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Dual-phase electrocatalysts for hydrogen evolution reaction: A synergistic approach to enhance catalytic activity and durability

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Abstract:

Sustainable hydrogen production depends on optimising the hydrogen evolution reaction (HER); however, the development of scalable and efficient electrocatalysts remains challenging, particularly in alkaline environments where catalyst degradation and slow reaction kinetics limit performance. This review explores the promising potential of dual-phase electrocatalysts, which integrate complementary materials to synergistically enhance catalytic activity and stability. Focusing on processes in alkaline media, recent progress in HER catalysts has utilised advanced techniques such as hollow nanostructures, metal doping, and atomic layer deposition (ALD). Key materials, including transition metal phosphides, oxides, and dichalcogenides, demonstrate notable advancements in electron transport and hydrogen adsorption, thereby enhancing HER efficiency. The challenges of scaling these materials for commercial application are also addressed, with an emphasis on how the integration of computational and experimental approaches could accelerate catalyst design. Consequently, dual-phase catalysts represent a viable pathway for cost-effective and efficient hydrogen production, supporting the transition to a hydrogen-driven energy future.

Keywords: **alkaline catalysis, atomic layer deposition, dual-phase electrocatalysts, hydrogen evolution reaction, metal doping.**

Classification numbers: **2.1, 2.2, 2.3**

1. Introduction

The large-scale production of hydrogen, a clean and efficient energy carrier, is facilitated by the hydrogen evolution reaction (HER), a pivotal process in renewable energy technologies. Owing to its high energy density and zero carbon emissions, hydrogen has the potential to serve as a sustainable alternative to fossil fuels, which face increasing pressures due to global energy demands and associated environmental concerns [1]. The applications of hydrogen are vast, spanning industrial uses such as ammonia synthesis and refining processes to fuel cells that power portable devices and transportation systems. For hydrogen to emerge as a globally viable and cost-effective fuel, efficient, scalable, and affordable production methods are essential. Among the most environmentally sustainable approaches to hydrogen production is electrocatalytic water splitting, and the development of high-performance HER electrocatalysts remains a central focus of this effort [2]. Fig. 1 provides an overview of various strategies employed to enhance catalytic activity in HER, particularly through the use of transition metal phosphide-based catalysts.

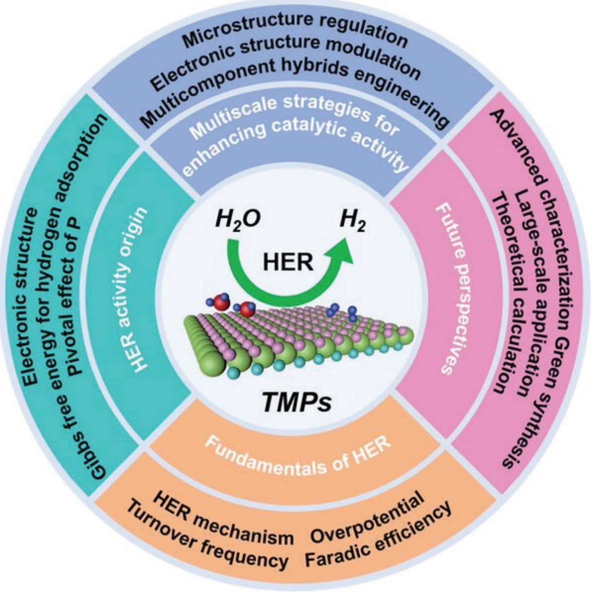

Fig. 1. Diagram of methods for using transition metal phosphide-based catalysts to increase catalytic activity in the hydrogen evolution reaction. Reproduced from G. Sdanghi, et al. (2022) [3].

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At its core, the hydrogen evolution reaction (HER) is an electrochemical process in which hydrogen gas is produced at the cathode through the reduction of water molecules. The high activation energy required often limits reaction efficiency, making the role of the catalyst essential. Platinum-based catalysts are typically considered the most effective due to their high reaction rates and low overpotentials. However, their reliance on costly and scarce materials presents significant drawbacks, necessitating an intense search for more affordable alternatives with comparable or superior catalytic performance [4]. Recently, dual-phase catalysts have gained considerable attention as a promising solution to these limitations. Dual-phase catalysts incorporate two distinct materials or phases, where one phase usually enhances stability or electrical conductivity while the other provides high catalytic activity. This combination enables unique synergistic effects, often leading to superior catalytic properties compared with those of single-phase catalysts. For example, combining various metal oxides or integrating transition metals with conductive carbon substrates can yield catalysts with enhanced electron mobility, higher active site densities, and optimised hydrogen adsorption energies [5].

In alkaline media, dual-phase systems offer a distinct advantage because of their ability to mitigate the high energy barrier associated with water dissociation, which typically reduces the activity of conventional catalysts. The interactions between the two phases in dual-phase catalysts can facilitate this water dissociation step, thereby improving both reaction stability and kinetics [6]. This feature makes dual-phase catalysts particularly suitable for alkaline HER applications, an area of growing importance in renewable energy technologies.

To optimise their catalytic performance, dual-phase catalysts have been developed through various advanced techniques in recent years, including atomic layer deposition, hollow structure designs, and heterostructures. For example, metal phosphides and nitrides exhibit enhanced stability and charge transfer capabilities when combined with a supportive phase, such as carbon or another metal [7]. These innovations underscore the versatility of dual-phase catalysts and their potential to deliver the high activity, durability, and scalability required for commercial hydrogen production.

This article provides a comprehensive overview of the landscape of dual-phase electrocatalysts for HER, with a focus on the distinctive mechanisms driving their enhanced performance. Our objective is to gain an in-depth understanding of the contributions of these materials to the progress of hydrogen production by exploring their synthesis methods, catalytic mechanisms, and structural modifications. We also address the challenges involved in scaling these materials for practical applications and consider potential future advancements. Through this synthesis, we highlight dual-phase catalysts as a promising pathway for the development of sustainable and cost-effective hydrogen energy systems.

2. Mechanisms and fundamentals of hydrogen evolution reaction in alkaline media

Owing to its potential for sustainable hydrogen production, the hydrogen evolution reaction (HER) in alkaline media has garnered considerable attention [8]. However, its slower reaction kinetics compared to those under acidic conditions introduce specific mechanistic challenges. This section examines the HER process, focusing on its fundamental mechanics, electron transfer mechanisms, the influence of adsorption energies on catalytic performance, and the distinct challenges posed by alkaline environments.

Research into the HER is essential to advance the frontiers of sustainable energy solutions. Emerging studies point towards various new methodologies to enhance HER efficiency, with most attention focused on non-precious metal catalysts and new synthesis techniques. These are crucial for reducing the dependency of HER systems' performance on relatively expensive noble metals.

Non-precious metal catalysts: Non-precious metal catalysts such as Fe, Co, and Ni are being tested as substitutes for platinum because they are cheaper and more readily available [9]. Optimising the electronic structures of these metals could significantly improve their HER capacity. However, challenges remain, such as the higher costs of noble metals and their limited availability. Non-precious metals suffer from inherent defects in hydrogen adsorption.

Innovative catalyst designs: 3D self-supported catalysts, such as the 3D P-Mo-NiFe LDH, demonstrate improved kinetics in neutral media, achieving 24 mV@10 mA cm-2 in phosphate buffer solutions [10]. Nevertheless, the kinetics of neutral media HER are still poor. Harsh conditions promote biocorrosion and present extreme pollution issues. A porous structure, such as that in NF/Ni@CoxPy catalysts, enhances electrocatalytic activity due to increased surface areas and hydrophilicity [11].

Synthesis techniques: Several techniques, including solution combustion synthesis and hydrogen reduction, have been used to synthesise high-entropy alloys (HEAs) following the discovery of good catalytic activity and HER stability [12]. These developments, although promising, also highlight the current challenges in adapting these technologies for commercial conditions and ensuring steady performance under long-term storage in diverse operational conditions. Further development is required to address these challenges and optimise catalytic dynamics across various operating conditions.

2.1. Hydrogen evolution reaction mechanism and electron transfer in alkaline medium

The HER mechanism in alkaline environments typically follows one of two main reaction pathways: the Volmer-Heyrovsky mechanism or the Volmer-Tafel. Both pathways begin with the Volmer step, the initial stage where water molecules dissociate, releasing hydrogen atoms (H*) that adsorb onto the catalyst surface while producing hydroxyl ions (OH^-). This step can be represented as follows:

The Volmer step: $H_2O + e^- \rightarrow H^* + OH^-$

In alkaline environments, the Volmer step poses particular challenges because water dissociation requires more energy than proton reduction under acidic conditions [9]. This added energy barrier slows HER kinetics, making the development of catalysts that facilitate this step crucial. Once H* is adsorbed onto the catalyst surface, the reaction can proceed in one of two ways:

Heyrovsky step: In this pathway, an adsorbed hydrogen atom (H*) combines with a solvated electron and a water molecule to release hydrogen gas.

$H^* + H_2O + e^- \rightarrow H_2 + OH^-$

Tafel step: Alternatively, hydrogen gas can be created by the direct recombination of two H* atoms on the surface.

$2H^* \rightarrow H_2$

The properties of the catalyst surface, which influence the adsorption and desorption energies of H*, determine the HER pathway. Catalysts with moderate adsorption energies optimise HER rates by facilitating both the formation of H* and its subsequent recombination or reduction.

The mechanisms and dependencies principally determine the different dynamics of the Heyrovsky and Tafel steps. The Heyrovsky step is a surface reaction involved in electrochemical desorption, where a surface-adsorbed hydrogen atom (Ha_{ds}) reacts with a proton (H+**)** to yield molecular hydrogen H_2. In contrast, the purely chemical desorption Tafel step is based on the direct recombination of two adsorbed hydrogen atoms on the catalyst surface. As the Heyrovsky step occurs via electron transfer, it is influenced by the applied electrode potential, whereas the Tafel step is independent of potential and depends on surface hydrogen coverage and catalyst adsorption strength. These differences are crucial for understanding rate-limiting processes and optimising catalysts for HER.

Effective HER requires a rapid electron transfer rate, which is closely linked to the electronic structure of the catalyst. Compared with single-phase catalysts, dual-phase catalysts often exhibit a higher exchange current density (j_0), resulting in lower overpotentials and faster HER rates. For example, Ni-Fe phosphide catalysts, which promote efficient electron transport, have demonstrated an exchange current density of approximately 0.6 mA/cm^2, significantly enhancing reaction kinetics.

In Fig. 2, the HER mechanism in an alkaline medium involves distinct reaction pathways, where the adsorption and desorption of hydrogen intermediates play a crucial role in determining overall catalytic performance.

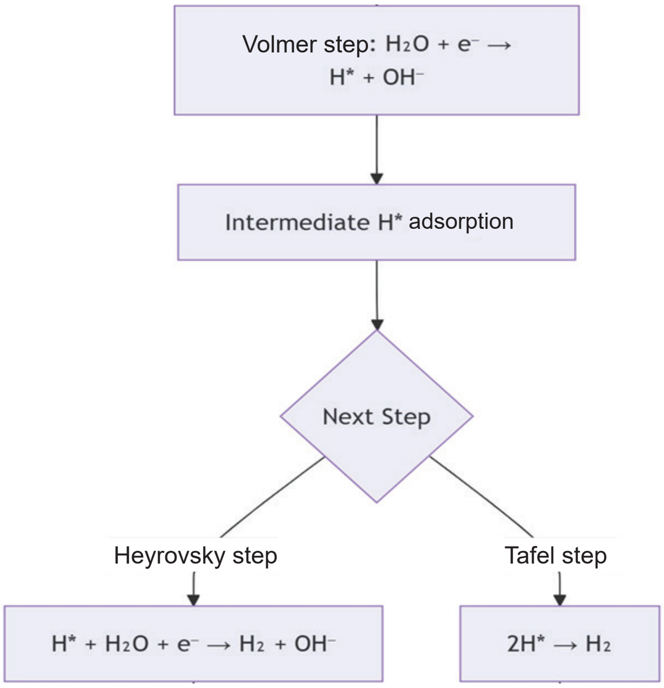

Fig. 2. Flowchart of the hydrogen evolution reaction mechanism in alkaline medium.

2.2. Influence of adsorption energies on catalytic performance

Adsorption energy is a primary factor in determining HER catalyst efficiency. Effective HER catalysts must balance competing requirements: Adsorbing hydrogen atoms strongly enough to facilitate the Volmer step, but not so strongly that desorption during the Heyrovsky or Tafel processes is hindered [13]. This delicate balance is often illustrated by a "volcano plot", where optimal HER performance is observed at moderate adsorption energies.

In dual-phase catalysts, synergistic interactions between phases adjust the electronic structure of active sites, thereby fine-tuning adsorption energy. For instance, NiFeP supported on carbon has a hydrogen adsorption energy (ΔG_H*) of approximately -0.05 eV, which lies close to the ideal range for HER, and enhances hydrogen adsorption and desorption rates [14]. This optimised ΔG_H* in dual-phase catalysts helps maintain a balance that improves overall reaction kinetics, enabling efficient HER.

2.3. Challenges of the hydrogen evolution reaction in alkaline solutions

Compared with acidic environments, HER in alkaline media faces greater kinetic challenges. One primary limitation is the energy-intensive water dissociation step, which slows down the reaction rate. Under acidic conditions, the availability of protons (H^+) simplifies the HER process by facilitating reduction. However, in alkaline conditions, the formation of H* requires water molecule dissociation, introducing an additional energy barrier that retards the reaction. Therefore, catalysts with strong activity toward water dissociation are essential for effective HER in alkaline applications [15].

Catalyst stability is another significant challenge in alkaline HER, as strongly basic environments can lead to corrosion and structural degradation. Dual-phase catalysts offer potential solutions by combining materials with complementary properties, such as high catalytic activity in one phase and corrosion resistance in the other. For example, transition metal phosphides and oxides exhibit enhanced stability and maintain high activity levels in alkaline solutions when combined with conductive materials such as carbon [16].

2.4. Summary of key parameters influencing alkaline hydrogen evolution reaction catalysts

The main factors affecting HER performance in alkaline media are summarised in Table 1. These factors include energy barriers, reaction stages, and common materials used in dual-phase catalysts.

Table 1. Factors affecting hydrogen evolution reaction performance in alkaline media.

Parameters	Description	Impact on HER	Examples of enhancements
Volmer step	Initial adsorption and dissociation of water to produce H*	Determines reaction initiation rate	Dual-phase catalysts with optimised water dissociation capabilities [17]
Heyrovsky/ Tafel steps	Subsequent steps involving H* combination to release H_2	Controls the rate of hydrogen evolution	Balanced adsorption energies achieved through synergy [18]
Adsorption energy	The energy required to bind and release H* on the catalyst surface	Influences reaction balance and kinetics	Optimised by combining metal and carbon phases [19]
Structural stability	Catalyst's resistance to degradation in alkaline environments	Affects long-term catalyst performance	Corrosion-resistant phases, such as oxides with conductive substrates [20]

The HER mechanism in alkaline media is depicted in the flowchart below, with special attention given to the sequential phases and the function of electron transfer at each level.

The versatility of dual-phase catalysts is further underscored by their comparative HER performance under acidic versus alkaline conditions. For example, MoS_2-$CoSe_2$ hybrids exhibit HER overpotentials of approximately 120 mV in alkaline media but only approximately 36 mV at 10 mA/cm² in acidic media, illustrating the additional energy barrier related to water dissociation in alkaline environments. Similarly, Ni-FeP/Carbon hollow nanorods achieve overpotentials of 95 mV in acidic media and 117 mV in alkaline conditions at a current density of 10 mA/cm², emphasising the importance of optimising catalysts specifically for alkaline HER applications [21].

3. Types of dual-phase electrocatalysts

Owing to their synergistic properties, dual-phase electrocatalysts have demonstrated significant potential in accelerating the hydrogen evolution reaction (HER). These catalysts typically consist of two phases-often a conductive material paired with a metal compound such as phosphides, sulphides, or oxides to increase both catalytic activity and stability. This section examines various types of dual-phase catalysts, focusing on transition metal phosphides, oxides, and dichalcogenide-based hybrids. Morphological advancements and specific characterisations further improve the HER performance of these systems.

Metal-compound hybrids:

- *Transition metal phosphide (TMP) hybrids:* TMPs (e.g., Ni_2P, CoP) combined with conductive supports (e.g., carbon, graphene), which exhibit high activity owing to the fast kinetics for hydrogen adsorption/desorption.

- *Transition metal sulphide (TMS) hybrids:* TMS (e.g., MoS_2, CoS) forms hybrids with conductive or catalytic phases, improving the conductivity and availability of active sites.

- *Transition metal oxide (TMO) hybrids:* Metallic phases, e.g., Fe_2O_3, NiO are used in conjunction with TMOs to improve stability and electron transfer rates.

Metal-metal hybrids: Combine two distinct metals, such as Ni-Co or Pt-Mo, which develop synergistic interfaces whereby modulations on electronic structure enhance catalytic performance while improving durability.

Metal-dichalcogenide hybrids: Pairing metal dichalcogenides (e.g., MoS_2, WS_2) with another phase (either metals or oxides) promotes the exploitation of their layered nature for augmented hydrogen adsorption capabilities.

Metal-organic framework (MOF)-derived hybrids: Potential templates from MOF were used for the synthesis of porous dual-phase structures incorporating active metal compounds with carbon-based conductive phases in order to obtain high surface area and boosted mass transfer.

Carbonaceous dual-phase hybrids: Carbon materials (e.g., CNTs, graphene) are integrated with metallic or non-metallic phases while providing good conductivity and ideal anchoring for active sites.

3.1. Morphology and characterisation of dual-phase electrocatalysts

The morphology of dual-phase electrocatalysts is a critical factor influencing their catalytic performance. Dual-phase catalysts frequently adopt nanostructured morphologies - such as hollow nanorods, core-shell structures, and porous frameworks - to increase the number of available active sites and facilitate electron transfer. These morphological features enhance mass transfer, surface area, and durability by reducing the diffusion lengths of both reactants and products.

For instance, Ni-doped FeP hollow nanorods supported on carbon demonstrate enhanced HER performance across a wide pH range. This improvement is attributed to their hollow structure, which provides an abundance of active sites and enables efficient charge transfer [22].

The synthesis, characterisation, and structural analysis of NiFe/CNT composites are illustrated in this figure. Fig. 3A demonstrates the application of melamine ink onto NiFe foam, followed by calcination, which generates NiFe/CNT composites via a solid-diffusion reaction.

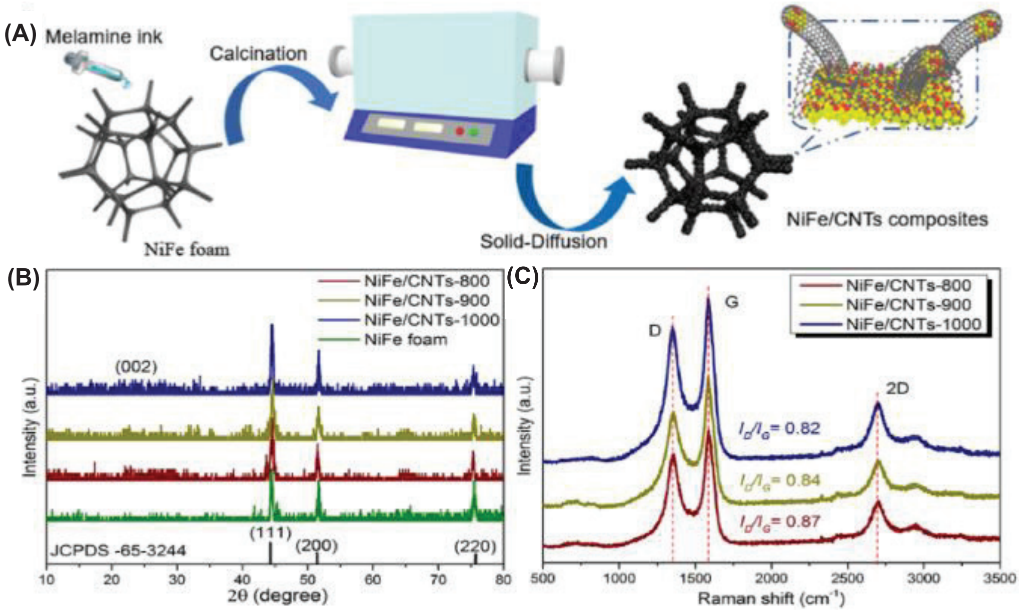

Fig. 3. (A) A schematic representation of the NiFe/CNT (carbon nanotube) composite preparation procedure; (B) NiFe foam and NiFe/CNTs synthesised at various temperatures (800, 900, and 1000°C) with X-ray diffraction (XRD) patterns demonstrating phase composition; (C) Raman spectra of NiFe/CNT composites at 800, 900, and 1000°C, showing how the structure changes with temperature adapted from H. Li, et al. (2020) [23].

Figure 3B presents X-ray diffraction (XRD) patterns for NiFe/CNTs synthesised at different temperatures (800, 900, and 1000°C), in comparison to those of NiFe foam. The successful integration of NiFe into the CNT structure is evident from prominent peaks at the (002), (111), (200), and (220) planes, which correspond to the JCPDS reference, indicating that structural integrity is maintained across the temperature spectrum.

Figure 3C shows Raman spectra with characteristic D and G bands associated with carbon-based materials. At higher synthesis temperatures, the ID/IG intensity ratios for the samples decrease significantly (from 0.87 to 0.82), indicating improved graphitisation and structural order in the CNTs. This analysis is crucial for understanding the crystallinity of composites and its potential influence on electrochemical performance.

Similarly, MoS_2-$CoSe_2$ hybrids exhibit enhanced HER activity due to their nanoscale morphology, which fosters synergistic interactions between MoS_2 and $CoSe_2$, contributing to improved stability and accelerated reaction kinetics, which is depicted in Fig. 4 [24].

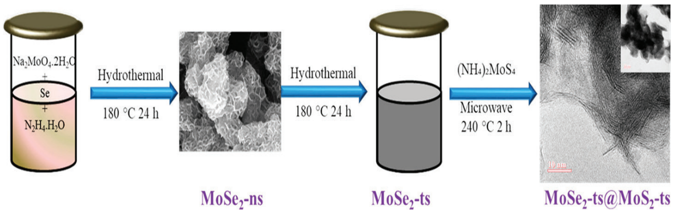

Fig. 4. Schematic illustration of the synthesis of $MoSe_2$ @ MoS_2 hybrid structures adapted from M.D. Sharma, et al. (2020) [24].

The synthesis process for $MoSe_2$-based composites, involving sequential hydrothermal and microwave treatments, is illustrated in this image. Initially, $MoSe_2$ nanosheets ($MoSe_2$-NSs) are synthesised by hydrothermally reacting a precursor solution of $Na_2MoO_4 \cdot 2H_2O$, Se, and $N_2H_4 \cdot H_2O$ for 24 hours at 180°C. A second hydrothermal treatment under similar conditions then yields $MoSe_2$ thin sheets ($MoSe_2$-ts), indicating controlled morphological evolution. In the final stage, the $MoSe_2$-ts@MoS_2-ts heterostructure is formed by adding $(NH_4)_2MoS_4$ and heating to 240°C for two hours. The TEM image shows layered features in this structure, suggesting a synergistic interaction between $MoSe_2$ and MoS_2 that may enhance properties such as electron transport and catalytic activity in electrocatalytic applications.

This synthesis process-utilising hydrothermal and microwave treatments, produces a layered, nanoscale morphology, increasing surface area and promoting synergistic interactions between MoS_2 and $CoSe_2$ components, thus supporting increased HER activity.

Characterisation techniques are essential for analysing the structural and electrical properties of these dual-phase systems. X-ray diffraction (XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) reveal the nanoscale morphology, crystal structure, and composition of the catalysts. A comprehensive understanding of how morphological and structural characteristics contribute to enhanced catalytic activity is achieved by integrating multiple characterisation methods.

3.2. Examples of dual-phase electrocatalysts

Transition metal phosphides, oxides, and dichalcogenides have been widely studied as dual-phase catalyst constituents due to their favourable electrical and catalytic properties. Below are some notable examples:

3.2.1. Ni-FeP/Carbon hollow nanorods

These catalysts exhibit high hydrogen evolution reaction activity and stability, attributed to their hollow nanorod structure, which enhances active site exposure and promotes electron transport. As shown in Fig. 5, the Ni-FeP phase provides active sites for hydrogen evolution, while the carbon phase enhances electrical conductivity and prevents agglomeration [25].

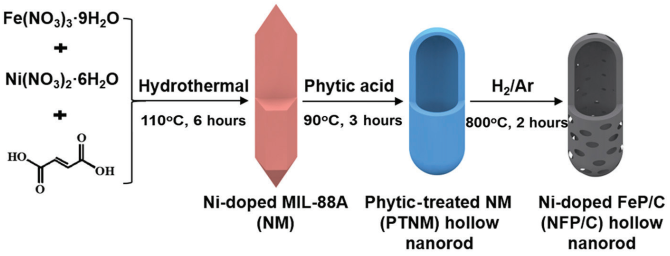

Fig. 5. Ni-FeP/Carbon hollow nanorod production and characterisation schematic synthesis adapted from X.F. Lu, et al. (2019) [25].

3.2.2. MoS_2-$CoSe_2$ hybrids

When MoS_2 and $CoSe_2$ are combined, the resulting composite benefits from the complementary properties of each material: $CoSe_2$ enhances stability and electron mobility, whereas MoS_2 offers active sites for the reaction. The synergy between these two phases leads to a catalyst with a low Tafel slope and high current density, indicative of improved catalytic activity and durability, which can be shown in Fig. 6 [26].

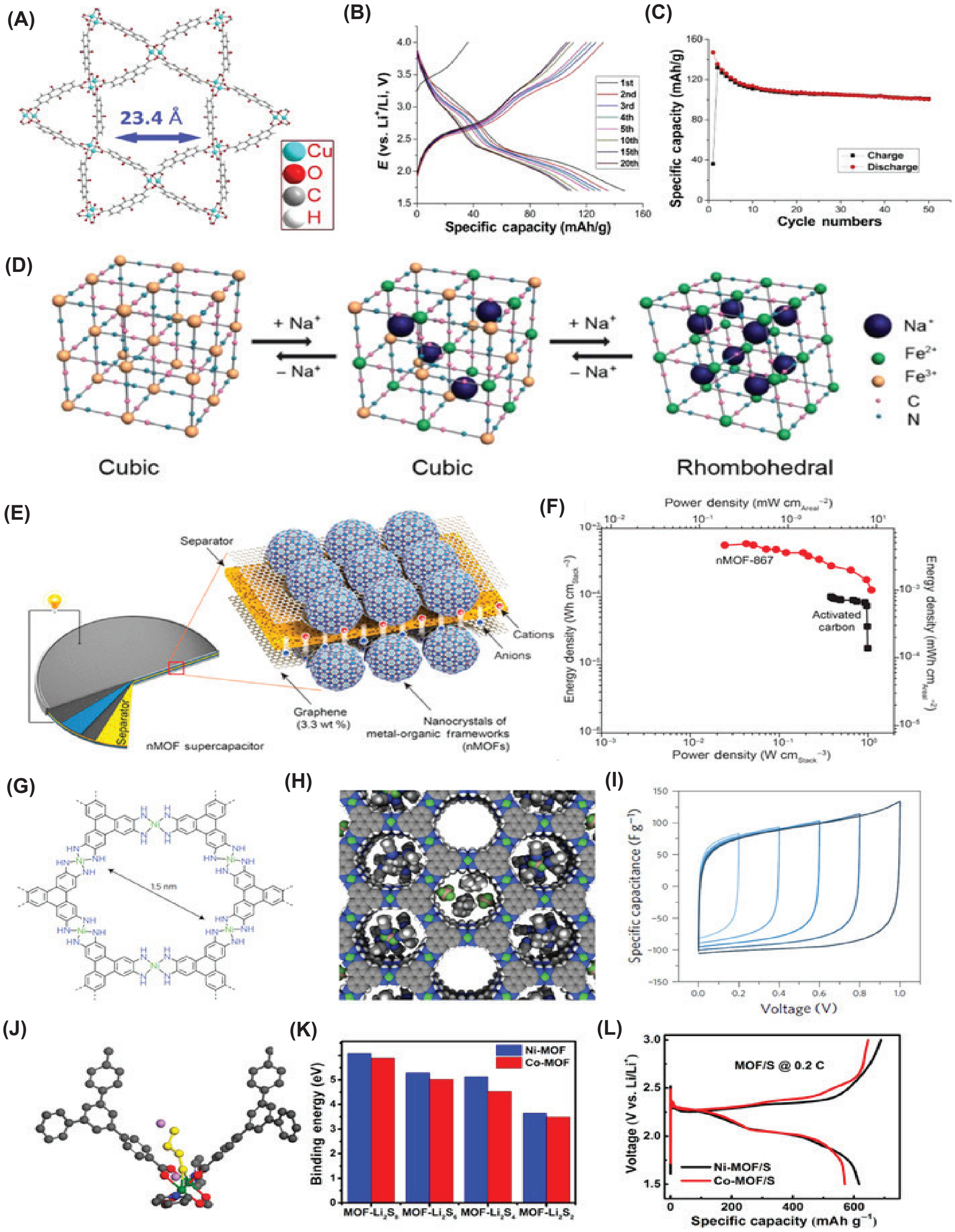

Fig. 6. MoS_2-$CoSe_2$ hybrids: Schematic and electrochemical characterisation reproduced from H.B. Wu, et al. (2017) [26].

Low Tafel slopes and high current density, which indicate enhanced catalytic activity and durability, demonstrate the synergistic effect between MoS_2 and $CoSe_2$. The MoS_2 layer provides numerous active sites, while the $CoSe_2$ component enhances stability and electron mobility, collectively resulting in improved HER performance.

3.2.3. Mn-Ni-Co oxide spinels supported on carbon

Spinel oxides, such as $Mn_{0.5}Ni_{0.5}Co_2O_4$, exhibit superior HER performance because of their large surface area, with the carbon support providing stability. This combination is particularly beneficial for alkaline HER applications, as it facilitates electron flow across the catalyst surface (Fig. 7) [27].

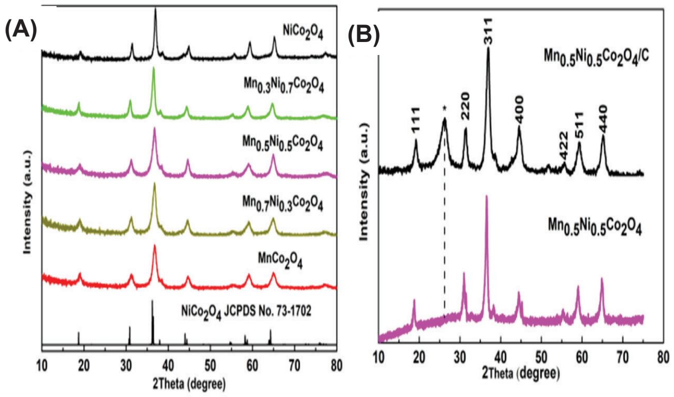

Fig. 7. X-ray diffraction (XRD) patterns of Mn-Ni-Co oxide spinels and their carbon-supported forms. (A) Shows the XRD patterns of various $Mn_xNi_{1-x}Co_2O_4$ compositions; **(B)** Compares the $Mn_{0.5}Ni_{0.5}Co_2O_4$ with and without carbon support. Adapted from T. Matthews, et al. (2021) [27].

The carbon support improves electron transmission and the diffraction peaks show the crystalline structure, these materials are appropriate for alkaline HER applications.

3.2.4. Pt-Ni-Co ternary alloy nano frame

A prominent example is the Pt-Ni-Co ternary alloy nano frame, a catalyst engineered to harness the unique functions of each metal. The inclusion of Ni and Co modifies the electronic environment of Pt, enhancing its catalytic efficiency for HER. Research has shown that this alloy structure surpasses conventional Pt/C catalysts by offering a larger electrochemical surface area, which promotes faster electron transfer and accelerates the reaction rate. The system's enhanced durability is due to the stabilising influence of Ni and Co during prolonged electrochemical reactions, making it a resilient choice for alkaline HER (Fig. 8) [28].

3.2.5. Ru@C_2N hybrid catalysts

Another innovative dual-phase system involves the Ru nanoparticles supported on nitrogenated holey carbon (C_2N). This hybrid catalyst leverages the high surface area and conductive properties of C_2N to achieve uniform dispersion of Ru nanoparticles, which enhances their interaction with the electrolyte. The C_2N structure aids in increasing water adsorption and subsequent dissociation - key steps in the HER process under alkaline conditions. The Ru@C_2N catalyst has demonstrated remarkable performance, achieving a low overpotential at 10 mA/cm² and, in some cases, surpassing the benchmark Pt/C. This performance increase is largely due to the effective modulation of the electronic structure of Ru by the nitrogen-doped carbon support (Fig. 9) [29].

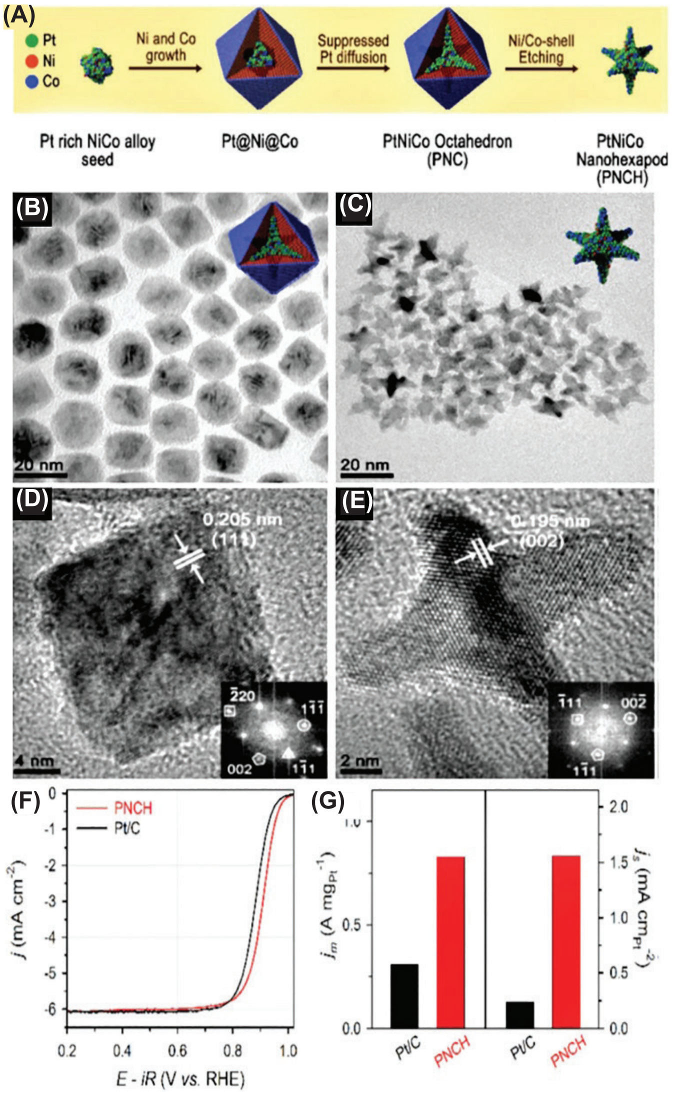

Fig. 8. Structural and electrochemical characterisation of Pt-Ni-Co ternary alloy nano frame catalyst for HER. (A) Schematic illustration of the synthesis process for Pt-Ni-Co nano frames, including the growth of Ni and Co on a Pt-rich NiCo alloy seed and subsequent etching; **(B-E)** TEM and high-resolution TEM images of the Pt-Ni-Co nano frames; showing their octahedral and nano hexapod structures with lattice spacings corresponding to the (111) and (002) planes; **(F)** Polarisation curves of Pt-Ni-Co nano frame (PNCH) compared to Pt/C, showing superior catalytic performance; **(G)** Comparison of mass and specific activities, demonstrating the enhanced activity of PNCH over Pt/C. Adapted from K. Eid, et al. (2022) [28].

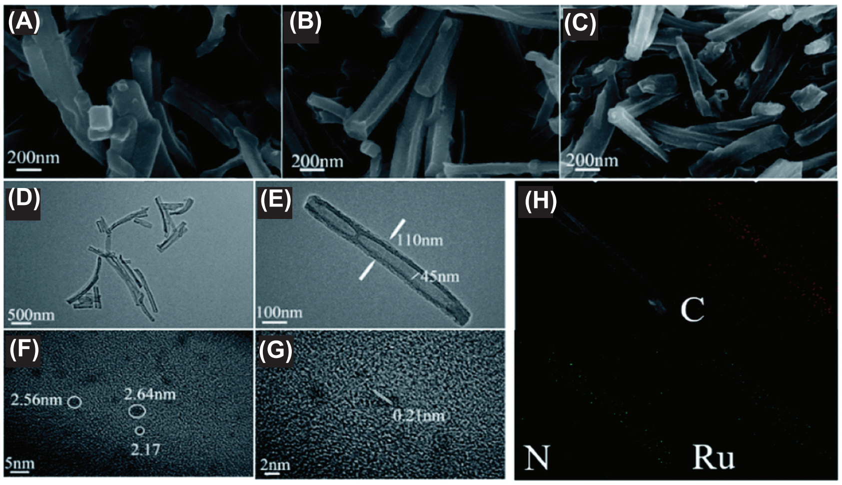

Fig. 9. Morphological and structural characterisation of Ru@C$_2$N hybrid catalyst. (A-C) SEM images showing the morphology of the Ru@C$_2$N hybrid catalyst; **(D-E)** TEM images reveal the tubular structure with uniform Ru dispersion on the nitrogenated holey carbon (C$_2$N) support, with dimensions labelled; **(F-G)** High-resolution TEM images displaying the lattice spacings corresponding to Ru and C$_2$N phases, confirming the structural integrity of the hybrid; **(H)** Elemental mapping of Ru, C, and N, indicating the uniform distribution of Ru nanoparticles within the C$_2$N matrix. Adapted from Q. Liu, et al. (2020) [29].

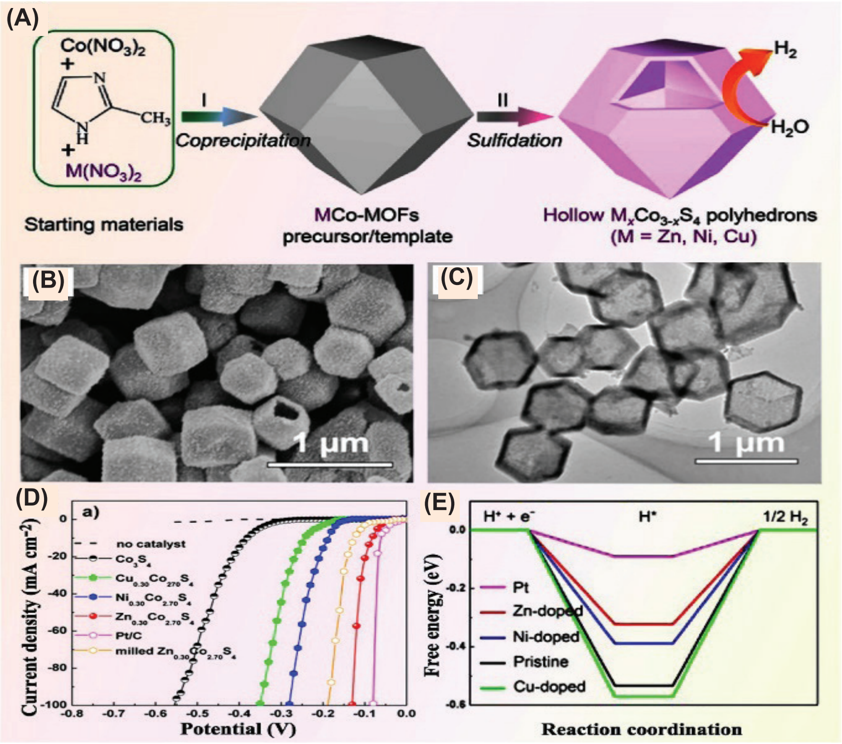

Fig. 10. Synthesis, morphology, and hydrogen evolution reaction performance of hollow MCo$_{3-x}$S$_4$ polyhedrons for dual-phase catalyst systems. (A) Schematic of the synthesis process for hollow MCo$_{3-x}$S$_4$ polyhedrons (M = Zn, Ni, Cu) via co-precipitation and sulfidation of metal-organic frameworks (MOFs); **(B-C)** SEM and TEM images display the hollow polyhedral structure; **(D)** Polarisation curves showing the HER performance of various MCo$_{3-x}$S$_4$ catalysts compared to Pt/C and Co$_3$S$_4$, indicating enhanced catalytic activity; **(E)** Free energy diagram for hydrogen adsorption. Adapted from Z. Chen, et al. (2019) [30].

3.2.6. CoP@BCN nanotubes

For transition metal phosphides, a dual-phase design with CoP encapsulated within boron and nitrogen co-doped carbon (BCN) nanotubes results in notable improvements in catalytic activity. The carbon matrix offers an excellent conductive network and structural stability, whereas the boron and nitrogen dopants enhance the catalytic properties of the CoP core by optimising the number of hydrogen adsorption sites. This synergy results in a lower overpotential and higher current density, indicating efficient HER performance in alkaline solutions (Fig. 10) [30].

These examples highlight the potential of dual-phase catalysts in addressing the limitations of single-phase electrocatalysts. Through strategic selection and engineering of constituent phases, researchers can attain substantial enhancements in both catalytic activity and stability, advancing the development of more cost-effective and efficient systems for hydrogen generation.

Table 2 offers an overview of recent dual-phase electrocatalysts for HER, detailing their morphology, active phases, testing conditions, particle sizes, performance metrics, and stability. The integration of diverse catalyst systems highlights the improvements in catalytic performance achieved through synergistic interactions in dual-phase designs, particularly under the demanding conditions of alkaline environments.

Table of reaction conditions, size, and performance: The key attributes of certain dual-phase catalysts, such as their reaction conditions, particle size, and HER performance parameters, are compiled in Table 3. This comparison shows how their catalytic performance is influenced by their morphological characteristics and reaction settings.

Table 2. Overview of dual-phase electrocatalysts for the hydrogen evolution reaction.

Catalyst system	Morphology	Active phases	Reaction condition	Particle size (nm)	Overpotential at 10 mA/cm²	Tafel slope (mV/dec)	Exchange current density (mA/cm²)	Stability
Pt-Ni-Co ternary Alloy	Nanoframe	Pt, Ni, Co	Alkaline (0.1 M KOH)	5-20	22 mV	59	0.9	High
Ru@C_2N hybrid	Hybrid nanosheet	Ru, C_2N	Alkaline (1 M KOH)	2-5	17 mV	38	0.75	Excellent
CoP@BCN nanotubes	Nanotube structure	CoP, BCN	Alkaline (1 M KOH)	20-30	215 mV	52	0.76	Good
Ni-FeP/carbon hollow nanorod	Hollow nanorods	Ni-FeP, carbon	Alkaline, acidic, neutral	20-50	~95 mV (acidic), ~117 mV (alkaline)	N/A	N/A	High
MoS_2-$CoSe_2$ hybrid	Nanosheet composite	MoS_2, $CoSe_2$	Acidic (0.5 M H_2SO_4)	5-30	N/A	36 mV/dec	N/A	Very High
$Mn_{0.5}Ni_{0.5}Co_2O_4$/carbon	Spinel structure	$Mn_{0.5}Ni_{0.5}Co_2O_4$, carbon	Alkaline (0.1 M KOH)	50-100	56 mV	N/A	N/A	High

Table 3. Hydrogen evolution reaction performance parameters.

Catalyst	Morphology	Reaction condition	Particle size (nm)	Performance (Overpotential at 10 mA/cm²)	Stability
Ni-FeP/Carbon hollow nanorods	Hollow nanorods	Alkaline, Acidic, and neutral	20-50	~95 mV in acidic, ~117 mV in alkaline	High
MoS_2-$CoSe_2$ Hybrid	Nanosheet-like composite	Acidic (0.5 M H_2SO_4)	5-30	36 mV per decade (Tafel slope)	Very high
$Mn_{0.5}Ni_{0.5}Co_2O_4$/Carbon	Spinel structure	Alkaline (0.1 M KOH)	50-100	56 mV at 10 mA/cm²	High

The data in the table underscores the influence of shape, size, and environmental factors on the electrocatalytic performance of dual-phase catalysts. For example, MoS_2-$CoSe_2$ hybrids and Ni-FeP/carbon hollow nanorods exhibit excellent performance across a wide pH range because of efficient electron transport pathways and optimised structural designs.

In conclusion, the shape and composition of dual-phase catalysts play a vital role in determining their HER efficiency. By fine-tuning structural elements such as particle size and active phase arrangement, researchers can significantly enhance the activity and durability of these catalysts. Transition metal phosphides, oxides, and dichalcogenides combined with conductive substrates represent a promising pathway for effective and durable HER electrocatalysis, especially in challenging alkaline conditions where stability is critical.

4. Enhancement strategies for dual-phase electrocatalysts

Interfacial engineering is pivotal in maximising the catalytic performance of dual-phase electrocatalysts. By modifying the interface between two phases, researchers can adjust electrical properties, improve charge transfer, and enhance catalyst stability under operational conditions. Recent studies, for instance, have shown that HER performance can be significantly enhanced through the controlled formation of heterojunctions between metal oxides and sulphides. A well-engineered $MoS_2/Ni_xFe_{1-x}S$ heterostructure, for example, demonstrated greater durability under alkaline conditions and a lower Tafel slope due to favourable band alignment at the interface, which facilitated electron transfer.

Another notable case is the $CoSe_2/MoSe_2$ hybrid system, where interfacial engineering enhances active site exposure and optimises hydrogen binding energies. This synergy led to high HER activity, achieving overpotentials as low as 120 mV at 10 mA/cm² in alkaline environments, which was attributed to effective charge transfer facilitated by the $CoSe_2$-$MoSe_2$ interface interaction. These advancements underscore the importance of interfacial control in dual-phase systems, where improved phase-to-phase contact can address limitations found in single-phase catalysts [31].

Future interfacial engineering research should focus on understanding atomic-level interactions at dual-phase interfaces. High-resolution techniques, such as high-resolution transmission electron microscopy (HR-TEM) and in-situ X-ray photoelectron spectroscopy (XPS), can capture real-time structural changes and reveal the mechanisms underlying enhanced catalytic activity (Fig. 11).

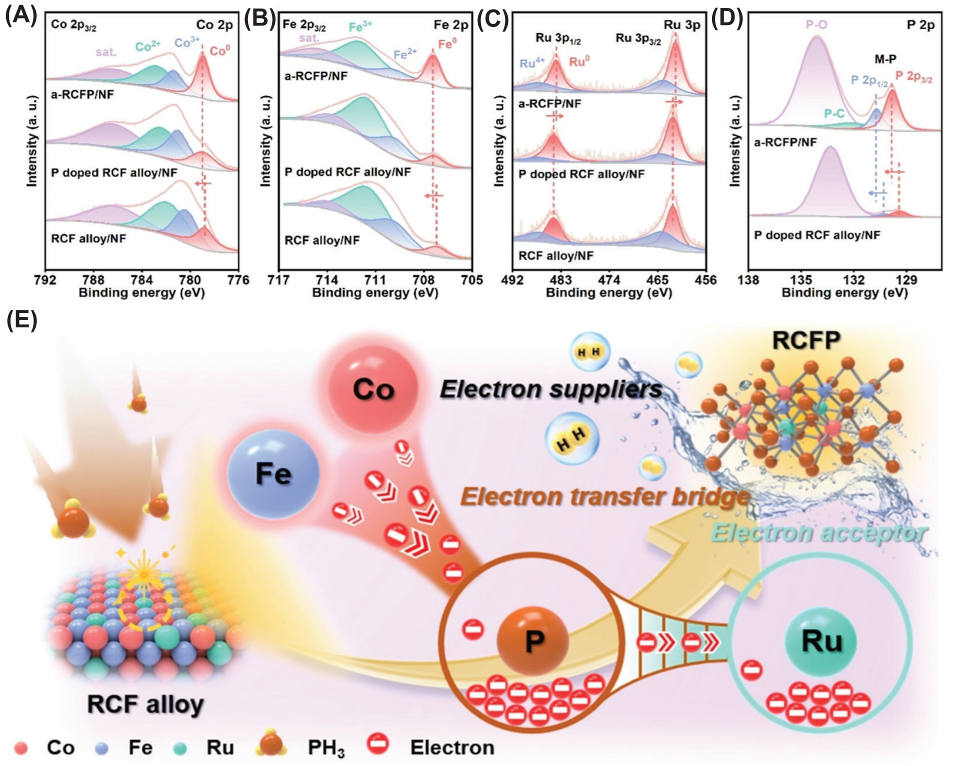

Fig. 11. Co-Fe-Ru-P (RCFP) dual-phase electrocatalyst for the hydrogen evolution process (HER): schematic representation of structural and electrical enhancement. Adapted from K. Jang, et al. (2023) [32].

4.1. Structural modifications: Hollow nanostructures

One of the most promising ideas for dual-phase HER electrocatalysts is the use of hollow nanostructures. In addition to enabling mass transit, these buildings greatly expand the surface area and reveal additional active places. Furthermore, hollow structures' internal holes lower material density, which can save production costs without sacrificing catalytic performance [33].

For example, because of their hollow design, which improves both mass and charge transfer, Ni-doped FeP/C hollow nanorods show good HER activity over a range of pH values [34]. Because of the enhanced stability of carbon support, which guards against material deterioration and structural collapse in the face of severe electrochemical conditions, these hollow nanorods also exhibit great durability.

4.2. Metal doping for enhanced activity and stability

Another essential tactic to increase the HER activity of dual-phase electrocatalysts is metal doping. Researchers can optimise the hydrogen adsorption and desorption processes by altering the electronic characteristics of the active sites by adding secondary metals to the catalyst structure. By lowering the rate of corrosion and limiting phase separation, doping can also increase the catalyst's structural stability.

In the case of Ni-doped FeP/C, Ni doping optimises the hydrogen binding energy and increases conductivity, which leads to quicker reaction kinetics [35]. In order to achieve excellent catalytic performance in a variety of pH conditions, Ni and FeP work in concert to improve electron transport and boost active site availability.

4.3. Atomic layer deposition for precision control

Atomic layer deposition (ALD) has become a potent method for creating atomic-level dual-phase catalysts with precise control. By producing high-density, precisely defined active sites, ALD enables the uniform installation of thin films or even single-atom layers, which is beneficial for improving HER. One noteworthy instance is the use of ALD to deposit Pt single atoms on nitrogen-doped graphene (NG), where the exact positioning of Pt on NG led to improved catalytic stability and optimum hydrogen adsorption [36].

However, atomic layer deposition has many drawbacks, especially in terms of cost and scalability. Because ALD requires expensive precursors and specialised equipment, its viability for large-scale manufacturing is limited, resulting in exorbitant prices. Furthermore, although fine control is possible with ALD's layer-by-layer growth process, it is time-consuming and would not be financially feasible for industrial-scale HER applications, where high-throughput synthesis techniques are usually preferred. The creation of hybrid ALD procedures that combine high accuracy with scalable methods, including chemical vapour deposition (CVD), may be one way to overcome these constraints while lowering costs and increasing throughput.

Combining atomic layer deposition with other scalable methods, including roll-to-roll processing or plasma-enhanced deposition, may help close the gap between commercial viability and laboratory efficiency in industrial applications. Investigating these hybrid strategies might offer a means to exploit ALD's precision advantages while also satisfying the scalability and cost constraints needed for sustainable hydrogen generation [37].

Table of enhancement strategies: The main enhancing techniques for dual-phase electrocatalysts are listed in Table 4, which also shows how each strategy affects catalytic performance, structural stability, and operational efficacy throughout various pH ranges.

Table 4. Parameters and performance of electrocatalysts.

Enhancement strategy	Description	Key benefits	Examples
Hollow nanostructures	Creating internal voids and reducing density	Increased surface area, better mass/charge transfer	Ni-doped FeP/C hollow nanorods
Metal doping	Incorporating secondary metals (e.g., Ni, Co)	Optimised hydrogen adsorption, enhanced stability	Ni-doped FeP/C for improved electron transfer
Atomic layer deposition (ALD)	Precise placement of single atoms or clusters	Maximised active site exposure, minimised precious metal use	Pt single atoms on N-doped graphene

4.4. Other structural enhancements

Other structural alterations, such as core-shell designs and nanoporous frameworks, in addition to hollow structures and doping, have also demonstrated efficacy in dual-phase HER catalysis. A sturdy, conductive core may be integrated with a catalytically active shell owing to core-shell architectures. Because the shell provides HER active sites and the core often improves electron transport, this arrangement optimises catalytic performance while preserving long-term durability.

In contrast, nanoporous frameworks provide a high surface-to-volume ratio and linked channels that enable effective mass movement. The fine-tuning of catalytic characteristics to meet certain operational needs is made possible by these frameworks, which also provide catalyst designers with more freedom [38].

There are many different ways to improve the performance of dual-phase electrocatalysts, and each one offers special benefits. While metal doping and ALD provide fine electrical alterations that improve catalyst durability and reaction kinetics, structural modifications such as hollow nanostructures and core-shell designs increase the accessibility of active regions. Owing to their integrated strategies, dual-phase catalysts have been developed to satisfy the requirements of scalable and effective hydrogen generation in a variety of operating settings.

5. Challenges and future prospects

Because of their synergistic characteristics, which improve their catalytic activity and stability, dual-phase electrocatalysts have demonstrated great potential in furthering HER. However, there are still several issues with their durability, scalability, and optimisation. To overcome these obstacles and advance the design of effective HER catalysts, this section addresses the present constraints and investigates potential future developments, especially through the combination of computational and experimental methods (Fig. 12).

Fig. 12. Flowsheet overview of key challenges and approaches in next-generation catalyst design.

5.1. Challenges in scaling and long-term durability

Despite significant advancements in HER performance using dual-phase electrocatalysts, challenges persist in terms of scalability, long-term durability, and environmental impact. Moving dual-phase catalysts from laboratory research to large-scale industrial applications requires addressing the following challenges:

5.1.1. Scalability issues

Dual-phase catalysts often require time-intensive and costly fabrication methods, such as atomic layer deposition (ALD) and multistep doping. While these techniques allow precise atomic control, they pose barriers to large-scale production. Hybrid methods, such as combining ALD with roll-to-roll manufacturing or chemical vapour deposition (CVD), show potential for achieving atomic-level precision while reducing costs [39]. Additionally, understanding the optimal interaction between phases for tuning adsorption energies and electron transfer at the nanoscale is crucial, especially for balancing hydrogen adsorption with water dissociation in alkaline media.

5.1.2. Stability under operating conditions

Stability during extended HER operation, particularly in alkaline environments, remains a significant concern. Earth-abundant catalysts (e.g., those based on iron, nickel, and cobalt) are vulnerable to oxidation and dissolution. Innovations in self-healing materials offer potential solutions; for example, catalysts with reversible bonding or phase transformation mechanisms exhibit resilience, allowing them to "self-repair" during reaction cycles. Self-healing catalysts incorporating dynamic covalent linkages may be essential for extending the stability of industrial HER applications [40].

5.1.3. Environmental impact and sustainability of scaling dual-phase electrocatalysts

The environmental footprint of scaling dual-phase electrocatalysts demands attention, especially with an increased focus on sustainability. The transition metals commonly used in these catalysts must be sourced responsibly. High-energy synthesis processes may contribute to carbon emissions, potentially undermining the sustainability of hydrogen production [41]. The use of eco-friendly, earth-abundant materials (e.g., iron or manganese as substitutes for platinum) aligns with green chemistry principles and could reduce costs. New synthesis techniques, such as bioinspired and low-temperature processes, present environmentally friendly alternatives. Life-cycle assessment (LCA) can further aid in identifying potential environmental impacts early on, enabling dual-phase catalysts to contribute positively to the hydrogen economy [42].

5.1.4. Catalyst poisoning and surface fouling

Catalyst poisoning-caused by contaminants accumulating on the catalyst surface and blocking active sites-remains challenging, particularly for dual-phase catalysts containing metal oxides or sulphides. Techniques such as in situ X-ray photoelectron spectroscopy (XPS) can track real-time surface changes and adsorbate behaviour during reactions, providing critical insights for mitigating fouling [43].

5.2. Future prospects: Integrating computational and experimental approaches

To design effective dual-phase electrocatalysts, a combined computational and experimental approach is crucial. This integration allows for efficient exploration and optimisation by leveraging structural and electronic synergies, leading to catalysts with enhanced performance.

5.2.1. Computational modelling and simulation

Techniques such as density functional theory (DFT) and molecular dynamics (MD) simulations are fundamental for designing HER catalysts, providing atomic-level insights into catalytic processes. DFT simulations can predict optimal hydrogen intermediate binding energies, allowing fine-tuning of active sites in dual-phase catalysts. Time-dependent DFT combined with Monte Carlo simulations can also model complex surface transformations and degradation cycles, offering accurate stability assessments under real HER conditions [44].

5.2.2. Machine learning and high-throughput screening

Advances in high-throughput screening and machine learning provide efficient tools for exploring large design spaces for dual-phase catalysts. Machine learning algorithms, trained on existing experimental and simulation data, enable rapid property and performance predictions for new material combinations. Automation-enabled high-throughput screening allows researchers to test numerous compositions under various conditions, streamlining the discovery process for optimal dual-phase catalysts [45].

5.2.3. Advanced characterisation techniques

Advanced techniques, such as scanning tunnelling microscopy (STM) and in situ XPS, are essential for validating computational predictions and observing catalytic behaviour in real time. These methods offer insights into dynamic processes such as surface fouling and degradation, providing crucial data for designing catalysts with long-term stability and efficiency [46].

5.2.4. Integration of computational and experimental workflows

A feedback loop combining experimental validation with computational predictions accelerates catalyst optimisation. For instance, computational models predicting doping effects on electronic structure can be confirmed experimentally, and iterative refinement enhances simulation accuracy, supporting the discovery of material combinations that optimise stability and activity [47].

5.3 Outlook: Designing next-generation dual-phase catalysts

Dual-phase HER catalysts show immense potential for future innovations, with promising avenues including the following:

Tailored nanostructures: Designing customised nanostructures, such as mesoporous frameworks, core-shell morphologies, or hollow nanospheres, can maximise the density of active sites and facilitate faster electron and mass transport. These architectures not only enhance intrinsic activity but also improve catalyst stability by reducing structural strain and preventing aggregation under operating conditions. Advanced synthesis techniques, such as atomic layer deposition or templating methods, offer opportunities for precise control over these nanoscale features, tailoring the catalyst properties to HER-specific demands [48].

Self-healing catalysts: Emerging developments in self-healing materials can address one of the most critical issues in HER catalysts: Degradation under harsh electrochemical environments. By integrating dynamic bonds, such as reversible covalent interactions or ionic cross-linking, self-healing catalysts can repair structural and chemical defects caused by prolonged operation. This could be particularly advantageous for dual-phase systems, where both phases can be engineered to exhibit complementary self-repair mechanisms, ensuring long-term durability and performance recovery [49].

Sustainable and abundant materials: As the global push for sustainability grows, the focus is shifting toward the development of dual-phase catalysts utilising earth-abundant elements, such as iron, cobalt, nickel, and molybdenum, paired with carbon-based materials. Future directions include exploring low-cost, scalable precursors such as biomass-derived carbon or recycled metals to reduce environmental impact. Additionally, innovative techniques like doping, alloying, or defect engineering can be employed to enhance the activity of these sustainable materials, making them viable alternatives to rare and expensive noble metals.

Multifunctional catalysts: Designing dual-phase catalysts that can simultaneously catalyse HER and other reactions, such as the oxygen evolution reaction (OER), could revolutionise overall water-splitting efficiency. By optimising the synergy between the two phases, multifunctional catalysts can provide higher energy efficiency and reduce operational complexity in integrated systems. Furthermore, introducing bifunctionality may enable their application in other energy-related reactions, such as CO_2 reduction, thereby broadening their utility.

While challenges in scalability, durability, and degradation resistance remain, integrating computational and experimental approaches offers significant promise for overcoming these obstacles. This combined strategy is likely to drive the development of next-generation HER catalysts, making scalable hydrogen production a viable and sustainable reality.

6. Conclusions

With notable gains in catalytic activity, stability, and durability over traditional single-phase catalysts, dual-phase electrocatalysts constitute a revolutionary development in the hydrogen evolution process (HER). The special advantages of dual-phase systems have been examined in this study, especially with respect to overcoming the difficulties of HER in alkaline media, where slow reaction kinetics and catalyst degradation are more noticeable. Dual-phase catalysts use complimentary materials to create synergistic features, such better electron transport and optimised hydrogen adsorption, which accelerate reaction kinetics and increase stability over a broad pH range. For example, when combined with conductive supports, transition metal phosphides, oxides, and dichalcogenides improve catalytic effectiveness by fine-tuning adsorption energies and increasing active site accessibility.

By employing cutting-edge improvement techniques, including metal doping, atomic layer deposition (ALD), and formation of hollow nanostructures, the design of dual-phase catalysts is further improved. Key catalytic features are optimised by each method: metal doping modifies electrical properties to promote hydrogen adsorption, hollow nanostructures increase surface area and mass transfer, and ALD allows for the exact placement of active atoms, resulting in highly effective, stable catalytic sites. When combined, these methods lessen the need for precious metals, cut production costs, and increase the long-term durability of catalysts.

Despite recent developments, dual-phase catalyst scaling for industrial applications is still difficult. The rapid industrial acceptance of these materials is constrained by the intricacy of synthesis techniques and problems with long-term stability, particularly in alkaline conditions. Innovative solutions including self-healing materials, the use of earth-abundant, sustainable materials, and sophisticated nano structuring processes will be needed to address these issues. High-throughput experimental screening combined with computational modelling and machine learning offers an intriguing chance to expedite the creation of affordable, high-performance catalysts by facilitating the quick investigation and verification of novel material combinations.

The integration of dual-phase catalysts with advanced electrolyser technologies, including membrane electrode assemblies and flow cell designs, can confer a further improvement in efficiency and industrial applicability. Most importantly, improved durability with variable operating conditions of temperature/pH shift remains a critical area of optimisation. Moreover, combining the dual-phase systems with renewable sources of energy, such as solar and wind, provides a pathway toward completely environmentally sustainable hydrogen production cycles. These integrated approaches will not only increase the practical utility of dual-phase catalysts but also support the transition toward a global hydrogen economy.

In conclusion, dual-phase catalysts are a significant advancement in the hydrogen economy and are ideally positioned to achieve the cost, efficiency, and scalability goals necessary for broad use. Their discovery offers a route to large-scale, economically feasible hydrogen generation at the nexus of materials science, electrochemistry, and computer modelling. Researchers are clearing the path for a sustainable hydrogen-powered future by utilising the special synergies present in dual-phase systems, which might make clean energy more widely available and reasonably priced.

CRediT author statement

Asad Ali Shah Zaidi: Conceptualisation of the review article, Literature search, Writing the manuscript as the main author and corresponding author; Zeeshan Ahmad: Reviewing, Data synthesis, Critical feedback; Iqbal Nisa: Reviewing, Data synthesis, Critical feedback; Sumayya Mumtaz: Editing, Refining the discussion and conclusions.

COMPETING INTERESTS

The authors declare that there is no conflict of interest regarding the publication of this article.

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