2025 4th International Conference on Computer, Electronic and Materials Engineering (ICCEME 2025)

"Research Progress and Application Prospects of Iron-Based Hydrogen Evolution Catalysts"

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Keywords: Hydrogen Evolution Reaction, Iron-Based Catalysts, Electrocatalysis

Abstract: Hydrogen energy is recognized as a key pillar of future sustainable energy systems due to its high energy density and zero carbon emissions. As the global demand for green hydrogen rises, water electrolysis powered by renewable energy has become one of the most promising methods for clean hydrogen production. However, the reliance on expensive and scarce noble metal catalysts such as platinum greatly limits the scalability of current technologies. In this context, iron-based hydrogen evolution reaction (HER) catalysts have attracted significant attention due to their earth abundance, low cost, environmental friendliness, and tunable catalytic properties. This review systematically summarizes recent progress in the design, synthesis, and application of iron-based HER catalysts. Key strategies including nanostructuring, heterointerface engineering, atomic doping, and single-/dual-atom catalysis are discussed, along with theoretical insights and advanced characterization techniques. Representative case studies are analyzed to elucidate structure–activity relationships and industrial feasibility. The challenges in durability, large-scale preparation, and mechanism clarity are also addressed. Finally, the prospects for integrating iron-based catalysts into practical green hydrogen systems are explored, providing guidance for future research and industrial applications.

1. Introduction

Hydrogen energy, due to its high energy density and zero carbon emissions, is widely regarded as a crucial pillar of future sustainable energy systems. According to projections by institutions such as the International Energy Agency (IEA) and China's National Development and Reform Commission, the proportion of hydrogen in the global energy consumption structure will significantly increase by 2050, playing a key role especially in the fields of industry, transportation, and electricity load balancing. However, over 90% of global hydrogen production currently relies on traditional fossil fuels (such as natural gas reforming and coal gasification), which not only results in massive carbon dioxide emissions but also contradicts the goal of a "green hydrogen economy." Therefore, developing efficient, clean, and sustainable hydrogen production technologies has become one of the core directions in current energy research.

Water electrolysis (WE), which can be powered by renewable energy sources (such as solar and wind), thus achieving zero emissions throughout the entire process, is considered the most promising method for hydrogen production. The core reactions of water electrolysis include the oxygen evolution reaction (OER) at the anode and the hydrogen evolution reaction (HER) at the cathode. Among them, HER in both acidic and alkaline electrolytes involves two-electron transfer steps. Although the reaction kinetics are relatively fast, it still heavily depends on efficient catalysts to reduce the overpotential and increase current density.

At present, noble metal catalysts such as Pt/C, Ru, and IrO_2 demonstrate HER performance close to the theoretical limit. However, their high cost, scarcity, and difficulty in large-scale deployment seriously limit their industrial applications. Therefore, developing efficient HER catalysts based on non-noble metal materials with high earth abundance, environmental friendliness, and low cost has become a research hotspot [3,17]. Among these, iron (Fe)-based materials have emerged as one of the most promising substitutes for noble metal catalysts due to their unique d-orbital electronic structure, good chemical stability, and abundant natural reserves [1,2,7 ,8].

DOI: 10.25236/icceme.2025.028

In recent years, with advancements in materials science and electrocatalytic theory, significant breakthroughs have been made in the research of iron-based HER catalysts. For instance, constructing heterojunction interface structures, introducing atomic-level doping, and developing single-atom/dual-atom catalytic mechanisms have not only significantly enhanced catalytic activity but also greatly improved durability and selectivity in both acidic and alkaline electrolytic environments. In addition, with the combined application of in situ electrochemical characterization techniques and density functional theory (DFT) simulations, researchers have gained deeper insights into the reaction pathways and active sites of iron-based catalysts during the HER process, providing a theoretical foundation for their rational design.

Nevertheless, iron-based HER catalysts still face several challenges that need to be addressed, such as structural degradation under industrial current densities, difficulty in balancing catalytic activity and electrical conductivity, and prominent issues in large-scale production and cost control. Therefore, a systematic review of current research progress on iron-based catalysts for hydrogen evolution, a clear understanding of existing problems and challenges, and an exploration of future research directions and application potential are of great theoretical and practical significance.

This paper aims to review the research background, material design strategies, representative research achievements, and application prospects of iron-based hydrogen evolution catalysts. It first introduces the performance and structural advantages of iron-based materials in HER, then focuses on commonly used structural regulation and performance optimization methods in current research, and finally looks ahead to their application prospects and future development directions under renewable energy systems, providing theoretical support and reference for relevant researchers.

2. Current Research Status of Iron-Based Hydrogen Evolution Catalysts

In recent years, iron-based hydrogen evolution catalysts have attracted widespread attention due to their low cost, high natural abundance, and excellent electrocatalytic activity. Extensive research has been conducted on structural regulation, interface engineering, elemental doping, and single-atom catalysis, which has significantly improved their HER performance in acidic, alkaline, and even neutral electrolytes. The following section systematically summarizes the current research status from four representative dimensions.

2.1 Nanostructure Regulation and Heterostructure Construction

Due to the various oxidation states of iron (Fe^{2+}, Fe^{3+}) [2,9,11,18] and its controllable crystal structures, iron-based materials can form a wide range of nanostructured morphologies under different synthesis conditions, such as nanowires, nanosheets, nanospheres, and 3D foam frameworks. These micro-/nanostructures can significantly increase the specific surface area, expose more active sites, and improve electron/ion transport capabilities.

Of particular interest is the strategy of heterostructure construction. For example, combining FeS with $Fe_5Ni_4S_8$ to form an n–n type heterojunction can create a built-in electric field at the interface, effectively promoting charge separation and transfer, thereby enhancing HER activity. In 2024, Su et al. constructed an $FeS/Fe_5Ni_4S_8$ heterostructure that achieved a current density of 10 mA cm^{-2} at only 178 mV overpotential under alkaline conditions, along with excellent stability, demonstrating the synergistic potential of nanostructures and interfacial effects.

2.2 Doping and Surface Modification Strategies

Introducing transition metals (such as Ni, Co, Mn, Mo) or non-metals (such as N, P, S, Se) for elemental doping can effectively regulate the electronic structure and d-orbital filling of iron-based materials, thereby optimizing the hydrogen adsorption free energy (ΔG_H*) and improving the reaction kinetics of HER intermediates.

For example, Wu et al. (2024) introduced an in situ sacrificial Fe protection layer on the surface of a CoP catalyst, which gradually released Fe species during the electrocatalytic process, significantly enhancing alkaline HER stability and current response. For non-metal doping, N-doping can lead to the formation of Fe–N_x coordination structures, providing high-density lone-pair electron active sites. In addition, surface modifications such as carbon coating and sulfide layers can effectively suppress metal dissolution and improve the durability of the catalyst.

2.3 Single-Atom Catalysis and Bimetallic Synergistic Strategies

Single-atom catalysts (SACs), which maximize atomic utilization and offer well-defined active site structures, have become a research hotspot for next-generation electrocatalysts. Anchoring Fe atoms on N-doped carbon substrates (Fe–N–C structures) can effectively enhance conductivity and catalytic selectivity. SACs have demonstrated HER performance superior to that of conventional polycrystalline metal materials in both acidic and alkaline systems [1,5,15].In recent years, researchers have further proposed the design of dual-atom catalysts (DACs), such as Ni–Fe or Co–Fe atomic pairs, leveraging electronic interactions and cooperative adsorption capabilities between two metal atoms to significantly improve reaction pathway selectivity. For example, Chen et al. (2023) fabricated a Ni/Fe dual-atom electrocatalyst that exhibited an onset overpotential of only 23 mV under acidic conditions, outperforming commercial Pt/C electrodes [3,4,24].

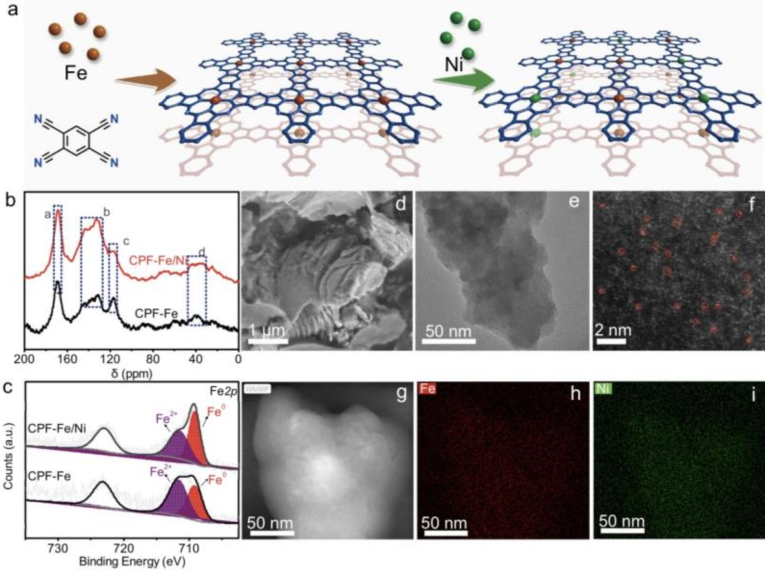


Figure 1: Schematic illustration and structural characterization of CPF-Fe/Ni.

As shown in Figure 1, the synthesis process of CPF-Fe/Ni, b Solid-state CP-MAS "C-NMR spectra of CPF-Fe and CPF-Fe/Ni,c High-resolution Fe2p spectra of CPF-Fe and CPF-Fe/Ni, the black curves are the fits data while the gray lines are the experimental results, d SEM and e TEM image of CPF-Fe/Ni,f-i HAADF STEM image and EDS-mapping results of CPF-Fe/Ni [5].

2.4 Advances in Theoretical Calculations and Characterization Techniques

In recent years, methods based on density functional theory (DFT) calculations have played a vital role in revealing the structure–performance relationships of catalysts. By simulating the interaction between Fe–X (X = O, N, P, S, etc.) active sites and hydrogen intermediates, researchers can screen material combinations with excellent catalytic performance. Meanwhile, theoretical calculations have also promoted the design of Fe-based materials in terms of charge density distribution and reaction pathway optimization at multiphase interfaces.

On the other hand, in situ electrochemical characterization techniques—such as in situ Raman, XPS, XAS, and TEM—have provided direct evidence of the structural evolution of iron-based materials during the HER process. For example, under high current densities, the surface of Fe_2O_3 can be transformed in situ into an $FeOOH/Fe^0$ active layer, and this dynamic reconstruction process may be one of the key factors contributing to the activity of iron-based catalysts.

3. Summary of Catalyst Design Strategies

To effectively enhance the electrocatalytic performance of iron-based catalysts in the hydrogen evolution reaction (HER), researchers have developed a series of structural engineering and interface regulation strategies focusing on three core objectives: "construction of active sites," "regulation of electronic structure," and "optimization of reaction pathways." The following summarizes five representative directions:

3.1 Nanostructure Construction and 3D Framework Design [3,9,29]

Constructing iron-based nanostructures with high specific surface areas and porous channels can significantly increase the number of electrochemical active sites and the efficiency of reactant transport. For example:

▪ Hollow nanospheres (Fe_3O_4@C) enhance specific surface area and prevent agglomeration;

▪ Nanosheet assemblies (FeP nanosheets) accelerate electrolyte diffusion.

These structures can effectively reduce internal resistance and simultaneously improve structural stability and long-term durability under high current densities.

3.2 Heterostructure and Interface Engineering Strategies [4,25,28]

By constructing interface heterostructures between iron-based materials and other transition metals or their compounds, it is possible to introduce built-in electric fields that enhance interfacial electron transfer efficiency. For instance:

▪ FeS/$FeNi_4S_8$ heterojunctions form n–n type interfaces that enhance charge separation ability during reactions;

▪ Fe@CoP biphasic structures exhibit electronic redistribution at the metal/metal phosphide interface.

The electronic “spillover” and charge polarization effects at the heterojunction interface accelerate the H^+ adsorption/desorption process, thereby optimizing the reaction pathway.

3.3 Doping Regulation and Active Site Engineering [2,16,21]

Iron-based catalysts are frequently doped with other metals (Ni, Co, Mn, Mo, etc.) or non-metallic elements (N, P, S, Se, etc.) to regulate electronic density, optimize d-orbital occupancy, and adjust hydrogen adsorption free energy (ΔG_H), thereby enhancing HER catalytic performance.

For example:

▪ N-doped Fe–C materials can form Fe–N_4 active sites, improving HER activity in acidic environments;

▪ Mo/Ni co-doped Fe_2O_3 can regulate surface electron cloud density, enhancing stability under neutral electrolyte conditions;

▪ Non-metal doping with S and P can also improve hydrophilicity and electrolyte affinity.

Doping strategies are diverse and are closely related to the oxidation state and coordination environment of iron, which ultimately determine the reaction pathways and catalytic performance. Figure 2 illustrates structure characterizations of the helical fibers.

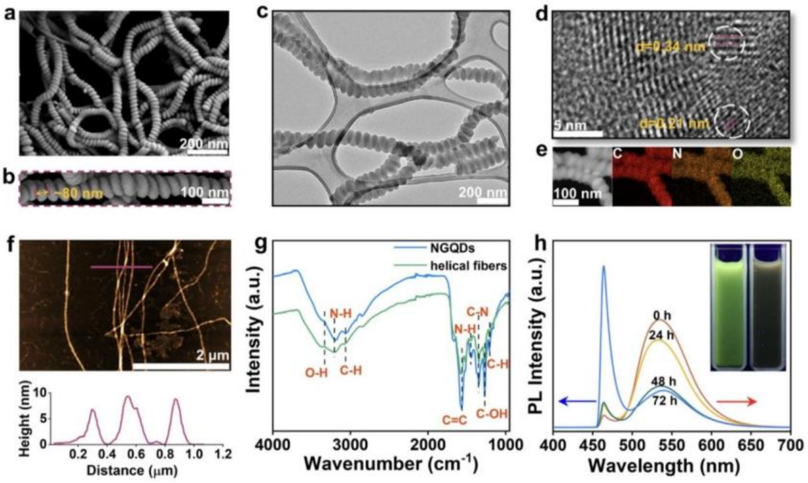


Figure 2: Structure characterizations of the helical fibers. Low-magnification

(a) and high-magnification (b) SEM images of the helical fibers. TEM image (c) and high-resolution TEM image (d) and STEM and elemental mapping images (e) of the helical fibers. fAFM image coupled with height-profile of the helical fibers. (g) FT-IR spectra of NGQDs and helical fibers. (h) Time-dependent PL spectra during the self- assembly of NGQDs, inset shows the optical photographs taken under UV (365 nm) and in dark [14].

3.4 Construction of Single-/Dual-Atom Catalytic Sites [1,5,6,14,15,19]

In recent years, single-atom catalysts (SACs) and dual-atom catalysts (DACs) have emerged as cutting-edge research directions for non-noble metal catalysts:

- $Fe–N_4$ single-atom sites provide uniform active centers and suppress aggregation;
- Ni–Fe atomic pairs enable synergistic adsorption and electron transfer regulation.

This strategy not only enhances atomic utilization but also simplifies the types of active sites, facilitating theoretical modeling and precise control. DACs are particularly suitable for constructing bifunctional catalysts (active for both OER and HER), thus supporting the overall optimization of water-splitting systems.

3.5 Surface Modification and Protective Layer Construction [27,29]

Iron-based catalysts are prone to corrosion and deactivation in strong acidic or alkaline electrolytes, making the development of surface protective layers and carbon coatings particularly important:

- In situ-formed Fe(OH)_x or FeOOH self-healing layers can enhance electrochemical stability;
- Graphitic carbon shell coatings can provide conductive pathways and prevent Fe^{2+} leaching;
- Oxide coatings (such as TiO_2, ZrO_2) can inhibit impurity corrosion from the electrolyte.

These protective layers also help regulate surface charge density and catalytic selectivity, ensuring long-term stability under high-intensity operation (e.g., >500 mA cm^{-2}).

3.6 Synergistic Multi-Strategy Optimization Design [20,26]

In practical applications, the integration of multiple strategies mentioned above has become a mainstream design approach. For example:

- Nanostructuring + doping + heterojunction interfaces;
- Single-atom sites + protective layer encapsulation;
- 3D conductive frameworks + interfacial electronic modulation + machine learning screening.

Through systematic structure–function–mechanism correlation design, challenges in catalyst activity, stability, and scalable preparation can be simultaneously addressed and overcome.

3.7 Comparison of Common Design Strategies for Iron-Based Catalysts: Advantages and Limitations

Design Strategy	Advantages	Shortcoming
Nanometer/3D skeleton	Increase active sites, accelerate mass transfer, facilitate electron transfer	Easy agglomeration, complex preparation
Heterostructure/integrand regulation	Forming built-in electric field, promoting charge separation, optimizing reaction path	Interface stability needs further improvement
Doping regulation	Optimize electronic structure, adjust adsorption energy, enhance selectivity	Difficulties in uniformity and load control during doping
Single/double atom catalyst	Maximize atomic utilization, site uniformity, and theoretical research convenience	Poor coordination environment stability, stringent preparation conditions
Surface coating/protection layer	Improve corrosion resistance and structural stability, extend service life	May hinder partial active site exposure, affecting activity
Multi-strategy optimization	Comprehensive performance improvement, suitable for industrial frontier fields	Cost increase, complex synthesis process, need to control parameters and their synergistic effects

Figure 3: Comparison Table of Advantages and Disadvantages of Common Design Strategies for Iron-Based Catalysts.

Here is a comparison of the advantages and disadvantages of common design strategies for iron-based catalysts, shown in Figure 3.

4. Representative Case Studies

In the study of iron-based hydrogen evolution catalysts, numerous representative material systems have been widely reported. These systems not only demonstrate excellent electrocatalytic performance in experiments but also reveal intrinsic structure–property relationships through theoretical simulations and in-situ characterizations. This section selects several recent exemplary iron-based catalytic systems and analyzes them from four perspectives: material design strategy, performance metrics, reaction mechanism, and industrial applicability, aiming to provide valuable references for future research.

4.1 Self-Supported Iron Foam Electrode (Fe@NF) [3]

Design Strategy:

Iron nanoparticles were in-situ grown on a nickel foam (Ni foam) substrate via electrodeposition, forming a 3D porous Fe@NF structure. This self-supported electrode avoids the need for polymeric binders.

Performance:

- Overpotential of only 87 mV to reach 10 mA cm^{-2} in 1 M KOH solution;Top: 2.54 cm;
- Maintains stable operation for over 1200 hours at industrial current densities (1000 mA cm^{-2}), with Faradaic efficiency >99%.

Mechanism Analysis:

In-situ characterization reveals that Fe reconstructs into an $Fe(OH)_2/Fe^0$ interface layer during HER, forming an efficient electron transport pathway and suppressing excessive adsorption of hydrogen intermediates, thus enhancing HER kinetics

Industrial Potential:.

The high stability and binder-free preparation method make it highly compatible with industrial application as a cathode in alkaline electrolyzers.

4.2 FeS/$Fe_5Ni_4S_8$ Heterostructure Catalyst [4,25]

Design Strategy:

A one-pot solvothermal method was used to construct FeS and $Fe_5Ni_4S_8$ heterojunctions, forming an n–n type semiconductor interface.

Performance:

- Overpotential of 178 mV at 10 mA cm^{-2} in 0.5 M H_2SO_4;
- Tafel slope of 38.6 mV·dec^{-1}, indicating excellent charge transfer ability;
- Maintains stable HER performance for over 100 hours with negligible degradation.

Mechanism Analysis:

The interfacial electric field facilitates rapid charge migration. The heterojunction interface offers optimized hydrogen adsorption energy, forming high-density active sites. DFT calculations identify the Fe–Ni–S interface as the reaction "hotspot".

Industrial Potential:

The facile synthesis and scalable production make it suitable for HER in both alkaline and neutral electrolytes.

4.3 Ni/Fe Dual-Atom Catalyst (Ni–Fe DAC) [5,21]

Design Strategy:

A metal–organic ligand adsorption strategy was employed to anchor Ni–Fe dual atoms on a nitrogen-doped carbon substrate, preventing agglomeration and decomposition.

Performance:

- Ultra-low overpotential of 23 mV at 10 mA cm^{-2} in 0.5 M H_2SO_4;
- Very low Tafel slope (29 mV·dec^{-1}), reflecting favorable reaction kinetics;
- Capable of switching between acidic and alkaline media.

Mechanism Analysis:

Electronic coupling between Ni and Fe regulates the adsorption strength of H* intermediates and modulates energy barriers. DFT simulations show Ni centers favor adsorption, while Fe centers facilitate hydrogen release—creating a synergistic effect.

Industrial Potential:

SAC/DAC design provides a blueprint for high-efficiency electrolyzers, especially in compact and portable green energy devices.

4.4 Fe–Co–P/N–C Dual-Doped Nanomaterials [2]

Design Strategy:

A one-step pyrolysis method was used to synthesize Fe–Co–P/N–C nanomaterials by co-doping Fe and Co into a nitrogen-doped carbon matrix, forming a highly conductive and metal–nonmetal synergistic interface.

Performance:

- Overpotential of 74 mV at 10 mA cm^{-2} in 1 M KOH;
- Current retention >95% after long-term cycling;
- Low charge transfer resistance.

Mechanism Analysis:

Co doping enhances electronic coupling, P incorporation modulates interfacial charge density, and the N-doped carbon matrix provides a high-mobility electron network.

Industrial Potential:

Suitable for scalable water-splitting devices, this system offers strong structural tunability, low cost, and a synthesis-friendly process.

4.5 SAC-Type Fe–N–C Catalyst (Fe Single-Atom Sites) [1,6,14]

Design Strategy:

Fe atoms were uniformly anchored on nitrogen-doped porous carbon to form Fe–N_4 coordination sites. This design prevents Fe aggregation and ensures homogeneous active site distribution.

Performance:

- Onset potential of only 85 mV in 0.1 M PBS;
- Over 48 hours of stable electrolysis without performance loss;
- Turnover frequency (TOF) significantly higher than Fe nanoparticle-based catalysts.

Mechanism Analysis:

Fe–N_4 sites precisely regulate the electronic state of Fe centers, optimizing H* adsorption and lowering the reaction barrier. This structure serves as a key model in current SAC-based HER studies.

Industrial Potential:

Highly suitable for micro-scale devices and hydrogen production in artificial photosynthesis systems. Figure 4 shows the mechanistic investigation of the GQD-based assemblies.

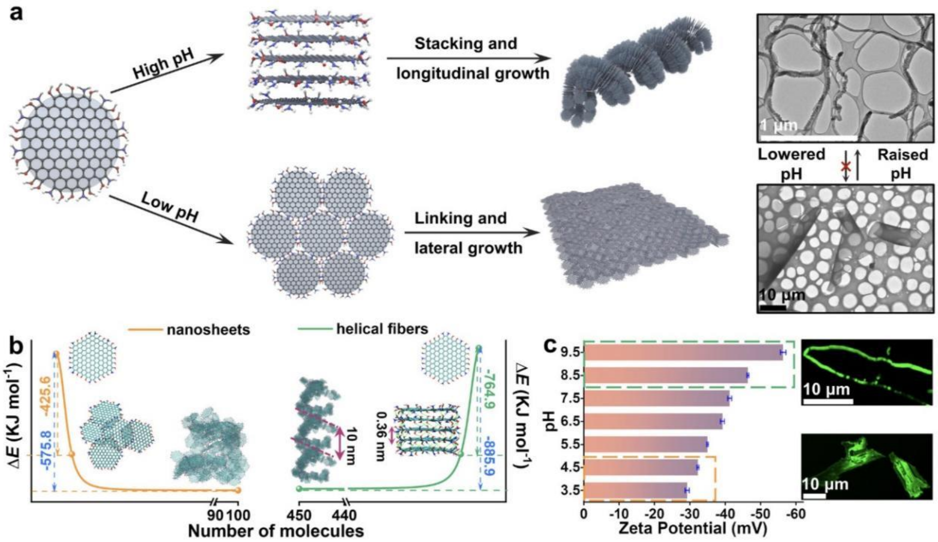


Figure 4: Mechanistic investigation of the GQD-based assemblies.

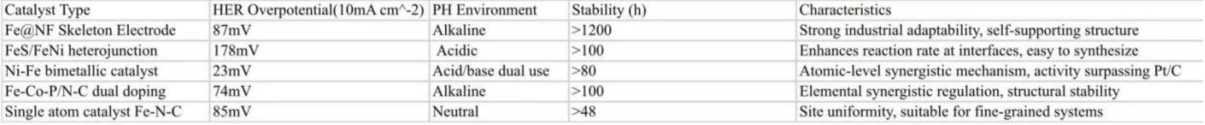
a) Schematic illustration of the NGQD self assembly under different pH. High pH promotes the formation of 1D nuclei, which stack up into helical fibers. Low pH lead to the formation of 2D nuclei, which link with each other into large 2D sheets. Shown in the up right are TEM images of the helical fibers and nanosheets.

b) Molecular dynamics simulation of the self-assembly process of NGQD at different pH as indicated by the calculated energy profile.

c) potential values of NGQDs-based architectures assembled under various pH conditions. Fluorescent optical micro- graphs of NGQDs-based architectures at high pH and low pH range [14].

4.6 Brief Summary

Different types of iron-based catalysts have achieved significant progress in structural regulation, activity enhancement, and stability maintenance. A comparison of the representative material performances is shown in Figure 5:



Catalyst Type	HER Overpotential(10mA cm^-2)	PH Environment	Stability (h)	Characteristics
Fe@NF Skeleton Electrode	87mV	Alkaline	>1200	Strong industrial adaptability, self-supporting structure
FeS/FeNi heterojunction	178mV	Acidic	>100	Enhances reaction rate at interfaces, easy to synthesize
Ni-Fe bimetallic catalyst	23mV	Acid/base dual use	>80	Atomic-level synergistic mechanism, activity surpassing Pt/C
Fe-Co-P/N-C dual doping	74mV	Alkaline	>100	Elemental synergistic regulation, structural stability
Single atom catalyst Fe-N-C	85mV	Neutral	>48	Site uniformity, suitable for fine-grained systems

Figure 5: Comparison Table of Performance Parameters of Representative Iron-Based Hydrogen Evolution Catalysts.

5. Application Prospects and Challenges [1,3,7,10,22,23,24]

Iron-based hydrogen evolution catalysts have become one of the most promising non-noble metal catalyst systems for future green hydrogen production due to their abundant resources, structural diversity, low cost, and good tunability. With the widespread adoption of renewable energy and the development of water electrolysis systems toward high current densities and long lifetimes, the transition of iron-based catalysts from laboratory research to industrial application is accelerating.

5.1 Application Prospects

5.1.1 Low-cost alternative catalysts for industrial water electrolysis systems

Commercial alkaline electrolyzers typically use catalysts such as Ni, Pt, and Ru, whose prices and resource limitations restrict further scale-up. In contrast, iron-based materials are easy to prepare and inexpensive (Fe metal market price < 1 USD/kg vs. ~30,000 USD/kg for Pt), offering potential for significant catalyst cost reduction. Some iron-based catalysts have demonstrated stable operation at 500–1000 mA cm^{-2} for over 1000 hours, indicating feasibility to replace Pt-based materials in alkaline industrial electrolyzers.

5.1.2 Ideal candidates for portable/micro-scale electrolysis systems

Systems such as micro wearable electrolyzers, artificial photosynthesis devices, and H_2 micro-gas sensors require compact size, high surface area, and stability. Lightweight and highly active materials like Fe–N–C single-atom catalysts can adapt to complex spatial and environmental conditions, making them especially suitable for future highly integrated micro-scale hydrogen energy devices.

5.1.3 Integration into multifunctional systems: overall water splitting, CO_2 reduction, photo/electrocatalysis

Iron-based catalysts exhibit excellent HER performance and multifunctionality, enabling participation in overall water splitting (OER + HER) or synergistic coupling with CO_2 reduction reactions. Some bifunctional Fe–Ni and Fe–Co materials can switch between oxygen and hydrogen evolution on the same electrode, advancing integrated water splitting systems.

5.1.4 Promoting the “green hydrogen–green electricity–energy storage” closed-loop development

Iron-based catalysts show good corrosion resistance in harsh environments (high temperature, high salinity, complex ions), suitable for coupling with seawater, industrial wastewater, and other electrolytes in wind/solar energy storage systems. This facilitates the construction of green closed-loop energy conversion systems and is promising for distributed hydrogen stations and remote unmanned energy supply equipment.

5.2 Key Challenges

Despite great potential, large-scale deployment of iron-based catalysts faces several critical bottlenecks:

5.2.1 Insufficient structural stability and active site deactivation [11,19,27,29]

At high current densities or in strong acid/base environments, iron-based catalysts often suffer from metal dissolution, uneven redox processes, and active site aggregation leading to performance degradation. The anchoring stability and dynamic evolution mechanisms of active sites in single-/dual-atom catalysts remain unclear. Achieving a dynamic balance between site stability and catalytic activity is a core research challenge.

5.2.2 Complex synthesis and lack of standardized preparation protocols [9]

Many high-performance iron catalysts require multi-step syntheses (templates, ionic liquids, sacrificial methods), leading to complicated processes, high energy consumption, and poor reproducibility. The absence of industrial-scale batch production standards restricts scaling and process adoption.

5.2.3 Unclear interface structure–performance relationships [12,28]

Although progress has been made in theoretical modeling and in-situ characterization, the exact active site configurations, electron rearrangement, and hydrogen adsorption/dissociation kinetics at heterogeneous interfaces (e.g., Fe/Ni, Fe/Co, Fe/S) remain debated, limiting predictive catalyst design.

5.2.4 Non-uniform performance evaluation standards [23,30]

Differences in electrolytes, reference electrodes, cell designs, and activity assessment methods among studies hinder cross-comparison of iron-based catalysts and slow industrial data consolidation.

5.2.5 High difficulty in coupled system integration [20,26]

In practice, iron catalysts must work synergistically with electrode materials, electrolytes, and mass transport interfaces. Properties such as conductivity, adhesion, and wettability directly affect overall efficiency. Currently, there is a lack of system-level coupling design standards for different reaction conditions.

5.3 Solutions and Research Trends

To accelerate industrialization of iron-based HER catalysts, researchers are tackling challenges through:

- Developing self-healing and in-situ reconstructing materials that form dynamic “active shells” induced by electric fields or pH to prolong lifespan.
- Employing machine learning/AI to rapidly screen novel active site combinations and enable performance prediction.
- Combining in-situ/operando characterization with theoretical simulation to elucidate active site dynamics and guide rational design.
- Optimizing macroscopic electrode structures by constructing self-supported, superhydrophilic, and electrolyte-philic 3D conductive networks to improve overall electrolyzer efficiency.

The organization is promoting standardized testing protocols and developing a database to unify HER testing conditions and data reporting, which will provide a solid foundation for engineering design.

5.4 Future Outlook

In the next 5–10 years, iron-based HER catalysts are expected to achieve breakthroughs in:

- Transitioning from “experimental optimization” to “theory prediction + experimental feedback loops,” enabling integrated design from materials discovery to industrial application.
- Expanding iron-based systems into acidic and neutral electrolytes to break the current “alkaline-only” usage limitation.
- Developing modular Fe-based electrode components for industrial hydrogen systems, facilitating integration with seawater electrolysis and flexible solar-driven devices.
- Becoming core components in energy–environment–chemical coupling systems, participating in carbon capture, nitrogen conversion, and multi-functional catalytic platforms for “multi-energy integration.”

6. Conclusion [7,11,13,16-17,19]

Iron-based HER catalysts, characterized by resource availability, structural diversity, and tunable properties, are increasingly becoming a research focus in green hydrogen production. Over the past five years, significant advances in material design, interface engineering, and electrocatalytic mechanisms have greatly expanded the applicability of iron-based materials across acidic, alkaline, and neutral electrolytes, with some systems exhibiting catalytic performances comparable to or exceeding noble metals like Pt.

This review systematically summarizes the development and current status of iron-based HER catalysts, emphasizing structural control strategies (e.g., nanostructuring, heterointerfaces, atomic site doping), performance enhancement mechanisms (electronic structure tuning, charge transfer optimization, stability improvements), and representative case studies. Further, it analyzes potential applications in industrial water electrolysis, portable devices, and renewable energy coupling systems.

Nonetheless, key challenges remain for translating iron-based catalysts from laboratory to industry:

- Stability and corrosion resistance: intrinsic iron activity suffers from structural reconstruction and metal dissolution in harsh media.
- Scale-up and synthesis consistency: many high-performance catalysts rely on delicate chemical syntheses, limiting mass production.
- Unclear coupling of mechanism and structure: active site microkinetics are not fully elucidated, lacking transferable design paradigms.
- Non-uniform testing standards and incomparable data: impede material performance benchmarking and engineering decisions.

Future research should focus on:

1) Developing controllable dynamic reconstruction catalysts with in-situ adjustable active sites for efficient “active center generation during reaction.”

2) Integrating computational simulations and machine learning for high-throughput material screening, combining DFT and neural networks to accelerate discovery.

3) Multi-scale interface regulation from atomic to electrode level to build synergistic conductive, ionic, and electrolyte-philic electrode systems.

4) Establishing standardized testing platforms and databases to harmonize catalyst evaluation parameters (pH, reference electrodes, stability metrics), enhancing reproducibility and comparability.

5) Cross-disciplinary integrated system development linking photo/electrocatalysis, artificial photosynthesis, and solid oxide electrolysis to promote iron-based catalysts in “electricity–hydrogen–chemical” hybrid platforms.

With the advancement of carbon neutrality goals and accelerated global hydrogen strategies, iron-based HER catalysts are poised to play an indispensable role in future clean energy systems. They represent not only key high-performance non-noble electrocatalysts but also potential bridges connecting low-carbon energy and traditional industrial infrastructures. In the pursuit of a green, sustainable, and secure energy future, iron-based catalysts offer vast exploratory space and engineering potential.

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