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Engineering internal electric fields in photoelectrochemical systems for enhanced hydrogen evolution: mechanisms, characterization and design strategies

Fen Qiao * and Bo Li

Photoelectrocatalytic (PEC) hydrogen production represents a pivotal technology for sustainable energy conversion, yet its efficiency is fundamentally limited by rapid charge recombination and sluggish reaction kinetics. This review highlights internal electric field (IEF) engineering as an innovative strategy to overcome these challenges by rationally designing catalysts at the nanoscale. We systematically discussed how tailored IEFs construction *via* heterojunctions, doping, surface modification, and strain engineering can dramatically enhance charge separation, transport, and surface redox kinetics in photoelectrocatalysts. By elucidating the underlying mechanisms (*e.g.*, band bending, dipole effects, and interfacial screening), we summarized universal principles for IEF manipulation across diverse materials, including metal oxides, chalcogenides, and 2D heterostructures. Furthermore, we critically evaluate performance breakthroughs in solar-to-hydrogen conversion enabled by IEF optimization. Challenges such as field stability under operational conditions and scalability are addressed, alongside emerging opportunities in machine learning aided design. This work not only provides a guide for next-generation photoelectrocatalysts but also extends IEF strategies to broader energy applications, underscoring their transformative potential in achieving carbon neutrality.

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1 Introduction

Photoelectrocatalytic (PEC) hydrogen production, a technology that directly converts solar energy into hydrogen, is regarded as a critical component of future clean energy systems due to its environmental friendliness, high efficiency, and sustainability.[1–5] The development of photoelectric hydrogen production traces its origins to Fujishima and Honda's pioneering demonstration of photocatalytic water oxidation on TiO_2 electrodes.[6] This work laid the groundwork for semiconductor-mediated photoelectrochemistry, extensive research endeavors have been dedicated to engineering advanced metal oxide materials with enhanced photocatalytic activity for solar-driven water splitting.[7–10] Follow-up studies prioritized visible-light-active materials such as Fe_2O_3,[11] $BiVO_4$,[12] and Cu_2O.[13] Progress in nanoscale morphology control and catalytic surface modification led to improved charge transport and reaction efficiency.[14–29] Contemporary strategies focus on tailored interface properties, internal field optimization, and device architectures to address challenges in efficiency and durability.[30–48] This ongoing advancement underscores a convergence of materials chemistry, photophysics, and catalytic engineering aimed at achieving scalable solar-driven hydrogen generation. However, current PEC hydrogen production technology still faces numerous challenges, including low catalytic efficiency, insufficient light absorption, and poor charge separation and transport

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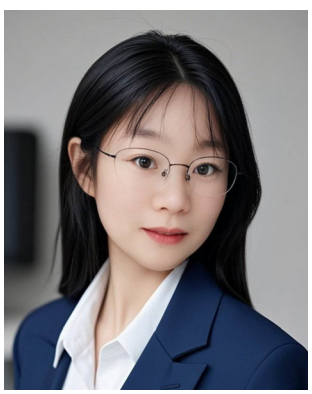

Fen Qiao

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properties, which significantly hinder its widespread application.

The urgent need for this review stems from the following critical gaps in the current research landscape. While built-in electric field catalysts have shown promise in enhancing PEC performance, no comprehensive analysis exists to unify the scattered mechanistic insights and design principles across heterojunctions, doping, and nanostructuring strategies. Recent breakthroughs in electric field modulation techniques (*e.g.*, atomic-level doping, interfacial engineering) have fundamentally reshaped understanding of charge dynamics but remain under-reviewed. Emerging applications of machine learning for electric field optimization present a paradigm shift in catalyst design that existing reviews have not addressed. This work uniquely bridges these gaps by establishing structure–activity relationships through a critical synthesis of cutting-edge studies, while providing a guide for next-generation catalyst development that distinguishes itself from prior summaries focused solely on material classifications or performance comparisons.

The design of catalysts with built-in electric fields has emerged as an innovative solution, offering a novel perspective to address these issues. By introducing an internal electric field within the catalyst, the separation, migration, and recombination processes of photogenerated electron–hole pairs can be effectively modulated, thereby enhancing the photoelectrocatalytic performance.[49] This strategy not only optimizes the band structure of the catalyst but also facilitates efficient charge transport at the nanoscale, providing a new approach for the development of high-performance photoelectrocatalysts.[50] In recent years, significant progress has been made in the development of catalysts with built-in electric fields, both domestically and internationally. By constructing heterojunctions, doping modifications, surface functionalization, and other strategies, researchers have successfully introduced internal electric fields within catalysts, markedly enhancing their photoelectrocatalytic (PEC) hydrogen production activity and stability.[51] These built-in electric field design strategies not only improve the light absorption capacity of catalysts but also optimize charge separation and transport pathways, thereby boosting catalytic performance.[52] However, despite the considerable potential of built-in electric field catalysts in PEC hydrogen production, research in this area remains in its early stages, facing several challenges.[53]

A key research focus and challenge lies in the precise control of the electric field's intensity, direction, and distribution within the catalyst to achieve optimal PEC performance. Additionally, issues such as fabrication processes, cost-effectiveness, and long-term stability of built-in electric field catalysts require further investigation and resolution.[54,55] The study of built-in electric field catalysts in PEC hydrogen production holds significant scientific and practical value.[56] These catalysts provide new insights into charge carrier behavior during PEC processes.[53] By modulating the internal electric field, researchers can gain a deeper understanding of the separation, migration, and recombination mechanisms of photogenerated electron–hole pairs, as well as their impact on catalytic performance.[54] This not only helps elucidate the fundamental principles of PEC hydrogen production but also offers theoretical guidance for developing more efficient and stable catalysts.[55] Built-in electric field catalysts hold promise for advancing the commercialization of PEC hydrogen production technology. By optimizing the band structure and charge transport properties, these catalysts can significantly improve efficiency, stability, and cost-effectiveness.[57] However, the practical application of PEC hydrogen production still faces numerous challenges, particularly in catalyst design and optimization.[58] Recently, built-in electric field catalysts have emerged as an innovative strategy to enhance PEC hydrogen production efficiency, warranting in-depth exploration of their current research status. The core principle of these catalysts lies in regulating the internal electric field distribution to optimize the separation and transport of photogenerated electrons and holes, thereby improving catalytic efficiency.[59] The realization of this strategy depends on precise control over the catalyst's band structure,[60] charge transport properties,[61] and surface chemistry.[62] Recent advances in catalyst design have demonstrated effective modulation of internal electric fields through strategic approaches including heterojunction construction, elemental doping, and nanostructure engineering. In heterojunction catalysts, the interfacial contact between materials with distinct band structures generates built-in electric fields that facilitate the separation of photogenerated electron–hole pairs. A representative example is the type II heterojunction formed by coupling wide-bandgap and narrow-bandgap semiconductors, which has shown remarkable enhancement in charge carrier separation efficiency.[63–65] Furthermore, the incorporation of dopants such as nitrogen or phosphorus enables precise tuning of the catalyst's band structure, thereby optimizing the spatial distribution of internal electric fields.[66] The architectural design of nanostructures plays an equally critical role in determining the performance of internal electric field catalysts.[67] Precise control over nanocatalyst morphology, dimensions, and spatial arrangement significantly improves charge carrier transport and collection efficiency. One-dimensional nanowires, two-dimensional nanosheets, and three-dimensional nanoporous frameworks have been widely employed in such designs due to their unique electronic transport properties and high specific surface areas.[68,69] These nanostructures not only promote charge separation and migration but also provide abundant catalytically active sites, collectively enhancing catalytic efficiency.

Beyond internal electric field modulation, the surface chemical properties of catalysts profoundly influence photoelectrocatalytic hydrogen evolution performance.[61] Surface modification techniques, including functional group grafting and chemical adsorption, can precisely regulate the electronic structure and surface chemistry of catalysts,

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thereby optimizing their interfacial interactions with reactants. For instance, the introduction of hydrophilic functional groups (*e.g.*, hydroxyl or carboxyl moieties) has been shown to improve both reaction kinetics and operational stability in PEC systems.[70] Several critical challenges remain to be addressed in the development of internal electric field catalysts for practical applications. Primarily, the stability and durability of these catalysts require substantial improvement to meet industrial operational demands. A second key challenge lies in the precise regulation of internal electric field distribution – achieving optimal spatial configuration and intensity remains both a research hotspot and a significant technical hurdle in maximizing photoelectrocatalytic performance. Furthermore, the scalability and cost-effectiveness of catalyst fabrication processes present additional obstacles that demand thorough investigation and innovative solutions. This review systematically summarizes recent advances in internal electric field catalyst design for photoelectrocatalytic hydrogen production, with particular emphasis on elucidating the fundamental mechanisms by which internal electric fields modulate catalytic performance (Fig. 1). Through comprehensive analysis of electric field construction principles and modulation strategies, we aim to reveal optimal pathways for photogenerated carrier separation and transport, establish structure–performance relationships to guide rational catalyst design and provide critical comparison of various electric field engineering approaches. By synthesizing current research findings, this work not only deepens the fundamental understanding of electric field-catalyst interactions but also provides new design principles for developing efficient and stable photoelectrocatalytic systems, ultimately facilitating their practical implementation.

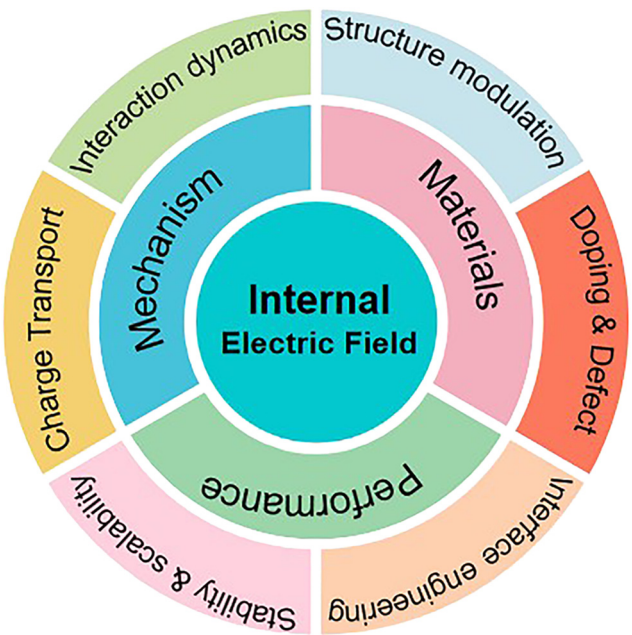

Fig. 1 Schematic illustration of internal electric field engineering strategies and their mechanistic roles in enhancing photoelectrocatalytic hydrogen evolution performance.

2 Theoretical foundations of internal electric field design

2.1 Mechanisms of electric field–catalyst interactions

The interaction mechanisms between electric fields and catalysts in internally designed electric field catalysts represent a critical factor for achieving high-efficiency photoelectrocatalytic hydrogen production. These mechanisms encompass multiple aspects including electric field-induced charge separation, migration acceleration, and band structure modulation.[71–73] In internally designed electric field catalysts, the established internal electric field promotes effective separation of photogenerated electrons and holes through field-driven forces.[74] Under illumination, photon absorption generates electron–hole pairs within the catalyst. The presence of an internal electric field induces directional migration of these charge carriers toward opposite directions, thereby achieving efficient charge separation.[75] Notably, both the intensity and orientation of the electric field significantly influence charge separation efficiency. Precise control over these parameters enables optimization of the separation process and enhancement of photoelectrocatalytic hydrogen evolution performance.[76]

Beyond charge separation, the internal electric field also facilitates accelerated charge migration within the catalyst.[77] Field-driven forces promote the transport of photogenerated electrons and holes toward the conduction and valence bands, respectively, where they participate in redox reactions with hydrogen and oxygen ions in solution to produce hydrogen and oxygen.[78,79] This field-enhanced migration process reduces charge recombination probabilities during transport, consequently improving both the reaction kinetics and operational stability of photoelectrocatalytic hydrogen generation.[80] The internal electric field further optimizes photoelectrocatalytic performance through band structure engineering. As a fundamental determinant of catalytic activity, the band structure can be precisely modulated by the internal electric field to favor both charge separation and migration processes.[81] Simultaneously, the electric field influences surface electronic structure and chemical properties, thereby optimizing catalyst–reactant interactions and enhancing catalytic activity.[82] Interface interactions between the electric field and catalyst surface constitute another critical factor affecting photoelectrocatalytic performance.[83] The electric field modifies surface charge distributions, consequently regulating reactant adsorption/desorption processes. Furthermore, it modulates surface redox reaction kinetics and optimizes reaction pathways to improve catalytic efficiency.[84,85]

The electric field–catalyst interaction mechanisms in internally designed systems thus serve as the foundation for high-performance photoelectrocatalytic hydrogen production.[86] Through strategic control of field intensity and

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orientation, optimization of charge separation/migration processes, band structure engineering, and interfacial interaction modulation, significant improvements in both efficiency and stability can be achieved.[87] Future research in this field promises deeper understanding of these interaction mechanisms, providing both theoretical guidance and practical strategies for developing advanced photoelectrocatalytic systems with superior performance characteristics.

2.2 Fundamental principles of internal electric field design

The design principles of internal electric fields are based on the photoelectric effect in semiconductor materials and the regulatory role of electric fields on charge carrier dynamics.[52] During photoelectrocatalytic hydrogen production, the catalyst absorbs photon energy to generate electron–hole pairs. However, the efficiency of this process is often limited by rapid charge recombination.[88] The internal electric field design addresses this challenge by establishing an intrinsic electric field within the catalyst structure, which utilizes electrostatic forces to facilitate effective separation and directional migration of photogenerated charge carriers, thereby reducing recombination probability and enhancing hydrogen evolution efficiency.[89]

The fundamental mechanism of internal electric field design lies in the precise modulation of the catalyst's band structure and charge distribution. The band structure determines two critical properties: (1) the light absorption capacity and (2) the energy conversion efficiency of the catalyst,[90] while the charge distribution governs the spatial separation and transport characteristics of photogenerated carriers.[91] Through strategic engineering of these two parameters, the separation pathways and migration trajectories of charge carriers can be optimized, leading to significant improvements in both the activity and operational stability of photoelectrocatalytic hydrogen generation systems.[92]

2.3 Design strategies for internal electric fields

The construction of internal electric fields in photocatalysts primarily employs three fundamental strategies: (1) heterojunction engineering, (2) elemental doping, and (3) nanostructure design.[56]

2.3.1 Construction of heterojunction. Heterojunction engineering involves the deliberate integration of semiconductors with distinct band structures to create interfacial electric fields.[93] Elemental doping modifies the electronic structure through the introduction of foreign atoms, thereby generating built-in potential gradients.[94] Nanostructure design enables precise spatial control of charge transport pathways through morphological engineering at the nanoscale (Fig. 2).[95] These synergistic approaches facilitate the establishment of directional internal fields that significantly enhance charge separation efficiency in photoelectrocatalytic systems.

2.3.2 Incorporation of dopant elements. The introduction of dopant elements represents another effective strategy for engineering internal electric fields within catalysts. By modifying the electronic band structure and charge distribution, dopant elements can induce the formation of built-in electric fields, which play a crucial role in facilitating charge carrier separation and transport (Fig. 3). The strength and direction of the resulting internal electric field are highly dependent on both the type and concentration of the dopants. Systematic optimization of these parameters enables precise control over the internal electric field, thereby enhancing both the efficiency and stability of photoelectrocatalytic hydrogen production.[96–100]

2.3.3 Nanostructure engineering. Nanostructure engineering represents a pivotal strategy for internal electric field design in photocatalysts. The unique structural characteristics of nanomaterials – including high specific surface area and abundant surface defects – provide numerous active sites and efficient charge transport pathways (Fig. 4).[101] Precise control over nanostructural morphology, dimensions, and spatial distribution enables optimization of both the intensity and spatial configuration of internal electric fields, thereby enhancing the efficiency and stability of photoelectrocatalytic hydrogen evolution.[102] Furthermore, tailored nanostructures can significantly improve light harvesting and energy conversion capabilities, leading to superior photocatalytic performance.[103] The design of internal electric fields through heterojunction construction, elemental doping, and nanostructure engineering offers an

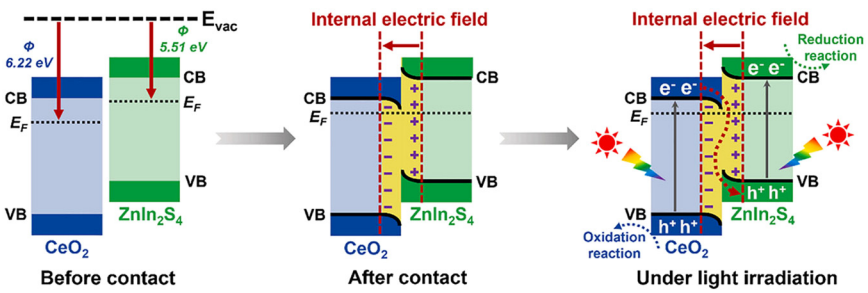

Fig. 2 Formation of $ZnIn_2S_4/CeO_2$ heterojunction photocatalyst and the proposed charge transfer paths, reproduced with permission from ref. 95 (Copyright 2023 Elsevier).

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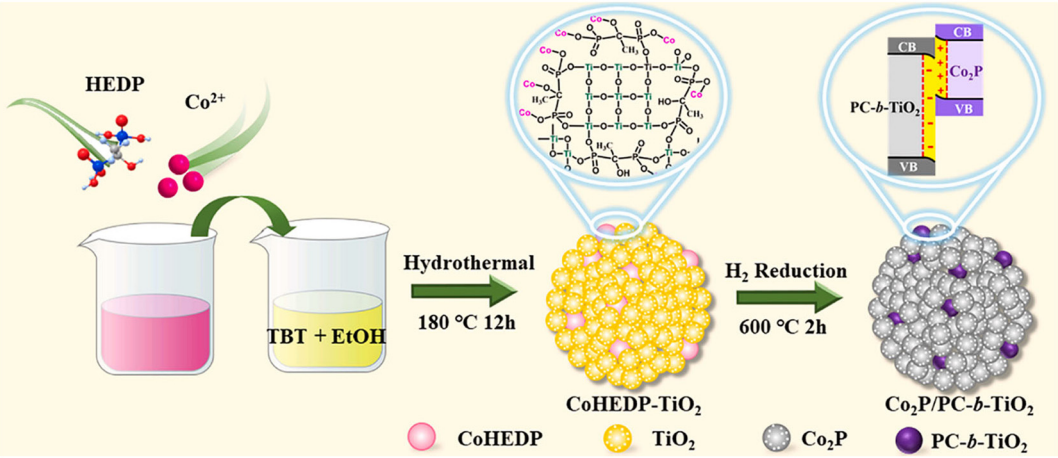

Fig. 3 Modification of P and C double-doped heterojunction, reproduced with permission from ref. 97 (Copyright 2022 Elsevier).

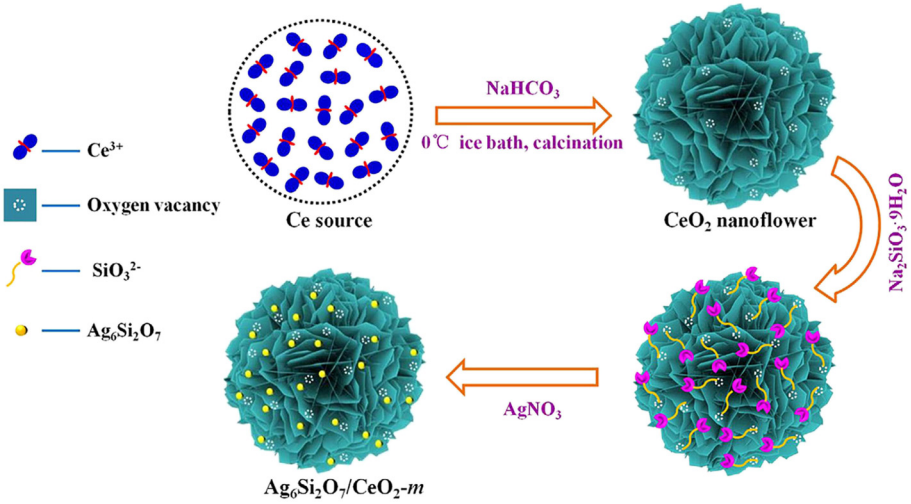

Fig. 4 Schematic diagram of $Ag_6Si_2O_7/CeO_2$-m nano structure, reproduced with permission from ref. 101 (Copyright 2020 Elsevier).

innovative paradigm for advancing photoelectrocatalytic hydrogen production. These approaches collectively enable precise modulation of electric field distribution within catalysts, optimization of charge carrier dynamics (separation, migration, and recombination), and substantial improvements in both activity and operational stability.[104,105] Future research should focus on elucidating the fundamental mechanisms governing internal electric field effects, which will provide crucial theoretical guidance for developing next-generation photocatalysts with exceptional performance.[106] Concurrently, practical considerations including catalyst durability, manufacturing costs, and scalability must be systematically addressed to facilitate the commercial viability of photoelectrocatalytic hydrogen production technologies.[107]

2.4 Critical factors influencing internal electric field design

2.4.1 Band structure of catalysts. The efficacy of internal electric field design is governed by multiple critical factors that require systematic investigation. The electronic band structure of catalysts constitutes a primary determinant in internal electric field design.[108] As a fundamental characteristic, the band structure governs three essential processes: (1) photon absorption efficiency, (2) energy conversion capability, and (3) the separation and migration pathways of photogenerated charge carriers.[109–112] Strategic engineering of the band structure enables optimization of charge carrier dynamics, thereby enhancing both the activity and stability of photoelectrocatalytic systems (Fig. 5a–d). Specifically, several band structure parameters critically influence the formation and intensity of internal electric fields, including the energy positions of conduction and valence bands, the bandgap width and the degree of band bending. These parameters collectively determine the built-in potential and charge separation efficiency in designed photocatalysts.

2.4.2 Dopant species and concentration optimization. Doping engineering represents a crucial approach for tailoring internal electric fields in photoelectrocatalytic systems.

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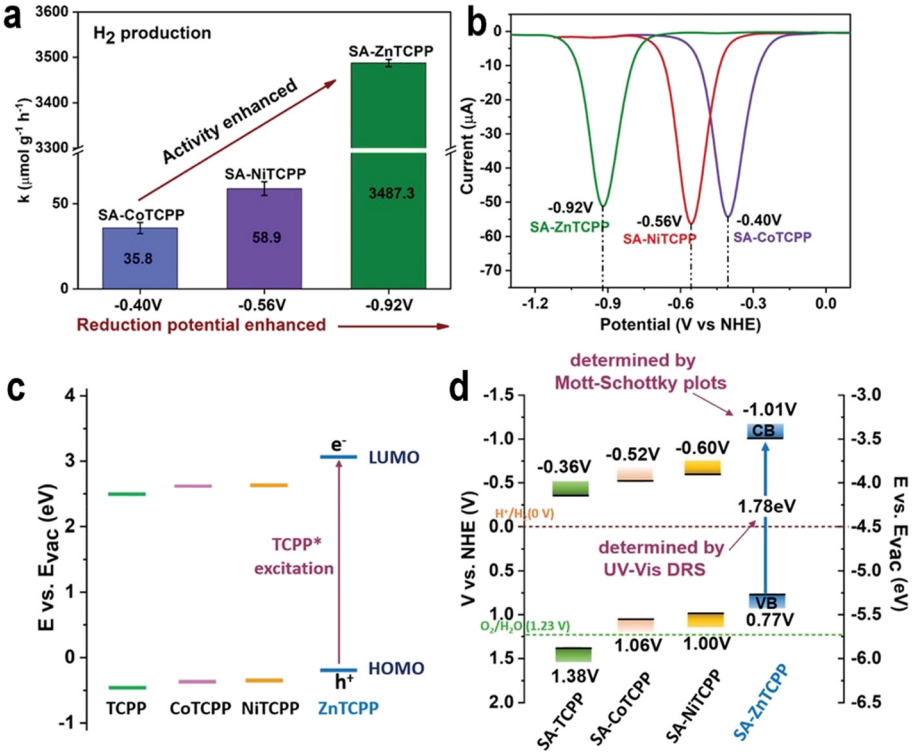

Fig. 5 (a) Comparative photocatalytic hydrogen generation performance of various supramolecular metalloporphyrins as a function of their elevated reduction potentials; (b) electrochemical characterization of redox potentials using differential pulse voltammetry; (c) HOMO and LUMO energy levels of the TCPP metalloporphyrin; (d) band alignment architecture for supramolecular porphyrins. Reproduced with permission from ref. 112 (Copyright 2021 Wiley).

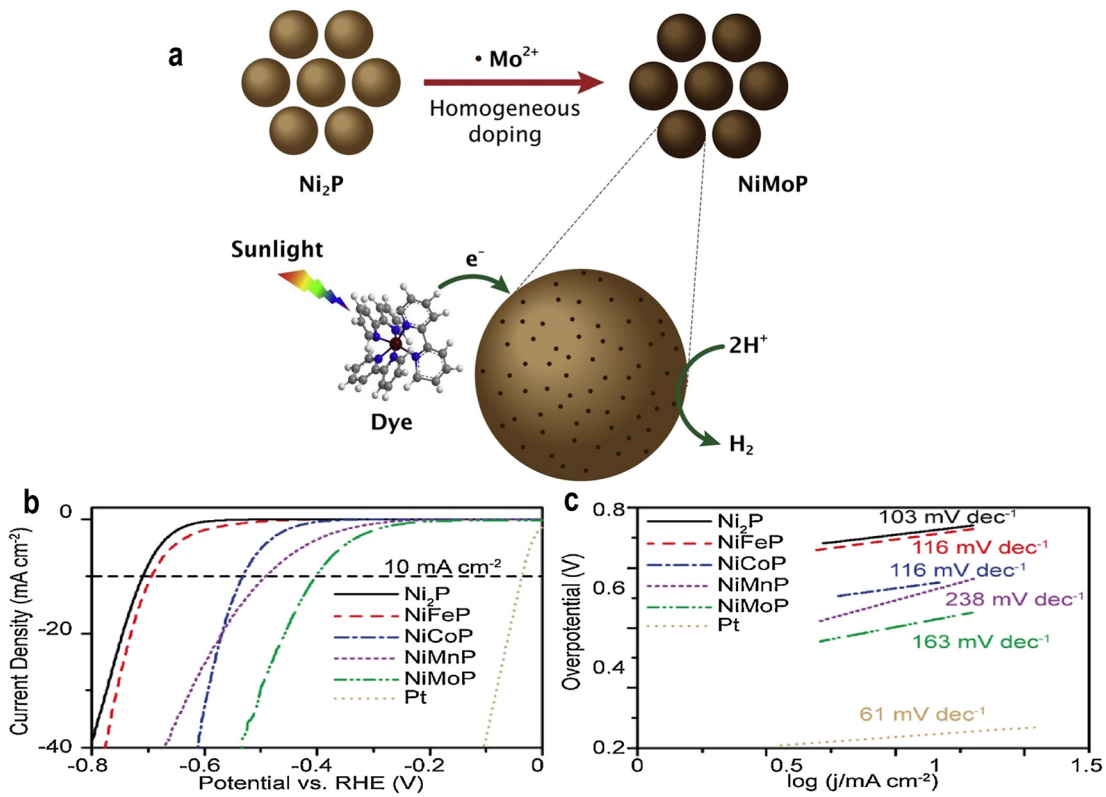

Fig. 6 (a) Optimized catalyst doped with transition metal Mo; (b and c) assessment of electrocatalytic activity for the HER. Reproduced with permission from ref. 113 (Copyright 2019 Elsevier).

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The strategic incorporation of dopant elements at optimal concentrations enables precise modulation of the catalyst's electronic band structure and charge carrier distribution, thereby facilitating the formation of desired internal electric fields. Extensive studies have demonstrated that both dopant species and concentration significantly influence the intensity and orientation of these internal fields.[113,114]

The selection of dopant elements must consider their fundamental physicochemical properties, such as the electronic affinity, which determines band structure modification. And the ionic radius, which affects lattice distortion and charge redistribution. These parameters collectively govern the electronic configuration and charge distribution characteristics of the doped catalysts.[115] Equally important is the dopant concentration, which directly controls the magnitude of the built-in electric field (Fig. 6a), the spatial distribution of potential gradients and the uniformity of charge separation efficiency (Fig. 6b and c).[113] Therefore, achieving optimal photoelectrocatalytic performance necessitates a systematic optimization protocol that simultaneously considers both dopant selection and concentration control. This dual-parameter optimization strategy is essential for maximizing internal field effectiveness, enhancing charge separation efficiency and improving overall catalytic performance. The rational design of doped photocatalysts should combine computational simulations with experimental verification to establish precise doping-property relationships, ultimately enabling the development of advanced photoelectrocatalytic systems with tailored internal electric fields.

2.4.3 Nanostructural engineering of catalysts. The nanostructural configuration of catalysts plays a pivotal role in the design of internal electric fields. Nanostructured materials possess two distinctive advantages, such as high

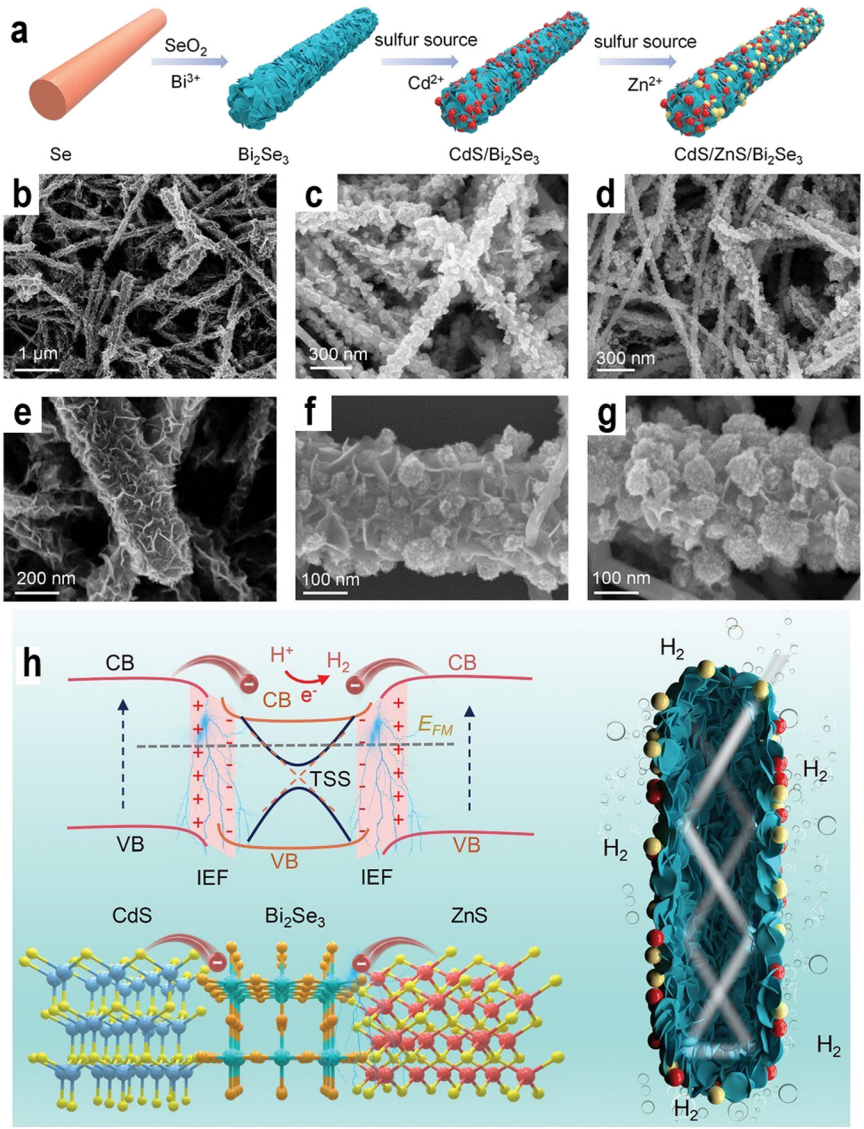

Fig. 7 (a) Fabrication process of the CdS/ZnS/Bi_2Se_3; SEM images of (b and e) Bi_2Se_3, (c and f) CdS/Bi_2Se_3, and (d and g) CdS/ZnS/Bi_2Se_3; (h) schematic diagram of multi-channel charge transfer in nanotubes. Reproduced with permission from ref. 117 (Copyright 2024 Wiley).

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specific surface area and abundant surface defects, which collectively provide numerous active sites and efficient charge transport pathways.[114] Precise control over nanostructural parameters (morphology, dimensional scale, *et al.*), and spatial arrangement, which enables optimization of both the spatial distribution and intensity of internal electric fields, thereby enhancing the efficiency and stability of photoelectrocatalytic hydrogen evolution.[115,116] Furthermore, tailored nanostructures can significantly improve photocatalytic performance through enhanced light harvesting capability, improved photon-to-electron conversion efficiency and optimized charge carrier dynamics (Fig. 7a–g).[117] Critical considerations in internal electric field design include morphology-dependent field distribution characteristics, size effects on electric field intensity, and structural–property relationships governing photocatalytic performance (Fig. 7h). These nanostructural parameters must be carefully engineered to achieve optimal electric field configurations and maximize photoelectrocatalytic activity. The rational design of catalyst nanostructures should therefore combine theoretical simulations with experimental characterization to establish fundamental structure–activity relationships.

2.4.4 Interfacial properties of catalysts. The interfacial properties of catalysts represent another critical factor influencing the design of internal electric fields. These properties govern both the interaction mechanisms between catalysts and reactants and the efficiency of charge transfer processes.[118] In internal electric field design, precise modulation of interfacial characteristics enables optimization of charge transfer across catalyst–reactant interfaces (Fig. 8a–d), thereby enhancing the efficiency and stability of photoelectrocatalytic hydrogen production (Fig. 8e).[119] Specifically, parameters such as surface charge distribution, defect states, and chemical properties significantly affect the formation and intensity of internal electric fields. Consequently, careful consideration of interfacial properties is essential for optimizing field distribution and overall photocatalytic performance.[120]

As an innovative catalyst design strategy, internal electric field engineering provides new perspectives for improving photoelectrocatalytic hydrogen evolution. However, its effectiveness depends on multiple interdependent factors, including the catalyst's band structure, dopant species and concentration, nanostructural features, and interfacial properties. Future research should focus on elucidating the fundamental mechanisms by which these factors influence internal electric field design and photoelectrocatalytic performance. Additionally, practical considerations such as catalyst stability, fabrication costs, and scalability must be addressed to facilitate the commercialization of photoelectrocatalytic hydrogen production technologies.

3 Application of internal electric field design in hydrogen production

3.1 Influence of internal electric fields on photoelectrocatalytic performance

The fundamental role of internal electric fields lies in their ability to facilitate efficient separation of photogenerated

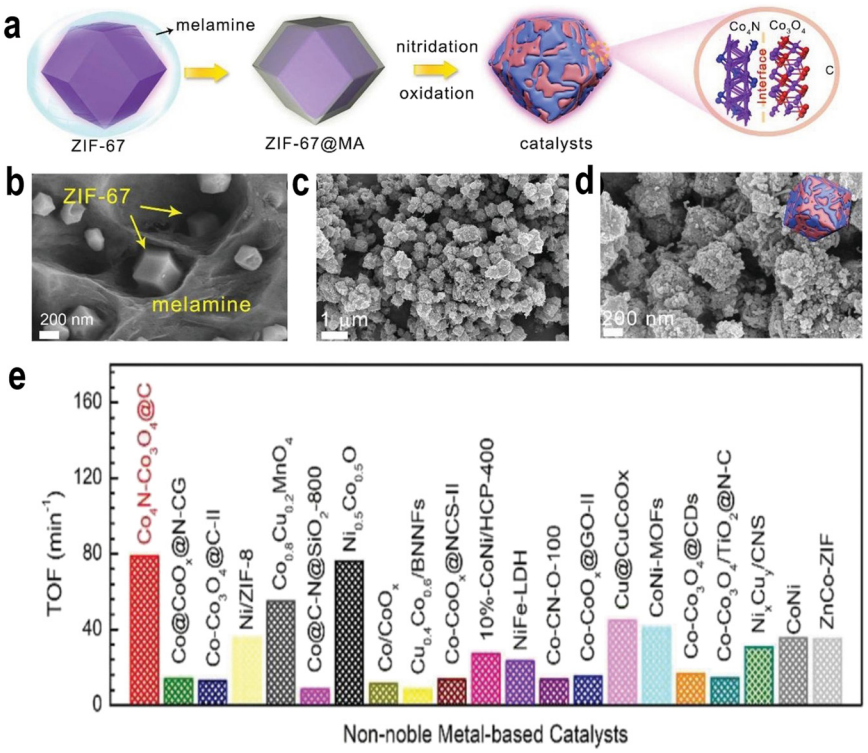

Fig. 8 (a) Schematic illustration of the synthesis procedure for Co_4N–Co_3O_4@C composites; scanning electron microscopy (SEM) characterization of (b) ZIF-67@MA, and (c and d) Co_4N–Co_3O_4; (e) comparative TOF of catalysts. Reproduced with permission from ref. 119 (Copyright 2022 Wiley).

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charge carriers. During photoelectrocatalytic processes, when catalysts absorb photon energy, electron–hole pairs are generated.[121] The presence of an internal electric field induces directional migration of these charge carriers along opposite directions under the influence of electrostatic forces, thereby achieving effective charge separation.[122] This field-driven separation mechanism substantially reduces the probability of electron–hole recombination while improving the utilization efficiency of photogenerated carriers, consequently enhancing the overall hydrogen evolution activity.[123] The spatial separation of redox-active sites further optimizes the catalytic process by minimizing backward reactions and improving charge transfer kinetics at the catalyst–electrolyte interface.

3.1.1 Band structure modulation and charge distribution optimization. The internal electric field plays a crucial role in optimizing charge distribution through precise modulation of the catalyst's band structure, which serves as a fundamental determinant of photoelectrocatalytic performance. The band structure governs three critical aspects: (1) the spectral range of light absorption, (2) the energy states of photogenerated carriers, and (3) their migration pathways.[124] By inducing controlled band bending, the internal electric field creates a favorable potential gradient that promotes directional charge separation. This gradient facilitates more efficient migration of electrons toward the conduction band and holes toward the valence band, thereby significantly enhancing both the reaction kinetics and overall efficiency of the photoelectrocatalytic process (Fig. 9a).[125] The synergistic effect of optimized band alignment and improved charge distribution contributes to superior catalytic performance by minimizing energy losses during charge transfer processes (Fig. 9b and c).

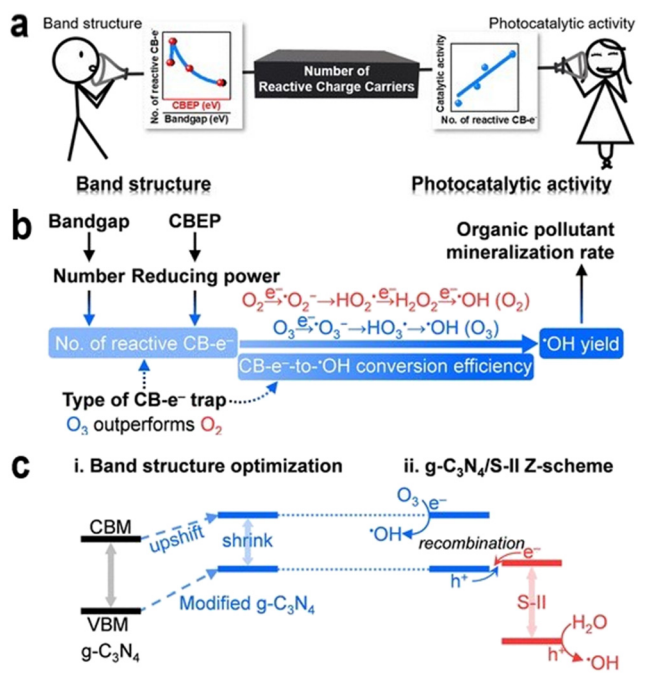

Fig. 9 (a) The influence of the number of active charge carriers on the band structure; (b) correlation of electronic band configuration with photocatalytic performance in g-C_3N_4; (c) strategic design principles for enhanced g-C_3N_4 photocatalysts. Reproduced with permission from ref. 125 (Copyright 2019 American Chemical Society).

3.1.2 Enhancement of light absorption and energy conversion efficiency. The internal electric field contributes significantly to improving both light absorption and energy conversion efficiency in photoelectrocatalytic systems.[126] This enhancement occurs through two primary mechanisms: first, the redistribution of charge carriers under the influence of the electric field can modify the catalyst's optical properties, including its refractive index and absorption coefficient, thereby optimizing photon capture efficiency.[127] Second, and more importantly, the internal electric field facilitates rapid separation and directional transport of photogenerated charge carriers. This process effectively minimizes energy losses associated with charge recombination, resulting in superior conversion of solar energy to chemical energy (Fig. 10).[128] The combined effect of these mechanisms leads to a substantial improvement in overall quantum efficiency, making the internal electric field a crucial factor in designing high-performance photoelectrocatalysts.

3.1.3 Regulation of surface reaction kinetics. The internal electric field exerts a profound influence on the surface reaction kinetics of photoelectrocatalysts. By modifying the charge distribution, the electric field can significantly alter both the surface charge state and spatial arrangement of active sites, thereby governing the adsorption and dissociation processes of reactants as well as subsequent chemical reaction rates (Fig. 11).[129] Furthermore, the electric field mediates reaction pathways through precise control of electron transfer processes, leading to enhanced selectivity and stability in photoelectrocatalytic hydrogen evolution.[130,131] As an innovative catalyst design strategy, internal electric field engineering demonstrates remarkable potential for advancing photoelectrocatalytic hydrogen production. The deliberate manipulation of internal electric fields enables comprehensive performance enhancement through: (i) optimized charge carrier separation and migration, (ii) improved light harvesting and energy conversion efficiency, and (iii) precisely tuned surface reaction dynamics. This multifaceted approach represents a significant advancement in the rational design of high-performance photoelectrocatalytic systems.

3.2 Current challenges in internal electric field design

Despite its demonstrated potential, the practical implementation of internal electric field design faces several critical challenges that must be addressed. The fundamental limitation lies in the difficulty of achieving precise spatial control over electric field distribution within catalyst architectures. This imperfect field modulation often results in non-uniform charge separation efficiency, ultimately compromising the overall photoelectrocatalytic hydrogen evolution performance.[132] Furthermore, the sophisticated

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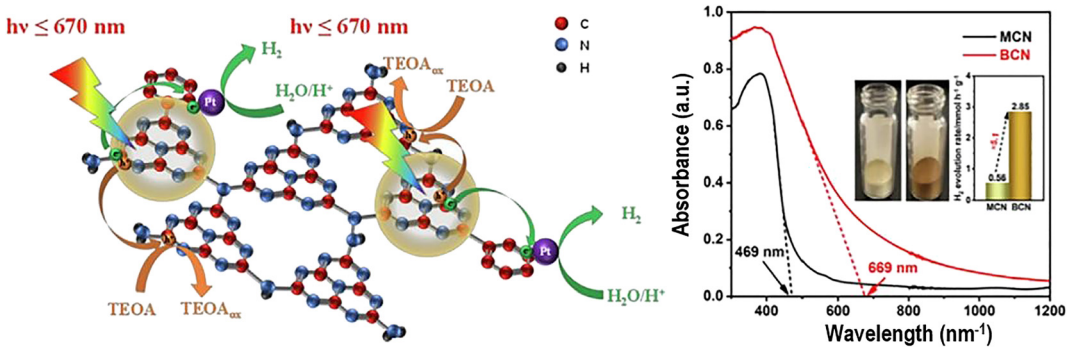

Fig. 10 Extended visible light phenyl-bound carbon nitride. Reproduced with permission from ref. 128 (Copyright 2022 Elsevier).

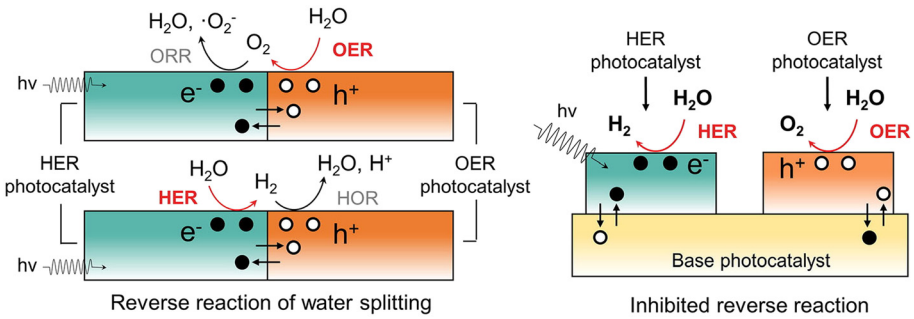

Fig. 11 Schematic diagram of the catalyst with varying charge distribution states. Reproduced with permission from ref. 129 (Copyright 2022, Elsevier).

structural configurations (*e.g.*, heterojunctions and nanostructures) commonly employed in internal electric field engineering exhibit inherent thermodynamic instability during prolonged operation (Table 1).[151–161] Such structural degradation not only diminishes catalytic activity but also severely impacts the long-term durability of photoelectrocatalytic systems.[133] From a practical perspective, the complex synthesis protocols and expensive precursor materials required for fabricating these advanced catalysts significantly elevate production costs, creating substantial barriers to commercial scalability. These collective challenges highlight the need for innovative approaches that can simultaneously address the fundamental limitations in field control while improving structural stability and cost-effectiveness.

Although the strategic design of internal electric fields has demonstrated remarkable efficacy in enhancing photoelectrocatalytic performance, the fundamental mechanisms underlying their influence on the separation, migration, and recombination processes of photogenerated electron–hole pairs remain insufficiently elucidated, thereby impeding further optimization of catalyst performance.[134] To address the challenge of imprecise electric field modulation, researchers should focus on developing high-precision

Table 1 Summary of preparation methods and fundamental properties of common photoelectrocatalytic materials for hydrogen evolution

Catalysts	Synthesize method	Morphology	Light absorption range	References
TNTs/STO/Ag_2O	Anodizing, hydrothermal and pulsed electrodeposition	Nanotubes	380–700 nm	151
NiS_2–ReS_2–V	High temperature calcination	Porous nanoparticles	—	152
S–$CoFe_2O_4$	Water bath vulcanization method	Nanorod-shaped	460–500 nm	153
$CoFe_2O_4$/CNS	Soaking calcination method	Nanotubular	200–800 nm	154
2D/2D$ZnIn_2S_4$/CeO_2	Low temperature solvent thermal method	Nanoflower-shaped microspheres	200–800 nm	155
$Ag_6Si_2O_7$/CeO_2	Co-cold precipitation method	Nanoflower-shaped	449–725 nm	156
SA-ZnTCPP	Precipitation method	2D nanosheets	300–698 nm	157
Mo(S,O)/Co(O,S)	Solvent thermal method	Rectangular nanorods	300–1500 nm	158
CdS/ZnS/Bi_2Se_3	Hydrothermal method	Hollow nanotubes	300–570 nm	159
Co(II)/PCN	Urea thermopolymerization method and high-temperature calcination method	Irregular nanosheets	200–800 nm	160
Re-CNN/CNN/Ox-CNN	High temperature calcination	Nanospheres	400–650 nm	161

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control technologies by employing advanced characterization techniques (*e.g.*, *in situ* spectroscopy[135] and electrochemical impedance spectroscopy[136]) to monitor field distribution, coupled with machine learning algorithms for optimized field design, enabling precise spatial regulation of electric fields within catalysts.

Enhancing catalyst stability can be achieved through structural modifications, including the development of robust heterojunction architectures,[137–145] utilization of corrosion-resistant materials,[146] and optimization of synthesis protocols. Surface engineering approaches such as protective coatings and functionalization may further improve the corrosion resistance during photoelectrocatalytic operations. Regarding cost reduction, exploration of abundant earth elements as active components, development of environmentally benign synthesis routes, and implementation of simplified fabrication techniques (*e.g.*, template-assisted methods[147] and self-assembly approaches[148]) represent promising strategies to minimize production expenses.

A comprehensive understanding of field-effect mechanisms requires synergistic integration of experimental characterization and theoretical simulations to elucidate the dynamic behavior of charge carriers under electric fields. The establishment of accurate physical models will be crucial for predictive catalyst design and performance optimization.[149] While internal electric field engineering stands as a potent strategy for advancing photoelectrocatalytic hydrogen production, existing challenges including limited field control precision, material instability, high manufacturing costs, and mechanistic uncertainties must be systematically addressed (Table 2).[152,162–169] Through concerted efforts in precision field engineering, stability enhancement, cost-effective fabrication, and mechanistic investigations, these obstacles may be overcome to facilitate the practical implementation of photoelectrocatalytic hydrogen generation technologies.[150]

3.3 Industrial challenges and IEF strategies for scalable systems

Although IEF engineering has demonstrated exceptional efficacy in laboratory-scale PEC hydrogen generation, its translation to industrial applications introduces multifaceted challenges. Achieving durable, cost-effective, and large-scale PEC systems necessitates a reassessment of IEF design principles through the dual lenses of scalability and practical integration.

3.3.1 Industrial challenges and the scalability gap. A primary obstacle lies in the scalable synthesis of nanostructured catalysts that maintain precise interfacial and dopant control. It is essential for establishing strong and uniform IEFs. Although techniques such as atomic layer deposition (ALD) afford excellent reproducibility at the research level, their low throughput and high cost hinder industrial adoption. Alternative high-volume methods, including spray pyrolysis and roll-to-roll printing, require further development to deliver the nanoscale accuracy necessary for consistent IEF implementation.

Operational durability presents another critical challenge. Industrial PEC environments is characterized by intense irradiation, extreme pH fluctuations, high electrolyte concentrations, and vigorous gas evolution, which can compromise the structural integrity of heterojunctions and interfaces responsible for IEF generation. Degradation mechanisms such as delamination, corrosion, and phase separation may lead to rapid attenuation of the built-in field and consequent loss of catalytic activity. Thus, sustaining IEF stability under continuous operation remains an imperative yet underexplored aspect of device longevity.

Moreover, system-level constraints including inefficient mass transport and non-uniform illumination impose additional limitations. Accumulated gas bubbles can block active sites and scatter incident light, diminishing overall efficiency. While IEF enhancement primarily targets interfacial charge dynamics, it does not intrinsically resolve these macro-scale engineering issues. Photoreactor designs must also ensure homogeneous light distribution across large electrode areas, as localized shading directly compromises photoexcitation and IEF driving force.

Finally, reliance on scarce (*e.g.*, Ga, In) or costly (*e.g.*, Pt) materials in many high-performance IEF systems undermines economic feasibility. Advancing toward industrial relevance mandates the adoption of earth-

Table 2 Comparison of catalysts based on built-in electric field design and their HER performance

Catalysts	IEF strategies	HER performance				
		Overpotential for HER (mV@10 mA cm^{-2})	Tafel slope (mV dec^{-1})	Electrolyte	Substrate	Stability
NiS_2–ReS_2–V	Re-vacancy and heterojunctions	42	84.8	1 M KOH	CC	120 h@10 mA cm^{-2} (ref. 152)
$Ni_2P/NiMoO_x$	Heterojunctions	49	—	1 M KOH	NF	200 h@300 mA cm^{-2} (ref. 162)
Ni_2P–CoCH/CFP	Heterojunctions	62	76	1 M KOH	CFP	50 h@10 mA cm^{-2} (ref. 163)
CoP–Nb_2O_5	Heterojunctions	69	72	1 M KOH	CC	12 h@200 mA cm^{-2} (ref. 164)
Co_2N/CoP	N-vacancy and heterojunctions	44	49	1 M KOH	CC	40 h@100 mA cm^{-2} (ref. 165)
Co/a-WOx	Heterojunctions	36.3	53.9	1 M KOH	CC	200 h@10 mA cm^{-2} (ref. 166)
Mo_5N_6–MoS_2	Heterojunctions	59	37.9	1 M KOH	PPy	33 h@10 mA cm^{-2} (ref. 167)
CoP@NiCoP	Heterojunctions	71	148	1 M KOH	CC	1000 cycles[168]
$MoNi_4$–MX_{10}	Heterojunctions	122.19	55.88	1 M KOH	NCs	300 h@10 mA cm^{-2} (ref. 169)

Notes: CC: carbon cloth; NF: nickel foam; CFP: carbon fiber paper; PPy: polypyrrole; NCs: nanocrystals.

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abundant alternatives without sacrificing IEF strength or catalytic functionality.

3.3.2 Adapting IEF engineering for scalable systems. To address these challenges, IEF design strategies must be reoriented toward scalable systems. One promising direction involves exploiting material processing routes compatible with industrial manufacture, such as macroscopic phase segregation in composite inks or electrophoretic deposition of anisotropic nanoparticles. These approaches can yield aligned dipoles and structured interfaces capable of generating substantial IEFs over large areas.

Enhancing operational resilience requires strategies that preserve IEF integrity under harsh conditions. Incorporating corrosion-resistant, conductive overlayers which can be designed to protect functional junctions without diminishing the IEF. It offers one viable pathway. Alternatively, embedding IEF-active components within a stabilizing amorphous matrix or implementing self-healing coatings may prolong functional endurance under operational stressors.

Reactor engineering also plays a crucial role in leveraging IEF effects at scale. Architecting three-dimensional hierarchical electrodes can simultaneously increase active surface area, improve photon capture, and facilitate bubble detachment. Such structures may synergize with IEF-induced charge separation to elevate overall system performance. Ultimately, bridging the gap between nanoscale IEF innovation and industrial-scale implementation demands interdisciplinary collaboration spanning materials science, catalysis, and chemical engineering. Computational tools and machine learning offer promising avenues for accelerating the discovery of scalable IEF architectures and predicting their long-term behavior.

4 Conclusions

The efficacy of internal electric field design hinges on the precise spatial modulation of field distribution to facilitate efficient separation and migration of photogenerated electrons and holes. However, current methodologies face significant challenges in achieving accurate and stable electric field control within catalysts, often resulting in performance degradation due to insufficient field uniformity and temporal stability. Overcoming these precision and stability limitations remains a critical hurdle in advancing electric field-engineered catalysts. Another major challenge lies in ensuring long-term durability under operational conditions, as catalysts are susceptible to photochemical and chemical corrosion during prolonged photoelectrocatalytic reactions. Additionally, the regeneration and reusability of catalysts present unresolved issues, necessitating strategies for cost-effective recycling to enable sustainable applications. Furthermore, the synthesis of such catalysts typically involves complex fabrication processes and expensive precursors, raising production costs and hindering scalability. Streamlining synthesis protocols while maintaining performance is thus imperative for practical implementation. Although internal electric field engineering has demonstrated substantial improvements in photoelectrocatalytic efficiency, the underlying mechanisms governing its influence on charge carrier dynamics including separation, migration, and recombination remain insufficiently understood. Establishing accurate physical and mathematical models to elucidate these mechanisms is crucial for rational catalyst design.

Future advancements should focus on developing more precise and stable electric field modulation techniques, such as integrating advanced *in situ* characterization tools with machine learning algorithms to optimize field distribution and enhance control accuracy. Concurrently, the exploration of robust field-stabilizing materials could improve catalyst longevity. To address durability and regeneration challenges, novel catalyst architectures, such as corrosion-resistant heterostructures and stable composite materials, should be investigated, alongside simplified and cost-efficient synthesis routes, including template-assisted and self-assembly strategies. Given the multidisciplinary nature of photoelectrocatalytic hydrogen production, fostering cross-disciplinary collaboration is essential. Synergizing insights from quantum chemical calculations, nanomaterials engineering, and advanced spectroscopy can deepen mechanistic understanding while optimizing catalyst performance.

Conflicts of interest

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

Data availability

Supplementary information is available. See DOI: **https://doi.org/10.1039/D5IM00112A**.

All data referenced and discussed are available from the original sources cited in the reference list.

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