indicated active sites and coarse surfaces both at the nanoscale and microscale. Also, it established appropriate electrocatalytic activity. Here, increased surface oxygen that developed on Mo_2C and interfacial mass transfer during HER was given credit for the superior performance of this MoS_2/Mo_2C heterostructure. Further research into actual industrial use should be done in light of these findings. Generally, 0D/2D heterostructures show promise in HER electrocatalysts, but further advancements are required due to their low long-term durability. [31,132].

2.3.2. Heterostructure 1D/2D

Materials with less than 100 nm sizes in two dimensions out of three are identified as 1D materials, such as Nanotubes, nanofibers, nanowires, etc. 1D materials with good conductivities are detected as unlike 0D materials, and they are able to be used as catalytic sites and also as conductive substrates. Furthermore, sized pores for gas diffusion or mass transfer can be optimally made by the construction of a 1D/2D heterostructure. To prepare high-performance electrocatalysts and optimize their microstructures and features, it is essential to put together several 1D/2D heterostructures [133,134].

Through indicating enhancing mass transfer mechanisms and more active sites, 1D/2D nanostructures can considerably improve electrocatalyst efficiency. These 1D/2D nanostructures have significant surface flaws and high surface areas, both of which are advantageous for surface reactions. Additionally, the numerous opening spaces between the adjacent 1D/2D nanostructures will promote improved electrolyte infiltration and bubble release. It is simple to create materials based on 1D/2D nanostructures by

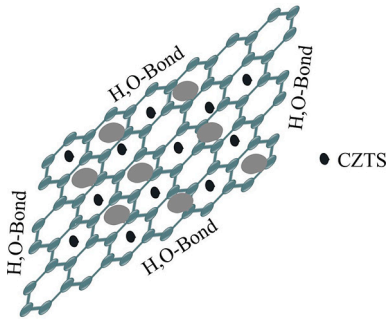

Fig. 7. CZTS/MoS_2-rGO heterostructure electrocatalyst.

growing them directly on the surface of conductive substrates, which is advantageous for effective charge transfer. To improve the catalytic activity of electrocatalysts water splitting, it is advantageous to construct 1D and 2D nanostructured self-supported electrocatalysts [131,135,136]. Using synergistic influences, catalytic enactment can be enhanced by the 1D/2D heterostructures. However, these 1D/2D hetero-structured catalysts cannot be used as self-supporting electrodes in a direct manner. Self-supporting electrodes can be successfully used, unlike substrate-supported electrodes. Through the layer-by-layer construction of graphene and CNTs, Chen et al. [137] fabricated a graphene-CNT hydrogel sheet electrocatalyst doped with both N and O (NG-CNT), which could employed as a self-supporting electrode for electrocatalysis. The structure of self-supporting electrodes can be improved. At this point, as graphene and CNTs have strong interactions, they were put together in a comparatively well-arranged manner in the hydrogel film. Researchers believe that charge transport may be facilitated and durability during catalytic processes can be enhanced.

The CZTS/MoS_2-rGO heterostructure electrocatalyst (Fig. 7) was synthesized by Renuka V. Digraskar et al. via a one-step sonochemical method. The CZTS/MoS_2-rGO exhibits an exceptional HER performance with an onset potential as low as 50 mV vs. RHE at 10 mA cm^{-2} accompanied by a Tafel slope of 68 mV dec^{-1} and an exchange current density of 962 mA cm^{-2}. When the CZTS is paired with MoS_2-rGO, the CZTS has demonstrated a synergistic effect that makes the heterostructure electrocatalyst a superior hydrogen evolution electrocatalytic system with long-term durability [31,138].

2.3.3. Heterostructure 2D/2D

2D/2D heterostructures have been confirmed as a type of adaptable nanomaterials. Further, they are suitable to address the issues related to the current of energy. It is essential to have consistent synthesis with strictly controllable chemical compositions so that several uses of 2D/2D heterostructures are obtained. Some reviews have pointed out the synthesis and fabrication of 2D based materials [119,139–142]. According to the fact that 2D materials have unique features, they indicate decent catalytic enactments. Nevertheless, these catalytic activities since these catalytic activities have severe restacking issues, they are not capable of challenging with noble metal-based catalysts. At this time, the Van Der Waals heterostructures came into existence. They contributed to provide new methods in order to realize the full likelihood of 2D materials in which two different 2D materials are used to make 2D/2D heterostructures so that the individual faintness and reduction interfacial contact resistances are compensated. This subjects to develop catalytic performances [143–147]. The chief gains of 2D/2D heterostructures for catalysis comprise:

1. indicate rich active sites resulting from interfacial defects and surface area.
2. fast charge transport of interfacial.
3. band twisting for developed red-ox fitness.
4. the enhancement in adsorption energy of intermediates for dropped reaction obstacles.

Therefore, the 2D/2D heterostructures have massive space to moderate the electrical structure to enhance the rate shaping steps of the catalysis reaction [119,148]. Yang et al. [149] used a hydrothermal reaction and they could synthesize a 2D WS_2 and 2D RGO heterostructure. Indeed, they stated decent performances for HER, using it, the researchers could improve charge transfer kinetics as there is near interaction between the two constituents notwithstanding being synthesized in solution with little control over their permeability and construction. Correspondingly, Tang et al. [150] made a vdW(van der Waals) heterostructure composed of graphene and nitrogen-doped MoS_2 using mesoporous magnesia as a template.

First, a porous graphene skeleton was created using CVD, and then Mo/S/N sources were added to grow nitrogen-doped MoS_2 nanosheets onto the graphene skeleton (G@N-MoS_2). The G@N-MoS_2 catalyst provided optimal HER activities with a low overpotential of 243 mV at a current density of 10 mA cm^{-2} in acidic media and an onset potential that was 100 mV higher than corresponding counterparts in alkaline media, according to the researchers who also looked into HER performances in this study. N-MoS_2 was found to have higher activities than pure MoS_2, they reported [131] (Fig. 8).

Some advancements have been made, including a reduced band gap, in considering the fact that nitrogen doping could effectively affect the electrical structures of MoS_2. Another reason is that the adsorption energy can be optimized by the interfacial contact between graphene and MoS_2. The next cause is that the active site exposure and proton transport can be improved by the subsequent 3D mesoporous structures. In addition to speeding up charge transfer, the inserted electrons from the gold substrate can also enhance the adsorption of hydrogen reactants onto the basal planes of 2H MoS_2, leading to improved electrocatalytic performances of 2H

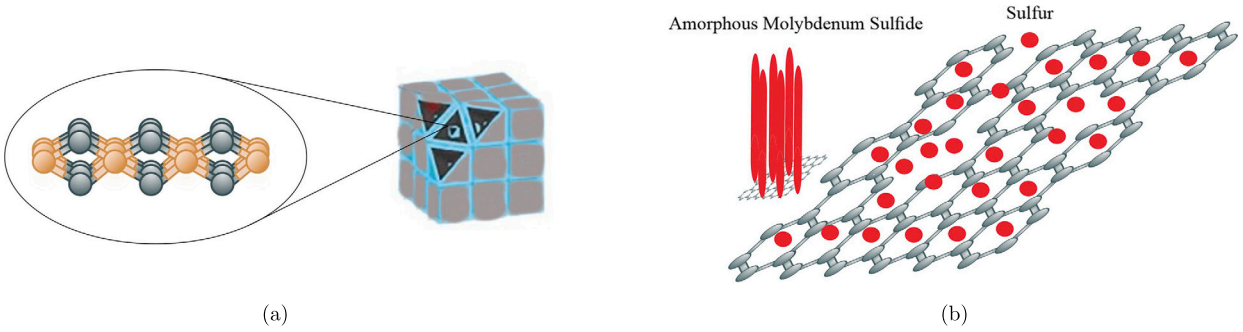

Fig. 8. (a) 2D/2D heterostructures, and (b) 3DMoSx/NCNT for electrocatalysis.

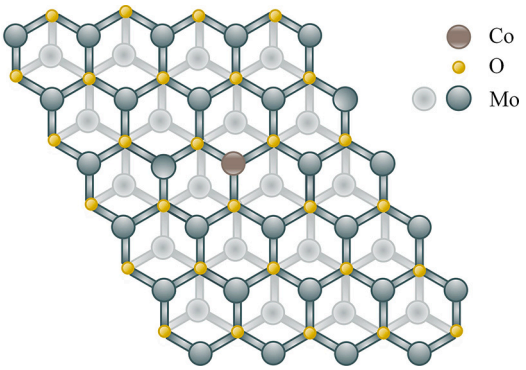

Fig. 9. Mo_2CO_2:Co model structure used for DFT calculations.

MoS_2. Interestingly, investigations revealed that the creation of 2D/2D heterostructures can significantly improve the catalytic performance of 2D materials, setting the stage for the expansion of 2D materials in electrocatalytic applications [131,151,152].

2.4. Mxene

So far, 30 different MXenes have been produced by selection etching *III*A or *IV*A group atomic layers from metal-ceramic phase MAX substance-laminar TMD such as carbonitride, nitride, and carbide [153]. The A-group element can be easily fixed from a chemical aspect since the M-X bond has a larger binding energy than the M-A bond. As a result, they produce inadequately attached multilaminar MXenes that many processing methods such as sonication can exfoliate [154]. Fluoride-containing and fluoride-free etching procedures are available. The etching and exfoliation are subject to the surface functionalization of MXenes with plentiful O and OH. The hydrophilic nature is increased by F groups. Furthermore, their top electrical and metallic conductivities (6000 – 8000 S cm^{-1}) are improved, as well as their huge surface area and strong interfacial contact. The ingredients of etchants in fluoride-containing techniques are HF, a combination of HCl, or NH_4HF_2 and LiF [155–157]. Fluoride-free techniques make use of the NaOH solution for the molten salt ways, alkaline etching approaches, and the mixture of NH_4Cl and $C_4H_{13}NO$ as an electrolyte for the electrochemical etching approaches [158]. MXenes with higher catalytic active sites and better electrical conductivity are prospective substitutes for 2D non-metal alkenes. In electrochemical HER, TMDs serve the same [159]. The distinct catalytic properties on the basal planes, including outstanding flexibility, good hydrophilicity, 2D morphology, and laminar structures are used to embrace a new and interesting group of 2D transition metal MXene as a promising HER electrocatalyst [2,158].

Hans et al. predicted the impact of the vacancy on $W_{1.33}C$'s HER accomplishment. Protons travel to vacancies and transform to hydrogen atoms under a metastable situation at high cathodic potentials, they discovered [160]. Gogotsi's group [40] conducted a combined experimental and theoretical study of MXenes as HER electrocatalysts, discovering that the basic planes of Mo_2CTx were catalytic activity and modulated HER activity with a modest overpotential of 283 mV to obtain 10 mA cm^{-2}. To identify the inherent cause of Mo_2CTx: increased Co's electrocatalytic efficiency, DFT calculations were done on a model Mo_2CO_2 structure with and without Mo substitution. According to calculations. As illustrated in Fig. 9, a low Co content in Mo_2CTx will impact catalyst performance. Functionalization of surfaces, like hydrogenation and oxidation, can boost the MXenes catalyst's reaction to the intermediate active adsorption capacity. Su et al. discovered oxygen-functionalized, extremely thin Ti_3C_2Tx nanosheets with accordion-like packing [161,162]. In addition, improved HER performance was shown by hydrogenated MXenes as the density of enclosed H atoms on the surface of catalysts was enhanced, giving diminished overpotential and near-zero $\Delta G_H^{\star}$ [163]. The quantity of conductivity and active sites can be also increased by the MXenes coupled with other materials. Zhang et al. [164] created a extremely conductive $MoSe_2$ heterostructure with oxygen-expired Ti_3C_2. Moreover, Lu and colleagues invented a Mo_2C/graphene unified structure with top crystal build and good electrical coupling that may be employed as a HER charge relay device [165]. Specifically,

the 11N-Ti_2CTx variant possesses a greater degree of nitridation demonstrating remarkable performance in the Hydrogen Evolution Reaction. It displayed a minimal overpotential of 215 mV at 10 mA cm^{-2} and a low Tafel slope of 67 mV dec^{-1} when tested in a 0.5 M H_2SO_4 solution, surpassing the performance of the original, pristine Ti_2CTx [251].

V. Thirumal et al. investigated 2D heterostructured reduced graphene oxides and Ti_3C_2Tx materials for electrocatalyst using simple hydrothermal procedures. Compared to bulk-reduced graphene oxides and MXene, the as-prepared MX@RG composite materials had higher HER activity. MX, RG, and MX@RG composite electrocatalysts have been developed. The MX, RG, and MX@RG composite electrocatalysts were found to have overpotential values of 220 mV, 193 mV, and 121 mV, respectively, at 10 mA cm^{-2} cathodic on set. Merging the other transition metals with MXenes can be used as perfect substrates, Heterostructures will be a sage and likely planned movement in multi-component catalyst systems to produce a sturdy MXene-based hybrid [52].

3. Summary of nanocomposites of 2D materials for HER

An overview of important advances in electrocatalysts is given in the Table 1 below:

Table 1
Comparing HER Electrocatalysts Recently Reported.

Type	Catalyst	Electrolyte	Morphology	Overpotential (at10 mA cm^{-2})	Tafel slope	Ref
TMD	C−MoS_2	1M KOH	Nanosheets	45		[117]
	Rh−MoS_2	0.5M H_2SO_4	Nanosheets	67		[117]
	2H−MoS_2	H_2SO_4 (PH = 0.2)	Monolayer	170		[117]
	1T−$MoSe_2$		Nanosheets	152		[166,167]
	MoS_2/Gr	0.5M H_2SO_4		110	67.4	[30]
	MoS_2/N−RGO			168	32	[119]
	MoS_2−P·SWCNT		Hetero-nanotubes	80		[168]
	MoS_2−BP		Heterostructure	85	209	[92,169]
	WS_2/Ni_5P_4−Ni_2P		Nanohybrid	94	74	[4]
Graphene	$MNi_{63}Co_{37}$/rGO			115	45	[63]
	MoSSe/rGO			258	98	[64]
	Gr doped with Ni (5wt%)		Mesoporous	239	109	
	defective Gr	0.5M H_2SO_4		150	55	[4]
	plasma-etched 3D N-doped Gr			128	66	[4]
Graphitic	g−C_3N_4 at 33 wt%	0.5M H_2SO_4		240	52	[66]
	Co_3O_4/MoO_3/g−C_3N_4			125		[67]
Black Phosphorus	BP(Co)			290	107	[52]
	Ni_2P@BP		Heterostructure	107		[52]
	NH_2−BP		Nanosheets	290	63	[52]
	MoS_2−BP			85		[52]
Heterostructure	CZTS/MoS_2−rGO		Heterostructure	50	68	[138]
	G@N−MoS_2	Alkaline media	Heterostructure	143		[170]
	G@N−MoS_2	Acidic Media		243		
Mxene	Ti_3C_2Tx/Rgo			121		[171]
	Mo_2CTx			609		[52]
	Ti_3C_2Tx	0.5M H_2SO_4	Nanosheets	190		[29]
	MoS_2/Ti_3C_2−MXene@C		Hierarchical	135		
	Mo_2TiC_2Tx−PtSA			77		

4. Optimization structure

Since 2D nanomaterials can be adjusted and consistently exposed to lattice planes, distinctive physicochemical features, and electronic structures, they have been widely practiced in electrocatalysts. The extrinsic and essential activities of electrocatalysts are considerably affected by these special specifications. Aside from the modifiable catalytic activities, 2D nanomaterials are able to serve as useful supports due to their large definite surface areas and strength for the growth of hybrid electrocatalysts. Most pure 2D electrocatalysts are sluggish or don't have enough catalytic activity owing to their low electrical conductivity, weak inherent activity, and low density of active sites [46,65,172]. Nevertheless, several methods as well as strain engineering, defect formation engineering, heteroatom doping, ion intercalation, defect constructing, and interfacial interaction, as shown, can enhance the catalytic

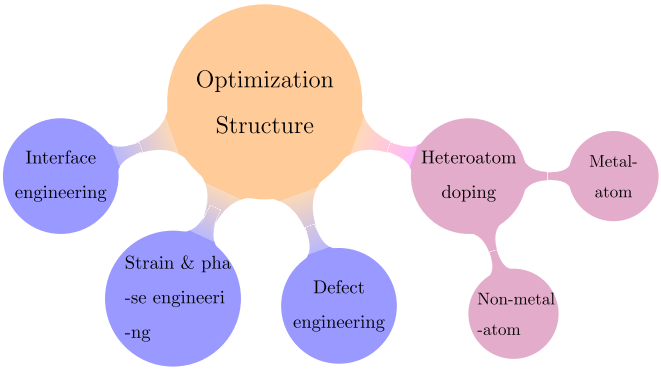

Fig. 10. Type of Optimization Structure.

performance of 2D materials through diverse mechanisms [31]. The purpose of these optimizations is to set the surface/interface features and electronic structures connected with H_2 adsorption free energy and transfer kinetics of charge/mass, which indeed influence catalytic kinetics [166] (Fig. 10).

In this part, different strategies for designing electrocatalysts of 2D nanomaterial-based are reported.

4.1. Interface engineering

It is necessary to construct highly active catalysts with definite heterointerface engineering. The surface/interface features and electronic structures of 2D can be moderated by the engineering hetero-interface using different components. Which can have an important role in the enhancement of electrocatalytic activities in 2D nanomaterial. [103,173]. Interface engineering is classified into two main types: synergistic interaction and heterostructure engineering, which are always related to each other. Synergistic interaction is actually the physical contact of two materials that are limited by the transport of electrons, while Heterostructure engineering usually includes intricate chemical bonding among two different materials [65]. Interface engineering can be an effective way to synthesize electrocatalysts with high-performance unique physical/chemical features.

Despite 2D TMD-based heterostructures, metal-free 2D materials can be em-practiced so that heterostructures are built. For enhanced HER kinetics, Qiao et al. coupled g-C_3N_4 with N-doped graphene (g−C_3N_4@NG) serve as a heterostructured catalyst [65]. Putting the DFT calculations and experimental findings together, they realized that the synergistic consequences of heterostructures are responsible for the promoted HER activities. The absorption of hydrogen results from the g-C_3N_4 and the electron transfer ability is increased by N-doped graphene. Next, they used porous C_3N_4 nanolayers as the HER electrocatalyst to make N-doped graphene nanosheets with [66].

Special HER performance with lower onset potential, greater exchange current density, and enhanced stability in comparison with commercial Pt/C are obtained by the heterostructured electrocatalyst. The synergistic effect of heterostructures affects the remarkable HER enactment, where porous C_3N_4 the exposed active sites are maintained by provides and more electron channels are provided by 3D conductive graphene network [166].

Also, dispersing atoms of metal on the 2D substrates can be a promising method to regulate the catalytic activity from the atomic point of view, since the distinct atomic interface between single metal sites and 2D platforms can reach the accurate inflection of the local direction environment and electronic structures thoroughly connected by the catalytic kinetics [174]. For instance, Qi et al. synthesized single cobalt atoms bonded to the slanted 1T MoS_2 nanosheets (SA Co−D 1T MoS_2) as an effective electrocatalyst for hydrogen evolution reaction from DFT calculations, bringing high activity and lasting durability [175]. Zhang et al. synthesized single-atom Pt and utilized MXene as support for boosting the electrocatalytic HER activity [176]. Several anchoring sites for immobilizing Pt active centers are maintained by the altered Mo_2TiC_2Tx nanosheets with plentiful Mo vacancies from Pt-C and Pt-O atomic interfaces are developed. A remarkable HER activity and high stability are displayed by the improved catalyst. Based on the DFT calculations, improved the ability of electron donor and greater electronic energy levels than bare $Mo_2TiC_2O_2$, are presented by the $Mo_2TiC_2O_2$−PtSA. Finally, an optimal hydrogen adsorption free energy is obtained [166].

4.2. Defect engineering

Engineering defects and vacancy are considered an appropriate method for modifying the physicochemical features and electronic structures of 2D nanomaterial-based electrocatalysts. Further, it is able to intensely influence ΔG_H and upsurge active sites. Indeed, the catalytic activity of HER electrocatalyst is enhanced [92,177–180,249] (Fig. 11).

For example, Xie et al. used an extensive method to present imperfections on the MoS_2 surface and produce more active edges [181]. Remarking on the HRTEM result, on one hand, atomic arrays on the basal planes have a disordered formation which is subject to the crack of the basal planes. On the other hand, more additional edges are made Ajayan's group applied H_2 treatment and O_2 plasma exposure to construct plentiful flaws in the monolayer of MoS_2 [182]. The quantity of the exposed active edge sites is considerably improved by the formation of these defects. In consequence, HER kinetics are significantly improved Additionally, the

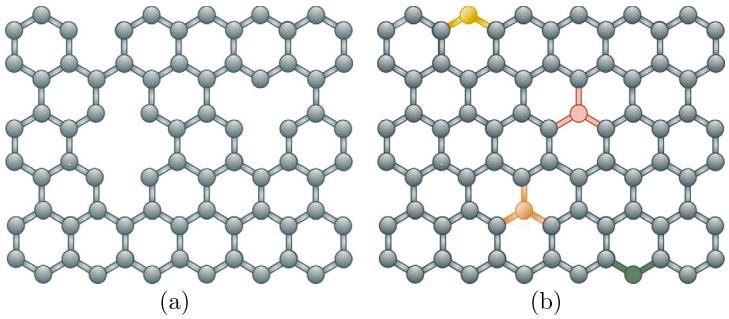

Fig. 11. Tuning the catalytic activity and properties of 2D materials by various methods, including (a) defect engineering, (b) heteroatom doping [31].

constructed defects are subject to lattice strains. The 2D materials band gaps are also modified. Li's group presented S vacancies and strains in the mono-layer 2H-MoS_2 basal plane to improve the HER activity [183]. The hydrogen adsorption can be facilitated by the S vacancies with band states forthcoming at the Fermi level. S vacancies induced strains controlling the ΔG_H, in that way, the HER kinetics is improved. As a result, an essential strategy for accelerating catalytic activity is to make flaws for 2D nanomaterial-based electrocatalysts. Though controllable tuning of defects It is essential to control tuning of defects in order to comprehend the consequences on reaction mechanisms [166].

For instance, Yao's group reported that creating defects improved the HER activities of graphene in both acidic and alkaline solutions since the conjunction carbons influenced the anticipated binding energy of hydrogen [184]. At the current density of $10\,mA\,cm^{-2}$ the overpotential was 150 mV for defective graphene in acidic solutions ($0.5\,MH_2SO_4$) (Fig. 3a). Which is lower than those of pristine graphene (420 mV) and nitrogen-doped graphene (350 mV). The defective graphene similarly presented a superior kinetic feature with a little Tafel slope of $55\,mV\,dec^{-1}$. Due to their DFT calculations, the defects and the adsorption site effectively affect ΔG_H (Gibbs free energy of hydrogen). They realized that the finest active site was the carbon at 4 on a 7557 defect was detected as the best active site as a calculated ΔG_H of −0.187 eV was provided by it [52].

4.3. Heteroatom doping

In order to modify electronic properties, changing the elemental composition of 2D nanomaterials, manipulating surface chemistry, and chemical doping with heteroatoms is an effective method. So far, due to heteroatom doping, it is capable of conveying catalytic activity for various 2D nanomaterials like MoS_2, graphene, g−C_3N_4, etc [6]. Non-metal-atom doping and metal-atom doping non-metal-atom doping are its two categories. The doping O^-, S^-, B^-, N^-, and P-atoms to the framework of nanomaterials are usually held in it. For instance, all of these elements have been effectively applied so that the carbon framework in graphene and CNTs is doped. To synthesize single-atom catalysts on a support structure, like Pt single atoms on grapheme, metal–atom doping is mostly practiced. In order to increase the electrocatalytic performance of catalysts, this method is efficient [6,166,185].

4.3.1. Non-metal-atom doping

The dopants include nitrogen, boron, sulfur, and phosphorous to reach the purpose by replacing carbon atoms in graphene, therefore the density of carriers (holes or electrons) is efficiently tuned. Since it is easy to fabricate N-doped graphene using different and the features of n-type doping are distinct, various studies have been carried out on Nitrogen [186–192]. For carbonaceous materials, one of the most common and efficient dopants is the N atom [193]. In the graphene matrix, the nearby C atom could be co-activated by the N dopants, it is the energy levels of valence orbital that are influenced to tempt a synergistically improved reactivity toward HER [186,189,192]. Furthermore, the values could be declined by the N integration so that the initial $H^\star$ adsorption improved. As a result, the HER process could be hastened [192]. Huang's group synthesized mesoporous graphene with nitrogen-doped at a concentration of 3.9 a% ($\backsim$ 5wt%) with an overpotential of 239 mV at $10mA\,cm^{-2}$ and Tafel slope of $109mV\,dec^{-1}$ [186]. Pyrrolic (edge site), pyridinic (edge site), and quaternary (edge and graphitic sites are identified as the probable structures observed in this situation. According to the investigations done by Qiao et al. [192] presented the substitutional sites decide on the improvement of HER activity of graphene by N-doping. In comparison with those at pyridinic positions, better catalytic activity is shown by the N dopants at the graphitic sites.

Ito's group [194] indicated that doping and defect were focused on the graphene curvatures by inspecting the association among doping and topological defect. From the π-orbital (POAV) theory, the catalytic activity of carbon nanostructures greatly relies on the strong chemical potential at curvatures [195,196]. Flaw and local curvature are identified as the two significant inherent factors. They remarkably influence the HER activity of graphene. S-doped graphene [197] was reported to have a similar HER performance as N-doped ones.

Tian's group presented that the graphene HER performance with doping of S could be enhanced by plasma etching for the sake of the increasing densities of doping and defects [197]. Sathe's group confirmed that the consequence of N and B doping on the development of hydrogen evolution reaction performance was alike to some extent [198].

Exceptional HER performance is shown by B-doped graphene [199], nonetheless, the activity is static lesser to those of the MoS_2-based and Pt-based electrocatalysts. Likewise, DFT calculations confirm that although the dopant of heteroatoms in graphene has

the ability to boost the adsorption of hydrogen adsorption capability, all the ΔG_H^* values are still positive, indicating an undesirable thermodynamic adsorption process [199].

Excluding doped graphene, non-metal-atom doping has been stretched to other materials for several reactions [38,200]. Xie et al. confirmed that the electronic structure of MoS_2 can be influentially regulated by oxygen incorporation. In consequence, its HER performance is developed [38]. Besides, optimization of their catalyst was completed through being capable of controlling the amount of fundamental disorder over oxygen doping. In comparison with single-doped materials, greater electrocatalytic activity has been done by two or three materials doping 2D nanomaterials. For instance, in comparison with their single-doped counterparts, multiple-atom-doped graphene nanosheets (N/P, N/S, N/B dopants) showed greater performance for HER was indicated by dint of multiple-atom-doped graphene nanosheets (N/B, N/S, N/P dopants) [199]. Remarking on the DFT calculations, synergistic intermolecular catalysis subjects to this improvement.

Evidently, the density of the exposed active sites is dominated by the intrinsic activity and the catalytic activity of active centers, which are related to the extrinsic geometric characteristics. For the graphene-based catalysts which have been doped, the total exposure quantity of active sites is closely coupled by definite surface area and the doping levels. Consequently, it is essential to consider the specific surface area and doping degree to improve HER activities of graphene-based electrocatalysts as well as selecting doped heteroatoms [166].

4.3.2. Metal-atom doping

In order to specify the performance of metal-based electrocatalysts, the main factor is the size of metal nanoparticles. According to theoretical and experimental research, more suitable catalytic activity or selectivity is recorded by sub-nanometer-sized metal clusters in comparison with nanometer-sized counterparts [201–203]. Another influential method for creating active sites for different catalytic processes is doping of the single metal in 2D nanomaterials [204]. Furthermore, extra active sites and tuning the electronic states of TMDs are effectively made by heteroatom doping. As a result, it directly enhances the extrinsic and inherent activity [38,205,206].

Small progress of acidic HER performance is delivered by Co- or Ni-doped $MoSe_2$ catalysts, nevertheless a significant improvement of HER electrocatalytic activity happened in alkaline media compared to the bare $MoSe_2$. DFT calculations and experimental outcomes prove that the ΔG_H(hydrogen adsorption free energy) is boosted by dint of Ni or Co doping on the $MoSe_2$ nanosheets basal plane as well as furthering the ability of water adsorption. Moreover, sluggish basal planes include the activation of in-plane S sites which could be activated through dopants of metals such as Fe, Ni, or Co, etc. The amount of active sites is enhanced through them [207–209].

Co-incorporation at the S-edges can lessen from 0.2 to 0.1 eV. Remarking the STM images of the synthesis of Co−Mo−S nanoparticles in a chemical way, it is concluded that the shape of pristine triangular MoS_2 to a truncated hexagonal plane with both Mo and S−Co exposure can be altered by Co incorporation [210]. This subject to a better length of active edges. This subject to a better length of active edges. Subsequently, DFT was practiced to monitor the HER activity leaning of MoS_2 tampered with a variety of transition metals [109].

4.4. Strain & phase engineering

The bandgaps can be altered by phase engineering for TMDs can alter and the electronic conductivity can be enhanced by Lattice strain. Mostly, alkali metal intercalation, the hydrothermal method, and heterostructure construction are comprised of the strategies for phase engineering [6,166].

In order to gain the exfoliated MoS_2 nanosheets with lots of metallic 1T phases as the vastly active HER electrocatalysts, Chhowalla's group used the solvent-free intercalation technique [211]. After the surface excess negative charges are removed, the delivered superior HER kinetics are provided by the MoS_2 nanosheets of 1T phase Furthermore, adding the conductive SWNTs can considerably endorse the HER performance of the 2H phase. Hence, the weak conductivity of the 2H phase disapproves of the electrocatalytic activity. Moreover, the outcomes determine that the 1T phase displays a superior electron transformation feature than the 2H phase, which is a significant factor for the improvement of the HER performance [166,211].

In addition, Jin et al. [167] organized somewhat crystallized 1T-$MoSe_2$ nanosheets made up of crystalline and disorderly phases through a hydrothermal approach. They stated that the tangled phase can deal with abundant flawed sites as the active centers, whereas the inherent activity and conductivity of the electrocatalysts can be effectively enhanced by the 1T phase. The synergistic result for this electrocatalyst shows superior activity with an overpotential of 152 mV at 10 mA cm^{-2}. As 1T inclines to alter into a thermodynamically stable 2H phase, it is unhinged. In order to stabilize the 1T TMDs phase, an effective way is to inject electrons from extra constituents. According to experimental consequences, both the layer spacing (which modifies the band gap) is increased, and altering the d-band filling decreases the oxidation state of Mo [212].

Zhang's group [213] described 1T-$MoSe_2$/NiSe heterostructures with 1T-$MoSe_2$ nanosheets fastened on metallic NiSe nanowires. Electrons can be injected into $MoSe_2$ nanosheets by the NiSe nanowires. Since the hybrid electrocatalysts benefit from the phase transition. As a result, excellent HER activity and decent stability are featured by the hybrid electrocatalysts. In order to design other 1T MX_2-based heterostructures for several use fields, this strategy can be practiced.

4.5. Summary of optimization structure

The present review scrutinized strategies for designing 2D nanomaterial-based HER electrocatalysts, such as interface engineering, defect engineering, heteroatom doping, and strain & phase engineering. The electrical conductivity, exposed active sites, electronic

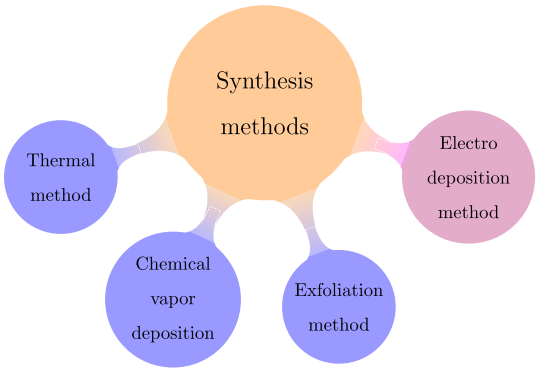

Fig. 12. Type of Synthesis methods.

states, and surface/ interface properties of electrode materials can be properly optimized by these strategies. It is still challenging to bring exactly measured synthesis, the purpose of actual active sites, perceiving the related mechanisms, and cost-effective profitable uses, although extensive attempts have been dedicated to designing the 2D nanomaterial-based electrocatalysts. Substantial consequences aim to produce suitable strategies to make the best out of the gains of these 2D nanomaterials in the route of the growth of efficient HER electrocatalysts [166].

5. Synthesis methods

An appropriate synthesis method is essential in order to design a very efficient electrocatalyst. Hence, a cheap or capable production approach applies to synthesize the catalysts with exceptional performance. Further, an applicable synthesis method is thought so that the particle morphology is controlled and the high purity of the catalyst is retained. After that, various significant synthesis techniques for water-splitting catalysts are clearly provided. The crystal structure and electronic morphology of the catalysts are controlled by the synthesis conditions [214] (Fig. 12).

5.1. Thermal method

One of the most frequently used synthetic methods is thermal synthesis. In order to dissolve and recrystallize powders, water, or an organic solvent is put into practice. Specifically, it is unnecessary to have a high temperature to separate ceramic powders through the hydrothermal method, which avoids impurity introduction, defect formation, and grain growth that can happen during the calcination procedure. Throughout the thermal process, modifying the reaction conditions is practiced to control the grain purity, crystal structure, and crystallization morphology [215–218]. When compared to other processes, thermal synthesis offers full tiny particle size, inexpensive raw material cost, stable distribution, grain development, comparably low particle accumulation, and easy control of chemical metering and crystallization shape [219]. Yu et al. [220] used a one-step hydrothermal method and made a MoS_2@PRGO composite. By using a hydrothermal technique, Niyitanga et al. [221] MoS_2 showed remarkable HER activity.

5.2. Chemical vapor deposition (CVD)

Chemical vapor deposition is a process that involves the reaction of two or more gaseous raw components to generate solid components, which are subsequently deposited on a substrate or catalyzed by other surfaces to form solid products [222]. Within the last century, CVD technology was initiated. CVD also has the advantages, such as the lowest energy usage, consistent and reliable output, and plain equipment. Consequently, it has gradually grown in importance as a technique for synthesizing nanocatalysts. Gas-phase reduction, hydrolysis, pyrolysis, and oxidation are among the methods applied to prepare nanomaterials by CVD. Because the pressures in the reactor vary, they may be classified as atmospheric, low pressure, super vacuum, and so on. Moreover, resistance, plasma, laser, flame, and other heating methods are used [214].

It is easy to control the CVD method and the particle shape of the produced catalyst is narrow. Also, in the commercial use of water electrolyzer catalysts, the catalyst can be uninterruptedly and firmly manufactured by CVD and it holds several benefits. Presently, it has been extensively used to prepare transition metal sulfides, graphene-supporting materials, and other water electrolyzer catalysts. Nevertheless, because of the utilization of gas sources and high temperatures and pressures, this approach has several safety flaws. Additionally, its deposition efficiency needs improving owing to gas deposition [214]. Browne et al. [223] made MoS_2 thin films by mixing the Mo precursor with a sulfur-containing solution and subsequently hardening it under slow gas to generate a fairly stable MoS_2 layer.

5.3. Exfoliation method

It is recommended to use the chemical and mechanical exfoliation method to synthesize single- or few-layer 2D nanomaterials [224,225]. Techniques such as plasma-assisted and liquid-phase exfoliation are among these stripping procedures; liquid-phase exfo-

liation is the most extensively utilized [226–228]. The downsides of this strategy include the high production costs of mass-producing huge numbers of items, which are considered flaws [30]. As well as the synthesis method, the morphologies and specifications of 2D materials set through exfoliation are greatly influenced by factors such as reaction temperature, the solution pH, type of solution, and surfactant [229–231].

The process of liquid-phase exfoliation was comprehensively discussed by Xu et al. (2014) [232]. Benabdallah et al. [233] investigated the influence of solvents on the peeling of black phosphorus and determined that the solution's restraint energy is the most important factor in layered material peeling. Because low pH is beneficial to the activation of inactive (002)-MoS_2, it was discovered that (002)-MoS_2 generated in a lower pH solution has a bigger exact surface area. Hu and coworkers looked at the effects of solvent and temperature on the properties of MoS_2 and came to the conclusion that (001)-MoS_2 has excellent hydrogen evolution capability [30].

The influence of the structure of layered materials on their properties is particularly remarkable. Intercalation structures, core-shell structures, and hollow structures can all be produced besides layered 2D structures. The expansion of the exposure of active sites is regarded as the gain of these constructions. Moreover, the stability of single 2D layers is not as good as that of heterostructures [234–236].

5.4. Electrodeposition method

Electrochemical deposition is a method that allows for the direct creation of a coating through a series of physical procedures and chemical reactions. Because of the electrochemical deposition's electric field, the electrical current passes through the electrolyte solution, and the reduction-oxidation process occurs on the electrode. Water-splitting nanocatalysts with the electrochemical deposition process have the advantage of being able to be reliably loaded on the support and are commonly employed for metal catalysts. The electrochemical deposition method is practiced to prepare electrodes with micro-nanostructure in the water electrolyzer reaction experiment. Because micro-nanostructures have a sizable specific surface, they provide more active sites for water electrolyzer devices. Additionally, the micro-nanostructure can enhance mass transfer efficiency throughout the reaction phase. Indeed, it essentially improves the basic overall water-splitting performance of the working electrode [237]. To finally regulate the catalyst, the current density or potential in the electrochemical deposition process is adjusted [214].

For instance, Zhang et al. [238] used electrochemical deposition to make amorphous MoS_2. To put it briefly, the electrochemical deposition method is easy to deal with, small cost, and is a simple approach to making water electrolyzer catalysts that can produce certain exclusive construction catalysts [239]. Despite this, electrodeposition has several disadvantages. Electrode polarization and solvent implications resulting from charge transfer, as well as the relative concentration in the solution, have a constant impact on deposition efficiency [214].

6. Challenges towards H_2 economy

It is cost-effective to use hydrogen as a substitute for present fossil fuels [240]. The major aim of a hydrogen economy is for hydrogen to be produced primarily from reliable energy sources in order to replace the present fossil fuels utilized in commercial sectors, industry, transportation, and residential [241]. The economic reasons indicate that some sources have recognized the lessening detection of new petroleum sources mixed with the exceeding worldwide energy claim as the main concern. According to some accounts, this will happen around the mid-century mark, when ½of the world's crude oil would have been utilized. However, in order to ensure a plane transition to "greener" prospects, appropriate vindication options must be implemented in the years ahead, maybe a time ahead of the true highest oil occurrence [242]. Using hydrogen as a fuel is considered being as one of the best greener alternatives. The fact is that the gravimetric energy density of fuel hydrogen is roughly 2.5-3 times greater than usually used fossil fuels nowadays (see Table 2) [240]. The hydrogen economy has been planned to be a precise advanced and long-term response to the consistent problems challenging the world today counting [241]: 1. worldwide environmental problems, 2. reduction of natural resources, 3. food deficiency and malnourishment in the developing countries, and 4. the increasing development of the world population.

According to the fact that hydrogen has proper combustion properties, it can be practiced in internal combustion engines. For example, the flash-point of hydrogen is very low which is almost −231 °C (see Table 3). This is significant as the gaseous or vaporized states are the most suitable ones in which fuel can be burnt [240].

The produced hydrogen is first used by the fuel cell vehicle to generate power and then for electricity. Ammonia synthesis, refineries, and methanol production are among the ones using lots of the produced hydrogen. Within the near future, this level will be declined [244]. Soon, hydrogen energy will be used in all aspects of life. Since hydrogen production is costly and there are not enough infrastructures for it, fossil fuels are used as an alternative. Nowadays, several studies and research are being carried out on hydrogen. It seems that hydrogen is a promising source of energy in the future. Currently, worries over general lifecycle expenditures and discernments over fuel safety are counted as the foremost restrictions behind the extensive use of hydrogen. The main factors touching lifecycle cost comprise investment expenditures, production cost, storage costs, market price, supply cost, and demand [245]. Nevertheless, hydrogen produced by renewable energy-powered electrolysis allows for improved well-to-wheel efficiency and, perhaps, lower fuel costs. The development problem of bringing out the electrolysis of water at realistic efficiencies appears to be obstructing progress in understanding this currently. It's worth noting that if the cost of hydrogen produced by electrolysis falls, the cost of renewable energy power generation will fall as well [240,245].

Table 2
Ordinary fuels' volumetric and gravimetric energy densities [240,243].

Fuel	Gravimetric Energy Density ($MJ\,kg^{-1}$)	Volumetric Energy Density ($MJ\,L^{-1}$)
H_2 (ambient pressure)	143	0.0107
LPG butane	49.1	27.7
Methane (ambient pressure)	55.6	0.0378
Natural gas	53.6	0.0364
H_2 (liquid)	143	10.1
H_2 (compressed, 700 bar)	143	5.6
Diesel	45.4	34.6
LPG propane	49.6	25.3
Gasoline (petrol)	46.4	34.2
Natural Gas (Compressed, 250 bar)	53.6	9
Natural Gas (Liquid)	53.6	22.2
Kerosene	46.4	36.7
Biodiesel oil	42.2	33

Table 3
Flash-point of some ordinary fuels [240,243].

Fuel	Flash-point (°C)
H_2	-231
Biodiesel	130
Jet Fuel	60
Methane	-188
Diesel	62
Ethanol (70%)	17
Methanol	11
Propane	-104
Kerosene	36
Gasoline	-45

7. Conclusion and future prospective

CO_2 is exceedingly increased. It is essential to improve more effective technologies for reaping, changing, and storing clean and renewable energy; and material inventions are the main factor. Globally, energy is remarkably used up and the release of CO_2 is greater than before, from now; it is indispensable. Indeed, CO_2 2D nanomaterials are a new promising generation displayed [246].

This review focused on and explored the most recent developments in 2D nanomaterial electrocatalysts, their methodologies for production and optimization, and their promising electrochemical applications for HER. The present review scrutinized their synthesis methods, optimization methods and their encouraging electrochemical uses towards HER. The development of the 2D electrocatalysts, which include heteroatom-doped, 2D porous carbons modified with transition metals and, or heteroatoms, 2D nanocarbon-based transition metal compounds, or metal-free hybrids, involved using well-known synthetic techniques like thermal, exfoliation, electrodeposition, and CVD method, etc. Furthermore, chemical and physical modifications, including defect, strain & phase engineering, and doping, can be promoted through optimization methods [29].

Several advances have succeeded that obviously prove the benefits of 2D materials as electrocatalysts for water splitting. It is notable that the interfacial structure of these types of materials evidently plays a key role in their electrocatalytic performance. Nonetheless, they deal with several challenges in which lots of studies report assorted consequences even though 2D materials can be considered promising electrocatalysis in the future [31]. The essential research and applied large-scale use of hydrogen energy is dependent on the electrochemical HER, which is currently in an evolving phase notwithstanding the important development realized. However, the future landscape of this issue brings about several critical challenges. These challenges comprise the indistinct source of the 2D material's electrocatalytic activity, and the incapability to unswervingly detect the electrocatalytic procedure, which averts the remark of the reaction phases dealing with the apparatuses, high charges related to the synthesis of most 2D material, inefficiencies, and the difficulties, are thwarting commercialization [62]. The main challenges are presented below:

1. More clarification and details are required to clearly figure out the exact active sites and progress of active sites in the water splitting electrochemically process [52].

2. The electrocatalysts and electrocatalytic reactions can be perfectly analyzed by the ex-situ representations. Within the electrocatalytic reactions, it is not possible to properly illustrate the surface chemistry and structure evolution of the electrocatalysts [166].
3. Electrocatalyst production has not been industrialized, yet. However, it is essential to carry out thorough research on large-scale production processes.
4. It should be pointed out that great developments have been made in high-performance 2D electrocatalysts. It is needed to realize improved hydrogen evolution reaction catalysts higher than the marketable electrocatalyst. It is better to mull over some external field coupling notwithstanding elevating the family with more 2D electrocatalysts and alteration approaches [247,248].
5. It is possible to figure out the practical use of energy catalysis by the electrochemistry of 2D materials. The economic issues and green chemistry synthesis techniques of the electrochemistry of 2D materials are the most important problems. Finding affordable materials and environmentally responsible synthesis is essential [29].
6. Because transition metal-based LDH systems contain two metals, metal type selection, specifically metal surface electronic structure regulation, directly affects catalytic activities. The surface electrical structure's precise regulation is still lacking. Thus, binary LDH materials should be produced and their surface electronic structures described to provide a database for preparing electrocatalysts with exact surface electronic structures [253].
7. Chemical interaction between the interface's surficial and interior structures determines LDH material design and manufacture. The chemical states of metal atoms in LDH materials can be seen during reactions, but the quantity of newly formed metal sites and component interfaces cannot be accurately measured. The newly formed species at the interface should be carefully considered while tuning electrocatalytic activity [254].

CRediT authorship contribution statement

Farshad Sobhani Bazghale: Writing – review & editing, Writing – original draft. **Mohammad Reza Gilak:** Writing – review & editing, Writing – original draft. **Mona Zamani Pedram:** Supervision, Project administration. **Farschad Torabi:** Writing – review & editing, Visualization. **Gowhar A. Naikoo:** Writing – review & editing, Validation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data included in article/supp. material/referenced in article.

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