Original Article

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TMU Journal of Basic & Applied Chemistry
Vol.5
Jan-December, 2025: P.43-50

Two-Dimensional Nanomaterials for Hydrogen Evolution Reaction: Emerging Electrocatalysts and Future Prospects

Abstract

The growing need for clean and renewable energy solutions has highlighted hydrogen as a sustainable energy carrier owing to its high energy density and zero carbon footprint. Among various production methods, electrochemical water splitting particularly the hydrogen evolution reaction (HER) is considered a promising pathway for large-scale green hydrogen generation. Although platinum and other noble metals are highly efficient HER catalysts, their scarcity and high cost hinder widespread application, leading to intensive research on earth-abundant alternatives. Two-dimensional (2D) nanomaterials such as black phosphorus, transition metal dichalcogenides, and MXenes have recently gained attention due to their unique physicochemical properties, including high surface area, tunable electronic states, and abundant catalytic sites. This review highlights recent progress in the synthesis, structural tailoring, and catalytic applications of 2D nanomaterials and their composites for HER. Emphasis is placed on strategies such as heterostructure construction and surface functionalization to improve activity and durability. Common synthesis methods exfoliation, hydrothermal processing, chemical vapor deposition, and electrodeposition are also discussed, alongside the crucial role of interfacial structures in determining catalytic performance. Key challenges, including limited stability, unclear identification of active sites, difficulties in large-scale synthesis, and high fabrication costs, are examined. Finally, future directions are suggested, focusing on scalable green fabrication, advanced in-situ characterization techniques, and hybrid catalyst design to enable practical hydrogen production. Overall, this review underscores the promise of 2D nanomaterials as

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Received on: 11.09.2025

Revised on: 21.09.2025

Accepted on: 30.09.2025

efficient and sustainable HER electrocatalysts, paving the way toward a hydrogen-based energy economy..

Keywords: HER, 2D Nanomaterials, Electrocatalysis, TMDs, MXenes

Introduction

Global energy demand is still largely dependent on fossil fuels; however, their finite availability and the environmental challenges they pose, including pollution and climate change, necessitate the development of cleaner energy alternatives (Sapountzi et al., 2017; Yuan et al., 2020; She et al., 2017). Renewable resources such as solar, wind, geothermal, and biomass have attracted significant interest, but their intermittent nature underscores the importance of reliable energy storage technologies. Hydrogen (H_2) stands out as a promising clean energy carrier owing to its high gravimetric energy density, carbon-free emissions, and water as the only combustion byproduct (Wang et al., 2020; Acar et al., 2014).

At present, most hydrogen is obtained from fossil resources like natural gas, oil, and coal, while only a minor share originates from water electrolysis (Sobrino et al., 2010; Mori et al., 2009). To enable large-scale and environmentally sustainable hydrogen production, water-splitting processes—including photocatalytic, electrochemical, and biomass-assisted methods—are being extensively investigated. Within electrochemical water splitting, the hydrogen evolution reaction (HER) plays a central role, proceeding through a sequence of Volmer, Heyrovsky, and Tafel steps in either acidic or alkaline electrolytes.

HER performance is typically characterized by key electrochemical properties, including low overpotential, high exchange current density, small Tafel slope, excellent electrical conductivity, rapid charge-transfer kinetics, and long-term catalytic stability. The optimization of these parameters is essential to reduce energy consumption and enhance hydrogen generation efficiency. Consequently, the design of efficient, stable and low-cost HER electrocatalysts has become a critical focus in the pursuit of sustainable hydrogen production.

In acidic media-

Volmer step-

$$\mathrm{H_3O^+ + M + e^- \rightarrow M-H + H_2}$$

Heyrovsky step-

$$\mathrm{M-H + H_3O^+ + e^- \rightarrow M + H_2 + H_2O}$$

Tafel step-

$$\mathrm{2M-H \rightarrow 2M + H_2}$$

In alkaline media-

Volmer step-

$$\mathrm{H_2O + M + e^- \rightarrow M-H + OH^-}$$

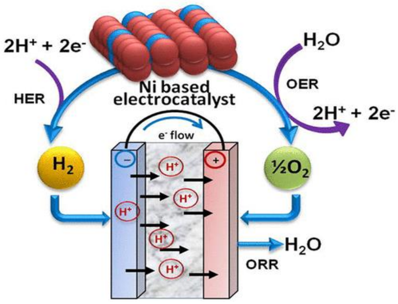
Heyrovsky step-

$$\mathrm{M-H + H_2O + e^- \rightarrow H_2 + M + OH^-}$$

Tafel step-

$$\mathrm{2M-H \rightarrow 2M + H_2}$$

Although noble metals like Pt are excellent HER electrocatalysts, their high cost and scarcity limit widespread use. Thus, research now focuses on earth-abundant, low-cost, and stable alternatives, particularly 2D nanomaterials (Black phophorus, MXenes, g-C_3N_4, transition-metal carbides, borides, and chalcogenides), which offer tunable structures, high surface areas, and enhanced catalytic performance (She et al., 2016; Gong et al., 2021; Popczun et al., 2013; Tan el al., 2017). Recent studies demonstrate that heterostructures, doping, and morphology engineering can significantly reduce overpotentials and improve HER efficiency



Schematic representation of HER, OER and ORR

This review focuses on the synthesis, characterization, and electrocatalytic behavior of 2 dimensional nanocomposites for HER, emphasizing key approaches to improve their efficiency, durability, and economic viability for next-generation hydrogen energy applications.

2D material-based nanocomposites as efficient HER electrocatalysts

The structural design and atomic arrangement of two-dimensional materials play a crucial role in determining their physical and chemical properties. Since the breakthrough discovery of graphene, these materials have attracted significant attention for energy storage and conversion applications. Owing to their large surface-to-volume ratio, abundant edge sites, and tunable electronic characteristics, 2D materials have emerged as promising electrocatalysts for hydrogen evolution. Their atomically thin layers expose plentiful active sites and promote fast electron transport, while approaches such as doping, defect engineering, and hybridization can further optimize catalytic efficiency.

In comparison with conventional nanomaterials, 2D systems present greater accessibility of active sites, ease of structural analysis, and cost-effectiveness, positioning them as viable substitutes for expensive noble-metal catalysts. This review emphasizes recent advances in three major classes of 2D electrocatalysts for HER: black phosphorus, TMDs, and MXenes.

Black phosphorus

Black phosphorus (BP), first synthesized in 1914 (Bridgman et al., 1914), is a layered semiconductor with a wrinkled honeycomb structure where each P atom bonds with three neighbors. Its tunable bandgap, surface lone-pair electrons, and anisotropic electrical properties make BP nanosheets attractive for electrocatalysis. The honeycomb lattice effectively exposes metal lone pairs, thereby enhancing HER activity.

Although black phosphorus (BP) possesses several advantages, its poor conductivity and limited stability hinder its direct application in electrocatalysis. Sofer et al. (2016) demonstrated that edge-plane BP exhibits superior catalytic activity (-0.35 V vs. SHE) compared to basal-plane BP (-0.93 V vs. SHE), but its performance still falls short of many non-precious catalysts. Doping with transition metals has been explored to enhance HER activity, with BP(Co) showing the highest performance, delivering an overpotential of 290 mV at 10 mA cm^{-2} (Liu et al., 2019).

Recent studies further reveal that BP-based heterostructures can generate strong synergistic effects. For instance, Luo et al. (2017) fabricated a BP–Ni_2P heterostructure that demonstrated excellent HER activity in acidic conditions, attributed to improved charge transfer and enlarged surface area. Similarly, MoS_2-BP composites have shown remarkable performance, achieving an overpotential as low as 85 mV at 10 mA cm^{-2} (He et al., 2017).

TMDs

Transition metal dichalcogenides represent a rapidly advancing family of 2D materials widely explored for applications in supercapacitors and water-splitting electrodes, owing to their hydrophilic surfaces, mechanical robustness, and large specific surface area. Structurally, they share similarities with graphene, featuring strong in-plane covalent bonding and weak van der Waals forces between adjacent layers, resulting in bulk crystalline forms. Depending on the stacking sequence, TMDs can crystallize into semiconducting (2H), metallic (1T), or other polymorphic forms such as 1T′ and 3R, each with distinct electronic characteristics (Voiry et al., 2015).

Among them, MoS2 has been the most extensively studied for the hydrogen evolution reaction (HER). Its catalytic activity is mainly attributed to Mo-edge sites, while the basal planes remain largely inert. Both density functional theory (DFT) and experimental investigations have confirmed that HER activity arises predominantly from edge sites, inspiring defect engineering and nanosheet thinning strategies to maximize exposure of active edges (Yu et al., 2014; Li et al., 2011). Few-layer or exfoliated TMDs exhibit enhanced conductivity, stability, and tunable bandgaps compared to their bulk analogs, making them particularly appealing for electrocatalysis, photocatalysis, and sensing applications. Notably, their band edge positions are well-aligned with the redox potentials required for water splitting, reinforcing their suitability as HER electrocatalysts.

TMDs are also promising due to low cost, chemical stability across wide pH ranges, and ease of synthesis, making them viable alternatives to noble-metal catalysts (Prabhu et al., 2020). They can form heterostructures with other nanomaterials, further boosting HER performance. Unlike graphene, TMDs possess inherent catalytic activity, tunable metallic/semiconducting phases, and broader doping flexibility with both transition metals and non-metals.

Dai Zhang et al. (Mei et al., 2022) reported the synthesis of amorphous MoS_2/N-RGO nanocomposites using plasma treatment, where the enhanced HER performance was attributed to the combined effects of abundant active sites, high electrical conductivity, and the intrinsic catalytic nature of MoS_2. In a related study, Badiger et al. (2024) fabricated $MoS_2/MnMoO_4$ composites through a simple hydrothermal approach. The composite exhibited superior electrocatalytic activity, delivering a low overpotential (-153 mV vs. RHE), a Tafel slope of 80 mV dec-1, and remarkable durability, maintaining stability for nearly 100 hours at 10 mA cm^{-2} in 0.5 M H_2SO_4.

Mxene

MAX phases, including carbides, nitrides, and carbonitrides, act as parent materials for MXenes, where the weaker M-A bonds are selectively etched away while the stronger M-X bonds remain intact. This process generates multilayered MXenes that can be further exfoliated through sonication. Various synthesis routes have been developed, including fluoride-based methods (using HF, HCl with LiF, or NH_4HF_2) and fluoride-free alternatives such as molten salt, alkaline etching, and electrochemical techniques (Ran et al., 2017). The resulting MXenes typically possess surface terminations (–O, –OH, –F) that enhance hydrophilicity, improve metallic conductivity (6000–8000 S cm^{-1}), and increase the density of active sites, rendering them highly attractive for HER applications, comparable to TMDs. Seh et al. (2016) demonstrated that Mo_2CTx displays intrinsic catalytic activity even at basal planes, achieving an overpotential of 283 mV at 10 mA cm^{-2}, while DFT calculations revealed that Co substitution in Mo_2CO_2 could effectively tune catalytic behavior. More recently, Thirumal et al.

(2023) synthesized MXene/graphene oxide heterostructures via a hydrothermal approach, reporting an overpotential of only 121 mV at 10 mA cm^{-2} significantly lower than that of pristine MXene (220 mV) or rGO (193 mV).

Synthesis strategies for efficient electrocatalysts

The choice of synthesis route is critical for designing efficient HER electrocatalysts, as it influences particle morphology, purity, and electronic structure. Several approaches, including thermal synthesis, chemical vapor deposition, exfoliation, and electrodeposition, have been widely explored.

Thermal methods (e.g., hydrothermal synthesis) allow controlled crystal growth at relatively low temperatures, minimizing impurities and grain growth. They yield small, uniform particles with stable morphology. Yu et al. (Yu et al., 2019) synthesized MoS_2/PRGO composites via hydrothermal method, while Niyitanga et al. (Niyitanga et al., 2019) reported excellent HER activity in hydrothermally prepared MoS_2.

Chemical vapor deposition (CVD) involves reacting gaseous precursors to deposit thin catalyst layers. It provides precise control over morphology, uniform deposition, and scalability, making it suitable for nano catalysts. However, high temperature/pressure and gas handling limit safety and efficiency. Browne et al. (Browne et al., 2019) prepared MoS_2 thin films via CVD using sulfur precursors, producing stable catalyst layers.

Exfoliation techniques (mechanical, plasma-assisted, liquid-phase) are commonly employed to obtain few-layer 2D materials. Properties depend strongly on reaction parameters such as pH, solvent, and temperature. Xu et al. (Xu et al., 2019) detailed liquid-phase exfoliation, while Benabdallah et al. (Benabdallah et al., 2020) showed solvent interaction governs black phosphorus peeling.

Electrodeposition enables direct catalyst growth on conductive supports by electrochemical redox processes. It offers low cost, structural tunability, and high surface area electrodes with enhanced mass transport. Zhang et al. (Zhang et al., 2019) fabricated amorphous MoS_2 via electrodeposition, while other studies highlight its practicality for producing nanostructured HER catalysts.

Challenges towards a hydrogen economy

Hydrogen is regarded as a cost-effective and sustainable substitute for fossil fuels, with the goal of powering commercial, industrial, transport, and residential sectors through reliable energy sources. Concerns over declining petroleum reserves and increasing global energy demand highlight the urgency of transitioning to hydrogen, with estimates suggesting that by mid-century nearly half of the world’s crude oil will be depleted. To ensure a smooth shift to greener alternatives, hydrogen is promoted as a long-term solution to challenges such as environmental degradation, depletion of natural resources, global food insecurity, and population growth.

Hydrogen presents several notable advantages as an energy carrier: its gravimetric energy density is about 2.5–3 times higher than that of conventional fossil fuels, and its favorable combustion characteristics, such as an extremely low flash point (−231 °C), make it suitable for internal combustion engines. At present, most hydrogen use is concentrated in refineries, ammonia production, methanol synthesis, and fuel cell vehicles, though its role is expected to expand into electricity generation and everyday energy applications in the near future. Despite this potential, large-scale deployment remains constrained by high production costs, inadequate infrastructure, safety considerations, and overall lifecycle expenses, including investment, production, storage, and distribution. Fossil fuels continue to dominate because of their lower cost. Nevertheless, hydrogen produced through renewable energy-driven electrolysis offers significant opportunities, particularly in improving well-to-wheel efficiency.

However, the relatively low practical efficiency of water electrolysis still poses a key challenge. Importantly, lowering the cost of hydrogen production is strongly dependent on reducing the cost of renewable power generation.

Conclusion and future prospects

The pressing challenge of reducing reliance on fossil fuels and curbing CO_2 emissions has intensified efforts toward sustainable hydrogen production. Among the available methods, electrochemical water splitting stands out as a highly promising route, with HER being a central step. This review emphasizes the potential of 2D nanomaterials—such as black phosphorus, TMDs, and MXenes as efficient and economical HER electrocatalysts. Their distinctive attributes, including large surface area, adjustable electronic structures, and plentiful active sites, make them strong candidates to replace conventional noble-metal-based catalysts.

Despite significant progress, several challenges remain before 2D electrocatalysts can achieve large-scale applications. These include limited stability under electrochemical conditions, incomplete understanding of active sites and reaction pathways, difficulties in real-time characterization of catalytic processes, and the high cost or scalability issues associated with current synthesis routes. Furthermore, the lack of industrial-scale production and the need for durable, reproducible, and eco-friendly fabrication methods continue to hinder commercialization.

Future research should focus on (i) accurate detection and control of catalytic active sites using advanced in-situ and operando characterization methods, (ii) green synthesis methods to enable industrial production, (iii) design of heterostructures, defect engineering, and external-field coupling to enhance activity and durability, and (iv) exploration of hybrid systems integrating 2D catalysts with conductive supports for improved charge transfer. Economic viability and sustainability must also guide future developments, ensuring environmentally responsible and cost-effective processes

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