Proceedings of CONF-MSS 2026 Symposium: Advanced Composite Materials and Polymer Chemistry
DOI: 10.54254/2755-2721/2026.AD34729

Research Progress on Hydrogen Evolution Reaction Driven by Nanostructure Regulation and Electronic Structure Engineering in Electrocatalysis

Jiahui Wang

School of Physics and Electronic Engineering, Harbin Normal University, Harbin, China
15331986505@163.com

Abstract. Electrolysis of water for hydrogen production is one of the key technologies for achieving the "dual carbon" goals and the sustainable energy transition. Developing efficient and stable hydrogen evolution reaction (HER) electrocatalysts is the core prerequisite for improving the overall efficiency of water electrolysis hydrogen production. This review systematically summarizes the research progress of HER electrocatalysts driven by nanostructure regulation and electronic structure engineering. This article elaborates on the reaction mechanism and structure-activity relationship of HER and reviews the latest progress of nanomaterial electrocatalyst systems. It systematically summarizes the multi-dimensional control strategies for performance optimization, including defect and vacancy regulation, crystal plane and crystal phase engineering, d-band electronic structure regulation, and design of multiple active sites in synergy. Finally, targeting practical industrial application demands, this work analyzes key challenges including long-term operational stability, structural reconstruction, electrolyzer compatibility, large-scale fabrication of nanomaterials and cost control, and presents a perspective on future research directions.

Keywords: Electrochemical hydrogen evolution, Nanostructure regulation, Electronic structure engineering, Transition metal compounds, Industrialization challenges

1. Introduction

Currently, the world is facing the depletion of fossil energy and the severe environmental pollution and greenhouse gas emissions caused by the combustion of fossil fuels. Hydrogen, characterized by sole water as its combustion product, zero carbon emissions, and high energy density, is regarded as one of the most promising clean energy carriers. Under the goal of "carbon peak and carbon neutrality" in China, hydrogen is encountering important development opportunities [1].

The current mainstream industrial hydrogen production methods include steam methane reforming, coal gasification, and electrochemical water splitting. Although the first two methods account for over 95% of the global hydrogen production, they consume a large amount of fossil fuels and produce CO_2. In contrast, electrochemical water splitting for hydrogen production uses water as the sole raw material and achieves zero carbon emissions, making it the greenest and most sustainable method [1].

The unique properties of nanomaterials arise from the small size effect, surface effect, and quantum size effect within the range of 1 to 100 nm [2]. These effects increase active sites, regulate the d-band center, and optimize ΔGH. Taking the nano-Ni-Mo alloy as an example, its hydrogen evolution overpotential decreases linearly with the reduction of grain size [3]. This work summarizes recent advances in nanostructure regulation and electronic structure engineering for HER catalysts.

2. HER reaction mechanism and structure-efficacy relationship

2.1. Analysis of energy barriers in the volmer-heyrovsky tafel mechanism

The HER mechanism is generally divided into three basic steps [3] (Figure 1). In acidic media, the first step of the Volmer reaction is $H_3O^+ + e^- \rightarrow H + H_2O$; subsequently, hydrogen is generated through the Heyrovsky reaction ($H + H_3O^+ + e^- \rightarrow H_2 + H_2O$) or the Tafel reaction ($2H \rightarrow H_2$). In alkaline media, the Volmer reaction is $H_2O + e^- \rightarrow H + OH^-$, the Heyrovsky reaction is $H + H_2O + e^- \rightarrow H_2 + OH^-$, and the Tafel reaction is the same [4]. The ease with which H is generated in the first step determines the speed of the entire reaction kinetics, so ΔG_h is widely used as a key descriptor for evaluating HER activity. Theoretical investigations reveal that ΔG_h exhibits a volcano-type correlation with the exchange current density. An overly positive ΔG_h corresponds to weak hydrogen adsorption, while an overly negative value leads to strong hydrogen adsorption; both cases hinder hydrogen production. Only when ΔG_h approaches zero can the catalyst balance efficient hydrogen adsorption and desorption simultaneously.

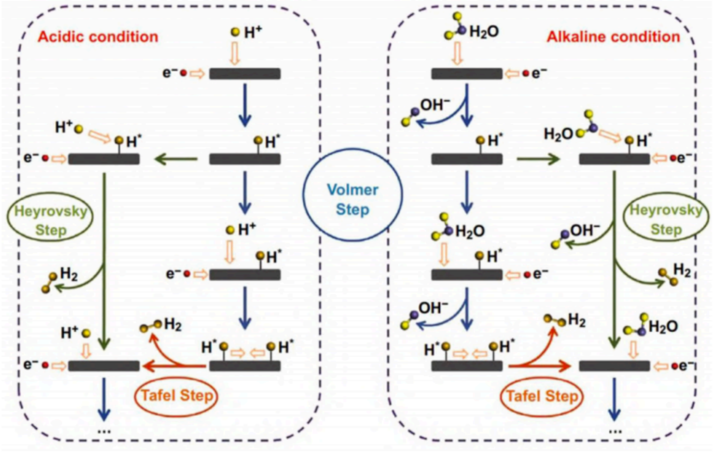

Figure 1. Schematic diagram of HER pathways [3]

2.2. ΔGH^* and the Sabatier principle

The Sabatier principle states that an ideal catalyst should form an "appropriate" adsorption strength with the reaction intermediate. In the HER, when ΔGH is too negative, H adsorption is too strong, making hydrogen desorption difficult and poisoning the active sites; when ΔGH is too positive, H adsorption is too weak, and the Volmer step is blocked. Only when ΔG_h is near thermodynamic neutrality (≈ 0 eV) can the catalyst deliver optimal electrocatalytic activity [5]. Defect engineering (oxygen vacancies, sulfur vacancies, metal vacancies, etc.) can effectively regulate ΔGH by changing the electronic structure of the catalyst surface and the position of the d-band center, and adjusting ΔGH* to the optimal range close to zero.

2.3. Hydrolysis kinetics and the bottleneck of alkaline systems

In alkaline HER, the hydrolysis step (Volmer step) is RDS, which requires breaking of the O-H bond with a high energy barrier and a large kinetic energy barrier. Although Pt has excellent H adsorption performance, its catalytic hydrolysis ability is relatively weak. In addition, the activity of alkaline HER is also influenced by the hydrogen binding energy and the hydroxyl binding energy together. Efficient alkaline HER catalysts need to simultaneously possess strong hydrolysis ability (usually requiring a higher hydroxyl binding energy) and moderate H adsorption ability [3] (Figure 2). This insight lays a theoretical foundation for the rational design of heterostructured catalysts.

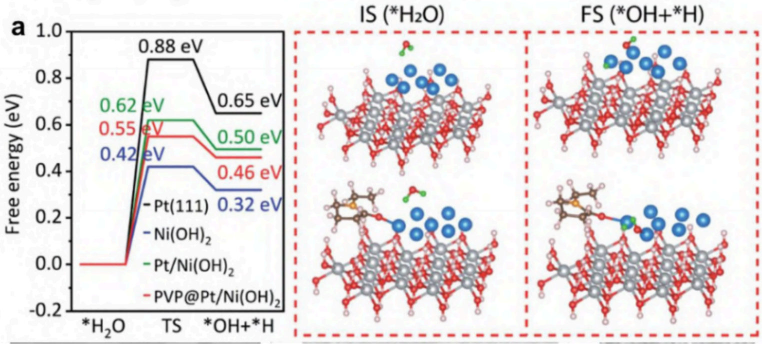

Figure 2. Schematic diagram of HER pathways in acidic and alkaline media [2]

3. Progress of nano-material electro-catalyst systems

3.1. Precious metals and their atomic-dispersed systems

Pt and its alloys are the benchmark catalysts for HER, but their high cost and low reserves limit their large-scale application. Alloying Pt with transition metals (such as Ni, Co, Fe, etc.) can increase the atomic utilization rate, and by utilizing ligand effects and strain effects, the d-band center of Pt can be regulated to optimize ΔGH* [6]. The core-shell structure (such as Pd@Pt) further finely regulates the electronic structure by taking advantage of the strain generated by lattice mismatch [7] (Figure 3). Monodisperse Pt catalysts anchor Pt isolatedly on the support, achieving nearly 100% atomic utilization rate, but the loading amount is low and the stability under high current density needs to be improved. Future research directions include: reducing Pt dosage via alloying, optimizing the coordination environment through monodisperse dispersion, and constructing a heterointerface by integrating a dissociation promoter.

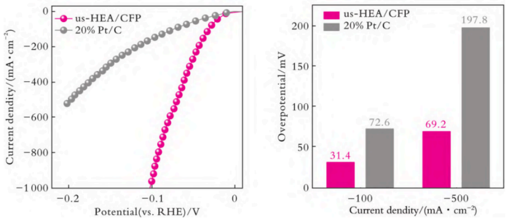

Figure 3. Microstructure and HER performance of ultra-small particle size PtRuFeCoNiCu high-entropy alloy [7]

3.2. Heterogeneous structures and interface engineering

Heterogeneous structures are formed by combining two or more functional components through interfaces, which can synergistically optimize water dissociation and H adsorption. Taking Pt/Ni$(OH)_2$ as an example, the edges of Ni$(OH)_2$ promote water dissociation, and H flows to the Pt surface to complete desorption, and the two work together to significantly enhance the activity. In Ru-CoO_x hollow nanoplatelet arrays, the Co sites accelerate water dissociation, and the Ru sites optimize H adsorption [3]. In terms of phase engineering, metallic 1T-MoS_2 has higher conductivity and more active sites than semiconductor 2H phase.Inducing the 2H→1T phase transition via strategies such as alkali metal intercalation can significantly enhance HER performance. The non-crystalline/crystalline heterojunction (such as CrO_x-Ni_3N) combines the advantages of the non-crystalline phase, which is rich in defects, high activity, and the crystalline phase with high conductivity, and the redistribution of interface electrons optimizes ΔGH.

4. Structural and electronic control strategies for performance optimization

4.1. Dimension and size engineering

Downsizing catalysts to the nanoscale induces the emergence of the small size effect and surface effect. The small size effect results in an increase in specific surface area and an increase in the number of active sites; the surface effect causes the surface atoms to be in an unbalanced coordination state, which has high chemical activity and makes it easier for H* to be adsorbed. Zero-dimensional nanoparticles, one-dimensional nanowires/nanotubes, two-dimensional nanosheets, and three-dimensional hierarchical structures each have their own advantages: two-dimensional materials (MoS_2, MXene) have large exposed surfaces, which are conducive to electron transmission; the three-dimensional hierarchical structure provides a larger specific surface area and a faster mass transfer path [2].

4.2. Electronic structure regulation and d-band engineering

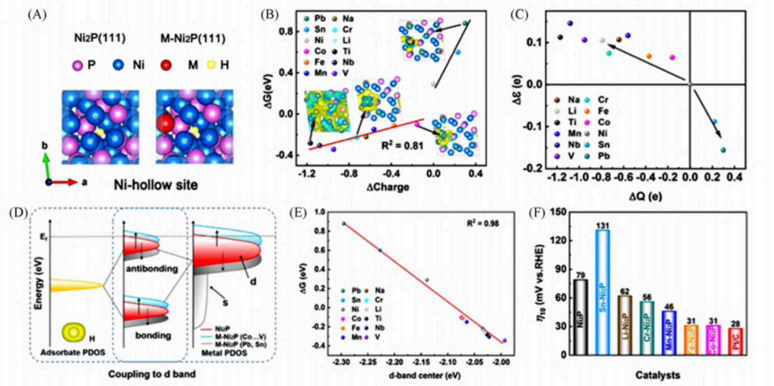

Figure 4. The correlation between the d-band center and the hydrogen adsorption free energy [8]

The position of the d-band center (εd) relative to the Fermi level determines the adsorption strength of H: an increase in εd leads to enhanced adsorption; a decrease in εd results in weakened adsorption. The optimal activity of HER requires ΔGH ≈ 0 eV, corresponding to an appropriate range of εd [8] (Figure 4). Doping is an effective means to regulate the d-band center: metal doping (Fe, Co, Ni, etc.) alters the d-band center of the host metal through ligand effects; non-metal doping

(B, C, N, O, S, etc.) optimizes the electronic structure through charge transfer. Strain engineering (lattice mismatch in core-shell structures) and hetero-interface coupling can also adjust the d-band center. Combining d-band theory with DFT calculations allows researchers to predict HER activity trends and guide the rational design of high-efficiency electrocatalysts.

5. Industrialization challenges and scaling issues

5.1. Performance degradation at high current density (>500 mA cm^{-2})

Industrial electrolysis of water requires a high current density to increase the hydrogen production rate. However, most laboratory catalysts perform well only at low current densities (<100 mA cm^{-2}), and their performance significantly degrades at high current densities [9]. The main reasons for degradation include: (1) Mass transfer limitation: A large number of H_2 bubbles adhere to the electrode, forming a "bubble shielding effect", which hinders the contact of the electrolyte; (2) Mechanical stability: Bubble scouring causes the catalyst to fall off; (3) Structural reconfiguration: Local pH and potential changes induce irreversible phase transitions; (4) Thermal effect: Joule heating leads to sintering and agglomeration. Corresponding strategies include fabricating 3D self-supported porous structures, introducing defect sites, heteroatom doping, and constructing heterointerfaces.

5.2. Long-term stability and structural reconstruction

The long-term operational stability of catalysts is crucial for their industrial application. Defect sites may undergo dynamic evolution, migration and even annihilation during long-term catalytic reactions, leading to irreversible structural reconstruction. For instance, sulfur vacancies may be refilled under reduction potential; some pre-catalysts may be in situ transformed into truly active phases (such as metal oxides/hydroxides reconfiguration), which may lead to an increase in activity but may also result in dissolution or collapse [5]. In-situ/operating condition characterization techniques (XPS, Raman, XAFS) can monitor electronic state changes and phase transitions in real time, identifying true active sites. By enhancing strong metal-based interactions, coating strategies, or designing adaptive catalysts, long-term stability can be improved.

5.3. Large-scale preparation of nanomaterials and cost control

Large-scale production and cost control are the core bottlenecks for electrolytic water hydrogen production to move from the laboratory to industry. Non-precious transition metal-based catalysts (Fe, Co, Ni-based oxides, hydroxides, chalcogenide compounds, etc.) have abundant reserves and low costs, and are regarded as ideal alternative materials. However, efficient catalysts in the laboratory often rely on complex synthesis processes (high-temperature, high-pressure hydrothermal, organic solvents, etc.), making it difficult to produce them at low cost, in large quantities, and with high reproducibility. It is imperative to develop facile, low-energy, and eco-friendly scalable synthetic strategies (e.g., room-temperature electrodeposition, solid-phase synthesis, continuous-flow reactions), establish evaluation criteria that better simulate industrial operating conditions, and advance anode alternative reactions such as urea oxidation and methanol oxidation to lower the overall energy consumption.

6. Conclusion

This review systematically summarizes the research progress of HER electrocatalysts driven by nanostructure regulation and electronic structure engineering. The kinetic bottleneck of the water dissociation step in alkaline systems remains key to enhancing performance. Strategies such as size and dimension engineering, defect and vacancy regulation, crystal plane and crystal phase engineering, d-band center tuning, and cooperative design of multiple active sites can effectively optimize catalytic performance. For industrial applications, major challenges include performance degradation at high current densities, long-term stability, structural reconstruction, electrolyzer compatibility, large-scale fabrication, and cost control. Future research should focus on developing novel catalysts with both strong water dissociation capability and moderate H* adsorption, leveraging multi-metal site synergy, exploring dynamic reconstruction catalysts under operating conditions, integrating AI and high-throughput computation to accelerate materials screening, and establishing material standards for GW-scale water electrolysis systems to advance highly active, stable, and low-cost HER electrocatalysts toward practical applications.

References

[1] Chen Yuefei, Xiao Ke, Wang Chaoyang, et al. Research progress of electrochemical water splitting catalysts [J]. Petroleum and Natural Gas Chemistry, 2024, 53(2): 62-70.
[2] Ma Haibin, Zhou Xiaoyan, Li Jiayi, et al. Rational design of heterogeneous structure electrocatalysts for promoting the kinetics of hydrogen evolution reaction in alkaline mediums [J]. Electrochemistry (Chinese and English), 2024, 30(1): 12-35.
[3] Xu Mingli, Zhang Zhengfu, Yang Xianwan. Research progress of nanomaterials and their applications in electrocatalysis [J]. Materials Report, 2006, 20(z2): 207-210.
[4] Song Jian, Yu Zongbao, Yang Zhanxu. Research progress on electrochemical hydrogen evolution using mo-based composites [J]. New Chemical Materials, 2022, 50(7): 67-72.
[5] Lang Chengguang, Xu Yantong, Yao Xiangdong. Optimizing Defects for hydrogen evolution reaction electrocatalysts: recent research progress and prospects [J]. Chinese Journal of Catalysis, 2024, 64(9): 4-31.
[6] Chen Ying, Yan Ronghua, Yin Weiyan, et al. Research progress on synthesis of metal monomer catalysts and their application in electrochemical hydrogen evolution [J]. University Chemistry, 2025, 40(9): 350-359.
[7] Chen Zheng, Sun Bing, Pan Yuan. Hydrogen evolution catalysis by transition metal phosphides: from nanoparticles to monomers [J]. Small, 2025.
[8] Zhang Qi, Zheng Dongqian, Liu Xinlu, et al. Research progress on high-performance hydrogen evolution electrocatalysts under high current density [J]. Low-carbon Chemistry and Chemical Engineering, 2024, 49(5): 96-104.
[9] Gao Qiulü, Diao Peng. Research progress and engineering application prospects of non-precious transition metal-based electrolytic water catalysts [J]. Journal of Engineering Science, 2025, 47(4): 923-939.