

CeF₃-modified Ni₈P₃ nanoarchitecture with built-in electric field for high-performance bifunctional water splitting electrocatalysis

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ABSTRACT

Developing efficient, stable, and earth-abundant bifunctional electrocatalysts is critical for advancing large-scale alkaline water electrolysis. Herein, we report a hierarchical Ni₈P₃-CeF₃/NF nanoflower catalyst grown in situ on nickel foam via a pH-controlled hydrothermal-phosphidation process. Electrochemical tests revealed excellent bifunctional performance, featuring low overpotentials of $\eta_{100} = 310$ mV (for oxygen evolution reaction, OER) and $\eta_{10} = 89$ mV (for hydrogen evolution reaction, HER), small Tafel slopes (51/87 mV dec⁻¹), as well as the highest electrochemical surface area (ECSA, 415 m² g⁻¹) among all tested samples. Impedance and Bode phase analyses reveal reduced charge transfer resistance and enhanced interfacial kinetics, resulting from the formation of a built-in electric field (BEF) and electronic redistribution from CeF₃ to Ni₈P₃. *In situ* Raman spectroscopy and Fourier-transform infrared (ATR-FTIR) spectroscopy studies confirm the accelerated formation of NiOOH and the accumulation of *OOH intermediates. When assembled into a symmetric electrolyzer, Ni₈P₃-CeF₃/NF delivers industrially relevant current densities of 100 mA cm⁻² at a cell voltage of 1.85 V and maintains 99.2% activity after 260 h of continuous operation at 100 mA cm⁻². These results position Ni₈P₃-CeF₃/NF as a highly promising candidate for cost-effective, scalable alkaline water splitting.

1. Introduction

The excessive reliance on fossil fuels continues to exacerbate both global energy insecurity and environmental degradation [1]. In light of these pressing challenges, hydrogen (H₂) has emerged as a promising energy vector, owing to its high gravimetric energy density and environmentally benign combustion byproducts [2]. Among the various production routes, water electrolysis offers a sustainable pathway to generate green hydrogen using intermittent renewable electricity sources such as solar and wind, thereby enabling long-duration energy storage and decarbonized energy transport [3]. However, the widespread implementation of water electrolysis—particularly in alkaline media—is limited by suboptimal electrocatalytic activity and inadequate long-term system durability [4]. Currently, platinum-based catalysts for the hydrogen evolution reaction (HER) and iridium/ruthenium

oxides for the oxygen evolution reaction (OER) are regarded as state-of-the-art [5]. Nonetheless, their reliance on scarce and expensive noble metals presents significant economic and scalability barriers [6]. To address this, extensive research has shifted toward developing noble-metal-free alternatives, particularly transition metal-based catalysts. These materials are not only earth-abundant and cost-effective, but also offer tunable electronic structures conducive to enhancing catalytic performance.

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simultaneous high activity and durability under industrial operating conditions remains a formidable challenge [8]. Recent strategies to overcome these limitations involve heteroatom doping, which effectively modulates the local electronic structure, lowers activation barriers, and enhances intrinsic activity [9]. In particular, rare-earth elements have garnered increasing attention due to their distinctive 4f orbital configurations, which afford additional avenues for tuning catalytic properties [10]. Cerium (Ce), for instance, has demonstrated the ability to manipulate electronic structures and introduce surface oxygen vacancies that enhance catalytic performance [11]. For example, Gao et al. synthesized Ce-doped CoP, reporting a significant enhancement in HER through electronic structure modulation [12]. Similarly, Yang et al. developed a Ce-doped $\text{Co}(\text{PO}_3)_2$ nanosheet array on nickel foam (NF), which exhibited efficient bifunctional HER and OER activity [13]. Fluoride (F^-) doping offers another promising strategy, given its high electronegativity and capability to introduce lattice and surface defects that serve as active sites. Zhang et al. demonstrated that F-doped $\text{LaNi}_{0.75}\text{Fe}_{0.25}\text{O}_3$ perovskite exhibited reduced oxygen vacancy formation energy, facilitating surface reconstruction and enhancing OER performance [14]. Zeng et al. extended this concept by combining fluorine doping with oxygen-defect engineering in Co_3O_4 , significantly improving OER kinetics and stability [15].

A complementary and emerging approach involves constructing built-in electric fields (BEFs) within heterostructured catalysts to promote spatial charge separation. The formation of BEFs drives electron accumulation in one component (e.g., HER sites) and hole enrichment in the other (e.g., OER sites), thereby optimizing the overall kinetics of water splitting. Although BEF engineering has shown great promise, its application in noble-metal-free phosphides remains underexplored, especially through simultaneous cationic and anionic co-doping. Such a strategy can induce asymmetric interfacial charge transfer and modulate the d-band structure, ultimately optimizing adsorption energies of key intermediates and enhancing reaction kinetics [16].

Recent advances in heterointerface engineering have greatly promoted electrocatalytic water splitting [17]. Nevertheless, the modulation effect of rare-earth fluorides (e.g., CeF_3) on Ni-based active phases is still insufficiently explored. The incorporation of CeF_3 into Ni_8P_3 is expected to tune the d-band center and optimize the adsorption strength of catalytic intermediates. Meanwhile, CeF_3 may introduce defect states or modify local coordination environments to stabilize key reaction intermediates [18]. Distinct from conventional oxide and phosphide heterointerfaces in previous studies [19], CeF_3 can donate electrons to in-situ formed NiOOH and construct a built-in electric field at the $\text{CeF}_3/\text{Ni}_8\text{P}_3$ interface, which optimizes intermediate adsorption and accelerates the generation of active sites. Accordingly, the $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ catalyst exhibits outstanding long-term stability, bridging the research gap between classic heterostructure design and fluoride-mediated electronic modulation. Therefore, the rational design of this self-supported transition metal-based electrode optimizes electronic configuration and catalytic kinetics, while effectively meeting the practical requirements of renewable energy-coupled water electrolysis.

Although many transition-metal phosphide electrocatalysts for water splitting have been reported, most studies have primarily focused on simple compositional regulation and routine performance optimization, with relatively limited attention to sophisticated hierarchical structural design, well-defined electronic modulation mechanisms, and the simultaneous enhancement of catalytic activity and long-term stability. Herein, hierarchical $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ nanoflowers were fabricated through an in-situ growth strategy. The incorporation of CeF_3 induces a built-in electric field, thereby significantly accelerating interfacial charge transfer. Benefiting from these unique structural and electronic characteristics, the catalyst delivers low overpotentials of 310 mV for the OER at 100 mA cm^{-2} and 89 mV for the HER at 10 mA cm^{-2} , together with 99.2% activity retention after 260 h of continuous operation in a symmetric cell. Furthermore, it exhibits remarkable durability at an industrially relevant current density of 1000 mA cm^{-2} over the

same testing period, with only minor current fluctuations and no noticeable performance degradation. These findings clearly distinguish our work from previous reported studies and provide a promising strategy for the rational design of highly efficient and durable non-noble metal electrocatalysts.

We further benchmark our work against representative reported water-splitting electrocatalysts [20–24]. Considerable progress has been achieved with Ni-based phosphides, alloys, sulfide-MOF composites, rare-earth-oxide-modified phosphides, and spinel-oxide catalysts. Nevertheless, most of these studies rely on conventional alloying, phosphidation, or relatively simple morphological optimization, while rare-earth-fluoride-derived hierarchical heterointerfaces for targeted electronic modulation remain scarcely explored. Moreover, long-term durability under industrially relevant ultra-high current densities of 1000 mA cm^{-2} , together with mechanistic understanding of rare-earth-fluoride-induced built-in electric fields, remains limited. Herein, we fabricate hierarchical $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ nanoflowers in situ on nickel foam. The incorporation of CeF_3 creates a heterointerfacial built-in electric field that outstanding bifunctional electrocatalytic performance and excellent durability over 260 h, even under high-current-density operation, highlighting a rarely reported rare-earth-fluoride interfacial engineering strategy for efficient and durable overall water splitting.

2. Experimental section

2.1. Synthesis of $\text{Ni}(\text{OH})_2\text{-CeF}_3$

A $1.5\text{ cm} \times 3.5\text{ cm}$ NF substrate was ultrasonically cleaned in $0.5\text{ M H}_2\text{SO}_4$, ethanol, and deionized water (15 min each) to remove surface contaminants. A precursor solution was prepared by dissolving $1.2\text{ mmol Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $2.0\text{ mmol NH}_4\text{F}$, and $2.5\text{ mmol CO}(\text{NH}_2)_2$ in 50 mL deionized water under stirring. The pH was adjusted to 2 using $\text{HNO}_3(\text{aq})$, followed by 30 min of continuous stirring. The cleaned NF was then immersed in the solution and transferred to a 100 mL Teflon-lined autoclave for hydrothermal treatment at 140°C (10 h). After cooling to room temperature, the resulting $\text{Ni}(\text{OH})_2\text{-CeF}_3$ product was washed with ethanol and deionized water and dried at 60°C for 3 h.

2.2. Synthesis of $\text{Ni}_8\text{P}_3\text{-CeF}_3$

$\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ (1.0 g) and pre-prepared $\text{Ni}(\text{OH})_2\text{-CeF}_3$ were respectively placed upstream and downstream of the same tube furnace. The tube furnace was slowly heated to 350°C for 120 min with a heating rate of 5°C min^{-1} in N_2 atmosphere to obtain $\text{Ni}_8\text{P}_3\text{-CeF}_3$.

To investigate the influence of $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ concentration and pH, samples were prepared with varying $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ amounts ($0.6\text{--}1.4\text{ mmol}$) and pH values ($1\text{--}7$) under identical hydrothermal conditions.

In comparison, $\text{Ni}_8\text{P}_3\text{-Ni}_2(\text{P}_4\text{O}_{12})$ and CeF_3 were synthesized in a manner similar to $\text{Ni}_8\text{P}_3\text{-CeF}_3$.

2.3. Synthesis of RuO_2/NF and 20 wt% $\text{Pt/C}/\text{NF}$ electrodes

RuO_2 was prepared by calcining commercial $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ at 400°C for 3 h in air. For catalyst ink preparation, 2 mg RuO_2 and 20 wt% Pt/C were dispersed in a mixed solvent ($200\text{ }\mu\text{L}$ deionized water + $200\text{ }\mu\text{L}$ ethanol + $10\text{ }\mu\text{L}$ 5 wt% Nafion solution) via 30 min ultrasonication. The resulting suspension was drop-cast onto a pristine NF ($1\text{ cm} \times 1\text{ cm}$) and dried under ambient conditions.

3. Results and discussion

3.1. Synthesis and characterization of $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ nanoarrays

The $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ catalyst was synthesized through a two-step hydrothermal-phosphidation process (Fig. 1a). In the first step, Ni

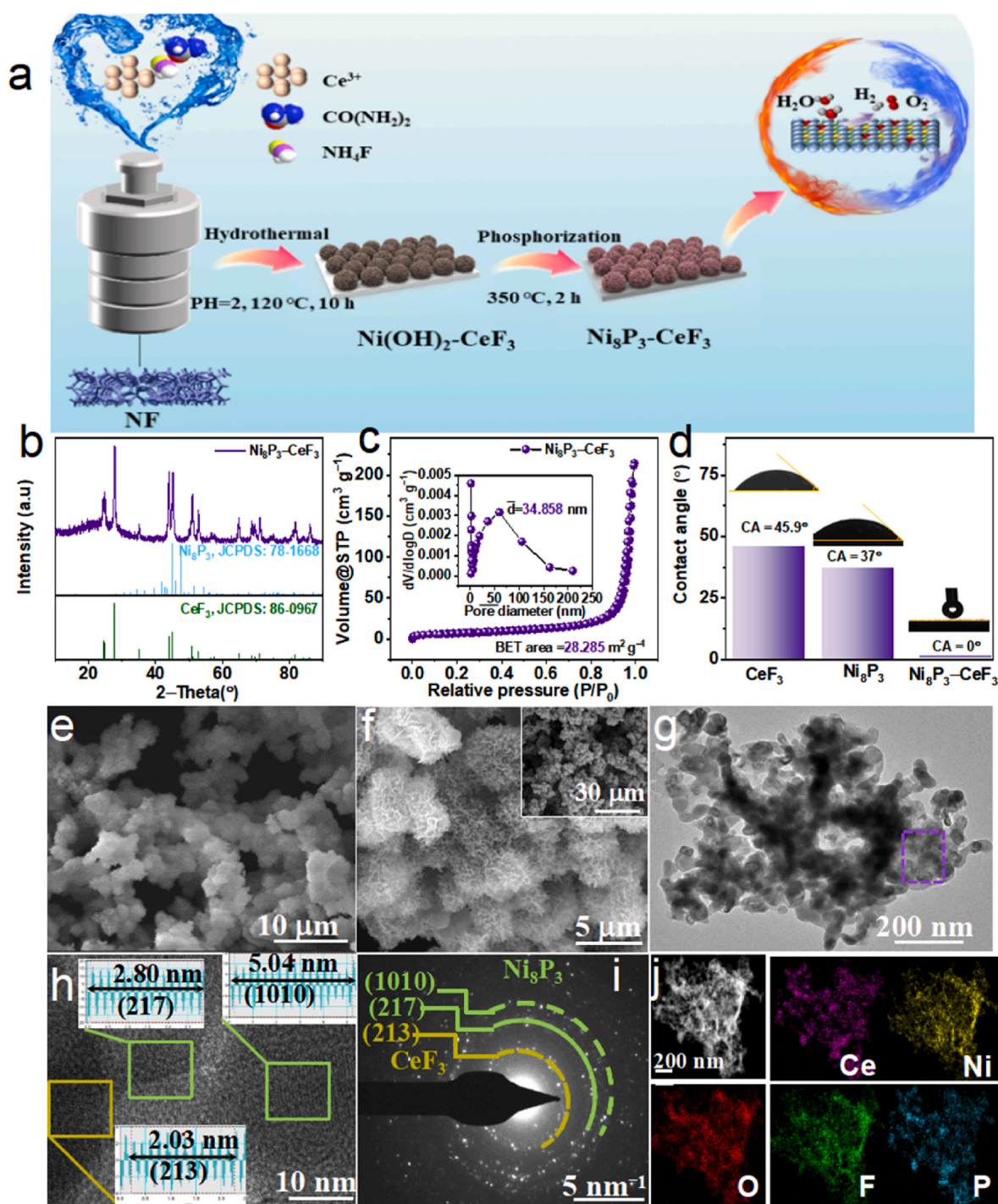


Fig. 1. (a) Schematic illustrations of the synthesis of $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$. (b) XRD pattern of $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$. (c) N_2 adsorption-desorption isotherms with the corresponding pore size distribution (inset) of $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$. (d) Contact angle test for CeF_3/NF , $\text{Ni}_8\text{P}_3\text{-Ni}_2(\text{P}_4\text{O}_{12})/\text{NF}$ and $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$. SEM images of (e) $\text{Ni}(\text{OH})_2\text{-CeF}_3/\text{NF}$ and (f) $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$. (g) TEM image. (h) HR-TEM image/as well as the intensity profile of corresponding areas (inset) of the $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$. (i) SAED image/HAADF-STEM image (inset) and (j) elemental mappings (Ce, Ni, O, F, and P) of the $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$.

$(\text{OH})_2\text{-CeF}_3$ precursors were grown in situ on NF under pH-controlled hydrothermal conditions, with the NF itself acting as the Ni source in the presence of Ce^{3+} ions (Fig. S2a). Subsequently, phosphidation using sodium hypophosphite transformed the precursors into the final $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ heterostructure (Fig. 1b). X-ray diffraction (XRD) confirmed that the resulting Ni_8P_3 and CeF_3 phases correspond well to their respective standard PDF reference patterns. For comparison, XRD patterns of $\text{Ni}_8\text{P}_3\text{-Ni}_2(\text{P}_4\text{O}_{12})/\text{NF}$ and CeF_3/NF —derived separately from Ni and Ce precursors—were also collected (Fig. S2b–c). Nitrogen

adsorption-desorption isotherms were employed to evaluate the surface area and pore-size distribution of $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ (Fig. 1c). The catalyst exhibits a distinct nano-flower morphology with a high specific surface area of $28.3 \text{ m}^2 \text{ g}^{-1}$ and an average pore size of 34.9 nm . This hierarchical structure not only increases the density of exposed active sites but also facilitates rapid mass transport, thereby enhancing electrocatalytic performance [25]. Wettability tests show that the $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ electrode has a contact angle (CA) of 0° (Fig. 1d), indicating excellent hydrophilicity compared to CeF_3/NF (45.9°) and $\text{Ni}_8\text{P}_3\text{-Ni}_2(\text{P}_4\text{O}_{12})/\text{NF}$

(37.0°). Such superior wettability plays a crucial role in promoting electrolyte penetration and efficient mass diffusion during electrochemical reactions [26]. Morphological evolution was tracked throughout the synthesis process. As shown in Fig. 1e, the initial Ni(OH)₂-CeF₃ nano-flower structure was formed via hydrothermal growth on NF. Upon phosphidation, the precursor was converted into Ni₈P₃-CeF₃/NF while preserving its original nano-flower morphology (Fig. 1f), highlighting the structural robustness of the material. Transmission electron microscopy (TEM) images reveal the flower-like architecture (Fig. 1g). High-resolution TEM (HR-TEM) further confirms the coexistence of Ni₈P₃ and CeF₃ crystalline domains (Fig. 1h). Selected area electron diffraction (SAED) patterns corroborate the polycrystalline nature of the composite (Fig. 1i). Finally, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) coupled with elemental mapping (Fig. 1j) confirms the uniform distribution of Ni, Ce, P, F, and O throughout the nanoarchitecture, providing strong evidence for the successful synthesis and homogeneous integration of the Ni₈P₃-CeF₃/NF bifunctional catalyst.

The mechanism of interfacial electronic modulation was systematically investigated using ultraviolet photoelectron spectroscopy (UPS) and Ultraviolet-visible (UV-vis) spectroscopy diffuse reflectance spectroscopy (Fig. 2a-c). As shown in Fig. 2a, the valence band maximum (VBM) of Ni₈P₃-CeF₃/NF was measured at 5.05 eV—intermediate between that of Ni₈P₃-Ni₂(P₄O₁₂)/NF (2.12 eV) and CeF₃/NF (8.60 eV). The significantly higher VBM of CeF₃/NF suggests a lower density of states near the Fermi level (EF), consistent with its d-band center lying

farther from EF. This electronic configuration weakens the interaction between the catalyst surface and adsorbed intermediates by reducing the occupancy of antibonding orbitals. Work function (WF) analysis (Fig. 2a) further supports the existence of distinct interfacial electronic properties. Ni₈P₃-Ni₂(P₄O₁₂)/NF exhibits a work function (WF) of 5.37 eV, slightly higher than that of CeF₃/NF (5.29 eV). This difference drives spontaneous electron transfer from CeF₃ to Ni₈P₃ domains, increasing the local electron density at catalytically active sites and facilitating intermediate adsorption/desorption processes [27]. UV-vis absorption spectra (Fig. 2b) further show that Ni₈P₃-CeF₃/NF possesses the narrowest bandgap (1.97 eV), compared with Ni₈P₃-Ni₂(P₄O₁₂)/NF (2.12 eV) and CeF₃/NF (3.08 eV), indicating enhanced electrical conductivity and charge mobility [28]. Combined UPS and UV-vis analyses (Fig. 2c) reveal a substantial energy-level mismatch between Ni₈P₃ and CeF₃, resulting in the formation of a built-in electric field at the interface due to a work-function difference ($\Delta\Phi \approx 0.08$ eV). The band alignment diagram in Fig. 2c is constructed from UPS-measured work functions and Fermi levels (see Supporting Information for calculation details), not from theoretical estimates. This internal electric field promotes interfacial charge separation and directional carrier transport. As illustrated in Fig. 2d, electron migration from CeF₃ to Ni₈P₃ enriches electron density on the Ni₈P₃ side while rendering CeF₃ electron-deficient. The effective interfacial barrier height is estimated to be $\Phi_B < 0.1$ eV, with a depletion layer width of approximately $W \approx 3$ nm [29]. Such an ultralow barrier height and thin depletion layer substantially reduce electron migration resistance, enabling efficient electron tunneling across the

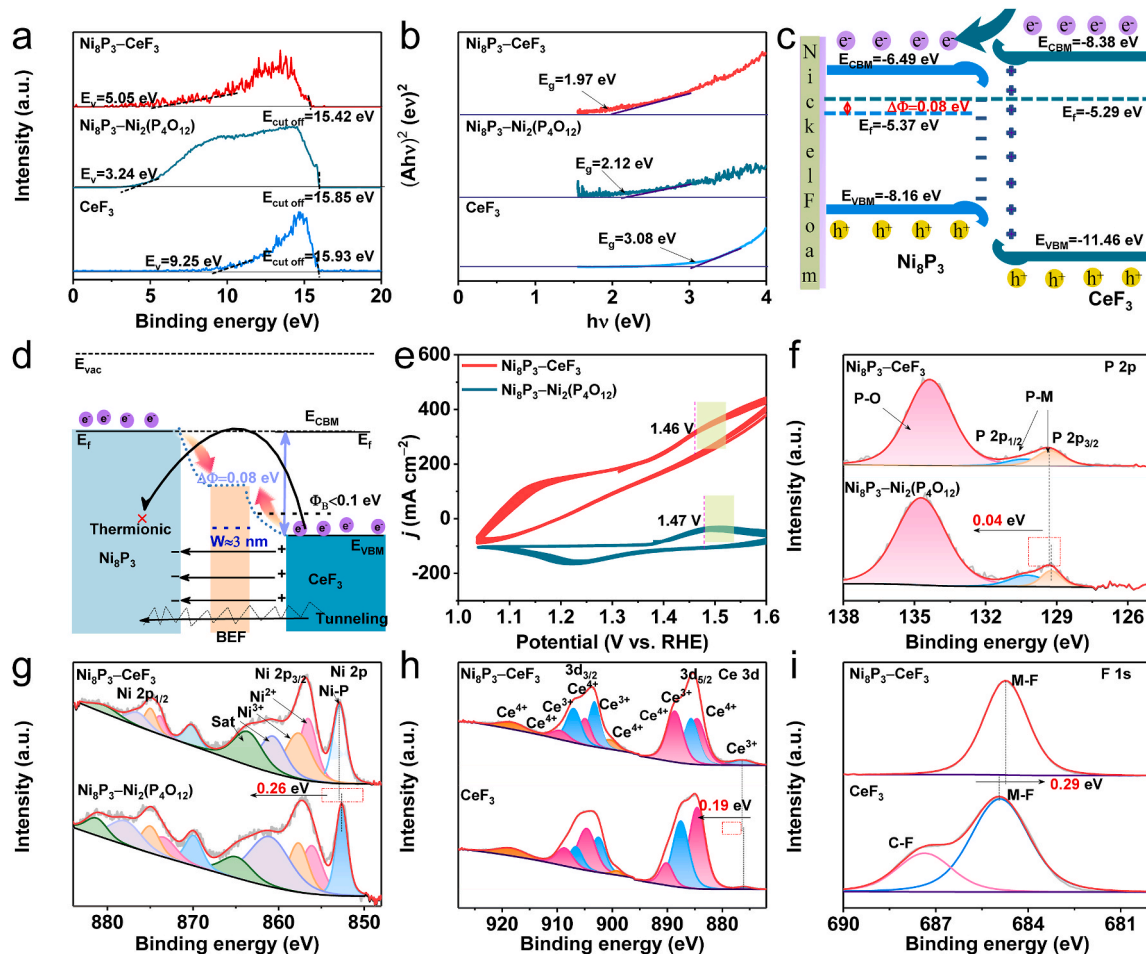


Fig. 2. (a) UPS spectra. (b) UV/Vis spectra and (c) Corresponding energy band diagram of Ni₈P₃-Ni₂(P₄O₁₂)/NF and CeF₃/NF. (d) Schematic of electron transfer based on BEF. The low barrier height ($\Phi_B < 0.1$ eV) and thin barrier width ($W \approx 3$ nm) enable feasible electron tunneling from CeF₃ to Ni₈P₃ under the built-in electric field. (e) Redox peaks of Ni in CV curves of Ni₈P₃-CeF₃/NF and Ni₈P₃-Ni₂(P₄O₁₂)/NF. High resolution XPS spectra of (f) P 2p, (g) Ni 2p, (h) Ce 3d and (i) F 1s of designed catalysts.

heterointerface. This favorable band structure accelerates charge separation and carrier transport, consistent with previously reported heterojunction tunneling behavior under low-barrier conditions. The resulting spatial charge separation enhances HER and OER kinetics by regulating adsorption energies and lowering activation barriers [30]. BEF-driven electron tunneling from CeF_3 to Ni_3P_3 serves both HER and OER pathways: during OER, electrons are extracted through the external circuit while holes participate in water oxidation; during HER, electrons directly reduce H^+ to H_2 on electron-rich Ni_3P_3 sites. Consequently, the same built-in electric field simultaneously supports OER and HER, accounting for the bifunctional catalytic activity of the $\text{CeF}_3/\text{Ni}_3\text{P}_3$ interface.

Cyclic voltammetry (CV) measurements (Fig. 2e) reveal a cathodic shift of ~ 10 mV in the $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox peak (~ 1.46 V vs. RHE) for $\text{Ni}_3\text{P}_3\text{-CeF}_3/\text{NF}$ relative to control samples, indicating a facilitated formation of NiOOH species—critical intermediates in the OER pathway [31]. This result underscores the role of interfacial electronic modulation in promoting surface reconstruction and accelerating reaction kinetics [32].

To gain further insight into charge redistribution mechanisms, X-ray photoelectron spectroscopy (XPS) was performed. The survey spectrum (Fig. S3a) confirms the presence of Ce, Ni, F, and P, with the C 1s peak at 284.8 eV used for charge referencing (Fig. S3b). The high-resolution Ni 2p spectrum (Fig. 2g) displays peaks at 852.87 eV and 870.17 eV, corresponding to the $\text{Ni } 2p_{3/2}$ and $\text{Ni } 2p_{1/2}$ levels of the Ni-P bond, respectively [33]. Additional peaks at 856.55 eV and 873.85 eV are assigned to Ni^{2+} states, while peaks at 857.64 eV and 874.94 eV are attributed to Ni^{3+} states. Satellite features at 863.59 eV and 880.32 eV

further support the presence of these oxidation states [34]. A positive binding energy shift of approximately $+0.26$ eV in $\text{Ni}_3\text{P}_3\text{-CeF}_3/\text{NF}$ relative to $\text{Ni}_3\text{P}_3\text{-Ni}_2(\text{P}_2\text{O}_7)/\text{NF}$ further confirms electron redistribution induced by CeF_3 -mediated interfacial hybridization. The Ce 3d spectra (Fig. 2h) exhibit Ce^{3+} features at 876.42, 885.67, 903.24, and 907.00 eV, along with Ce^{4+} peaks at 884.61, 888.64, 900.46, 904.94, 909.44, and 918.21 eV [35]. In $\text{Ni}_3\text{P}_3\text{-CeF}_3/\text{NF}$, an approximately 0.19 eV positive shift in Ce binding energies together with an increased $\text{Ce}^{4+}/\text{Ce}^{3+}$ ratio indicates Ni-induced electronic modulation, consistent with enhanced charge transfer and increased electron-withdrawing capability, both contributing to improved catalytic activity [36]. In the high-resolution P 2p spectrum (Fig. 2f), peaks at 129.27 eV and 130.38 eV are assigned to $\text{P } 2p_{3/2}$ and $\text{P } 2p_{1/2}$ of the P-Ni bond, while a peak at 134.36 eV is attributed to oxidized phosphorus species [37]. Notably, CeF_3 incorporation induces a positive shift in P 2p binding energies, reflecting substantial modulation of the phosphorus electronic environment through interfacial electronic interactions. The F 1s spectrum (Fig. 2i) shows a primary peak at 685.9 eV corresponding to metal-F bonding. Following CeF_3 incorporation, this peak shifts by approximately 0.29 eV toward lower binding energy, indicating electron redistribution and surface reconstruction [38]. A secondary peak at 686.19 eV is attributed to Teflon contamination from the Teflon liner and was excluded from subsequent analysis [39].

3.2. OER performance analysis

The OER and HER activities of the $\text{Ni}_3\text{P}_3\text{-CeF}_3/\text{NF}$ catalyst were systematically evaluated in 1 M KOH. By optimizing both the cerium

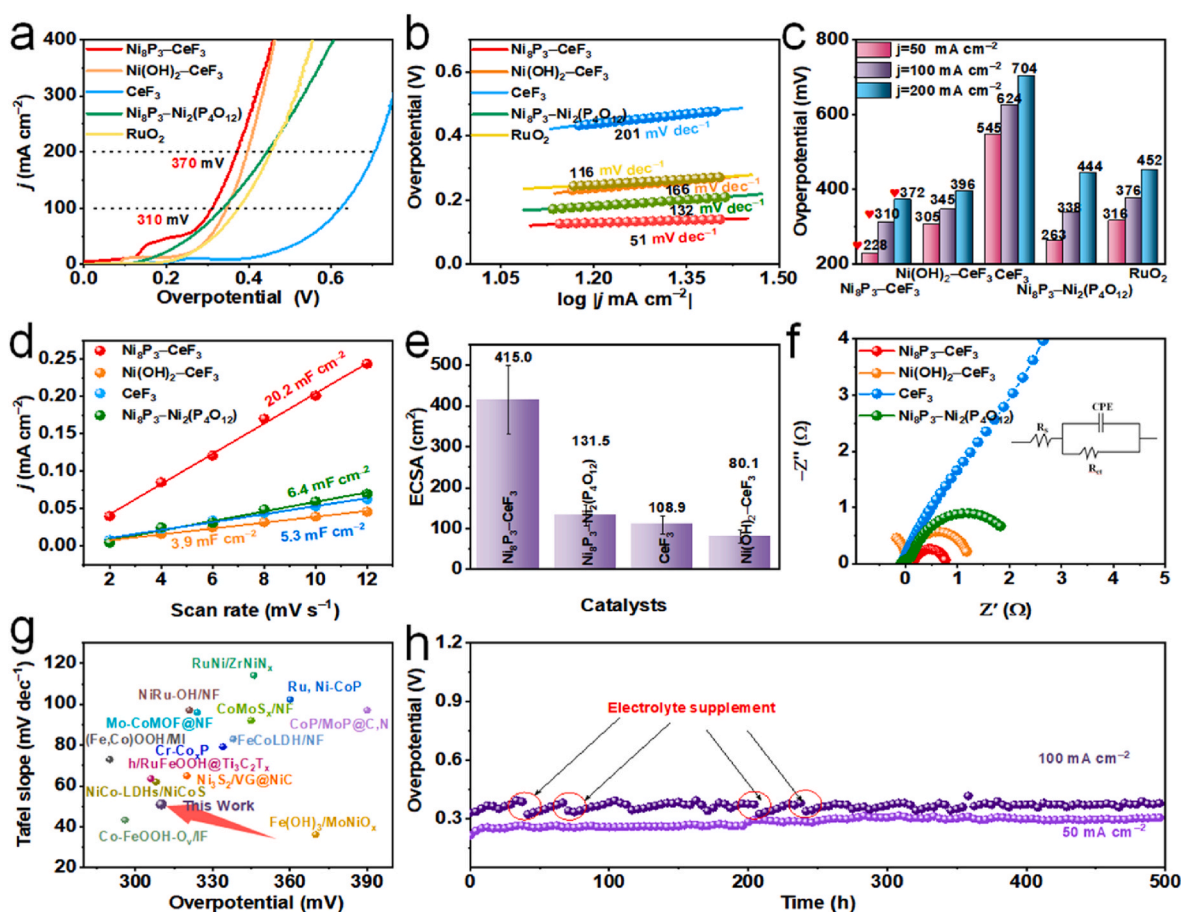


Fig. 3. OER performance of various samples measured in 1 M KOH. (a) Polarization curves. (b) Tafel slopes. (c) Overpotential at different current densities. (d) Ca_1 . (e) Summary of ECSA for the designed catalysts. (f) Nyquist plots. (g) comparison of η at 100 mA cm^{-2} and Tafel slopes with benchmark OER catalysts. (h) Stability test of $\text{Ni}_3\text{P}_3\text{-CeF}_3/\text{NF}$ at static overpotentials of 50 and 100 mV.

content and synthesis pH, the catalyst doped with 1.2 mmol of Ce and synthesized at pH = 2.0 was identified as the optimal formulation, exhibiting outstanding bifunctional performance (Fig. S4–7). The OER performance of the catalysts was systematically assessed using linear sweep voltammetry (LSV) in alkaline media (Fig. 3a). $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ exhibits outstanding catalytic activity, requiring overpotentials of only 228, 310, and 372 mV to achieve current densities of 50, 100, and 200 mA cm^{-2} , respectively (Fig. 3a and c). These values outperform most state-of-the-art OER catalysts under comparable conditions, as evidenced by the comparative analysis presented in Fig. 3g and summarized in Table S2. The catalyst also demonstrates excellent reaction kinetics, as reflected by a low Tafel slope of just 51 mV dec^{-1} (Fig. 3b), significantly surpassing those of $\text{Ni}(\text{OH})_2\text{-CeF}_3/\text{NF}$ (166 mV dec^{-1}), CeF_3/NF (201 mV dec^{-1}), $\text{Ni}_8\text{P}_3\text{-Ni}_2(\text{P}_4\text{O}_{12})/\text{NF}$ (132 mV dec^{-1}), and even the benchmark RuO_2 (116 mV dec^{-1}). The Tafel slopes for most catalysts (Figs. 3b and 4b) exceed 100 mV dec^{-1} , indicating that the adsorption of OH^- ions is the rate-limiting step in the alkaline electrolyte. In contrast, $\text{Ni}_8\text{P}_3\text{-CeF}_3$ exhibits a significantly lower Tafel slope of 51 mV dec^{-1} , suggesting a change in the rate-determining step. This improvement is attributed to the electronic modulation of Ni–P active sites by CeF_3 , which enhances OH^- adsorption kinetics, as further supported by cyclic voltammetry (Fig. 2e) where an earlier onset of OH^- adsorption is observed. This remarkable improvement is attributed to the synergistic interaction between Ni_8P_3 and CeF_3 , which enhances charge transfer efficiency and accelerates the rate-determining step of the OER pathway [40]. CV measurements reveal that $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ possesses the highest double-layer capacitance (C_{dl}) of 20.2 mF cm^{-2} and the largest electrochemical active surface area (ECSA) of 415 $\text{cm}^2 \text{mg}^{-1}$ among all samples (Fig. 3d and e, and S8). This enhancement is attributed to the catalyst's hierarchical nano-flower morphology and high porosity, which expose more active sites and facilitate efficient diffusion of reactants [41]. Electrochemical impedance spectroscopy (EIS) measurements were conducted to investigate charge transport properties. Among all tested samples, $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ exhibits the lowest charge transfer resistance, confirming its superior electrical conductivity and rapid interfacial electron transfer (Fig. 3f). Long-term durability was evaluated through chronopotentiometric measurements at current densities ranging from 50 to 100 mA cm^{-2} .

$\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ maintained stable performance with negligible degradation over 500 h of continuous operation (Fig. 3h). These results underscore the catalyst's potential for practical water oxidation applications, offering a rare combination of high activity, rapid kinetics, and excellent long-term stability.

3.3. HER performance analysis

For HER, $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ exhibits an overpotential of just 89 mV at a current density of -10 mA cm^{-2} , outperforming benchmark samples including $\text{Ni}(\text{OH})_2\text{-CeF}_3/\text{NF}$ (143 mV), CeF_3/NF (173 mV), and $\text{Ni}_8\text{P}_3\text{-Ni}_2(\text{P}_4\text{O}_{12})/\text{NF}$ (Fig. 4a and c). The catalyst also displays a lower Tafel slope of 87 mV dec^{-1} compared to 91–121 mV dec^{-1} for the control samples, indicating superior reaction kinetics (Fig. 4b). Notably, the HER performance of $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ surpasses that of most previously reported non-noble-metal-based electrocatalysts, as illustrated in the inset of Fig. 4d and Table S1. The catalyst's long-term operational stability was evaluated via chronopotentiometry at -10 mA cm^{-2} . Remarkably, $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ retained 99.2% of its initial activity after 320 h of continuous operation (Fig. 4e), further demonstrating its exceptional durability. Post-stability SEM characterization of $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ (Fig. 4e, inset) revealed a slightly roughened nanoflower surface, likely due to hydroxide adsorption at defect sites during extended HER operation. However, the overall structural integrity remained intact, confirming the catalyst's outstanding morphological stability under electrocatalytic conditions.

3.4. In situ technology investigation

As illustrated by the Bode phase plots (Fig. 5a and b), both $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ and $\text{Ni}_8\text{P}_3\text{-Ni}_2(\text{P}_4\text{O}_{12})/\text{NF}$ exhibit no significant phase angle arching below 1.30 V vs. RHE. This behavior is attributed to the high interfacial resistance between the electrocatalyst and the electrolyte at low potentials, which hinders effective charge transfer [42]. Upon reaching 1.35 V, both materials begin to show arching phase angles, indicating the onset of interfacial charge transfer. Notably, $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ exhibits lower phase angles within the 1.35–1.50 V potential range, suggesting that CeF_3 incorporation promotes more

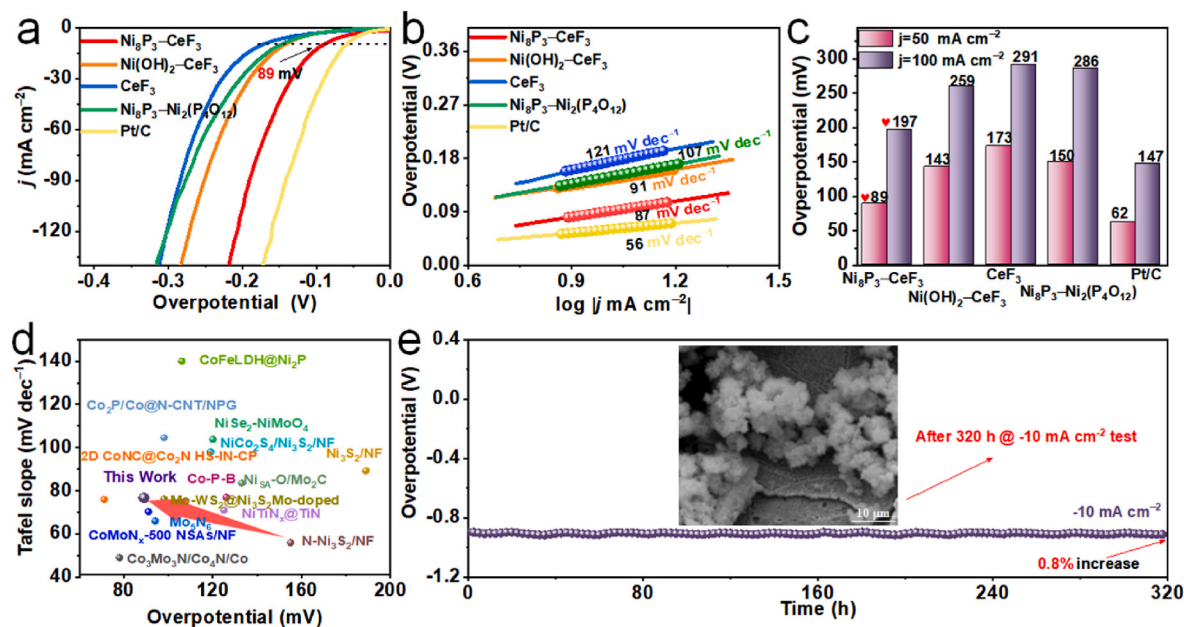


Fig. 4. HER performance of various samples measured in 1 M KOH. (a) Polarization curves. (b) Tafel slopes. (c) Overpotential at different current densities. (d) comparison of $\eta@10 \text{ mA cm}^{-2}$ and Tafel slopes with benchmark HER catalysts. (e) HER stability of $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ at $\eta = 10 \text{ mA cm}^{-2}$ (inset: shows the morphology of $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ after stability at -10 mA cm^{-2}).

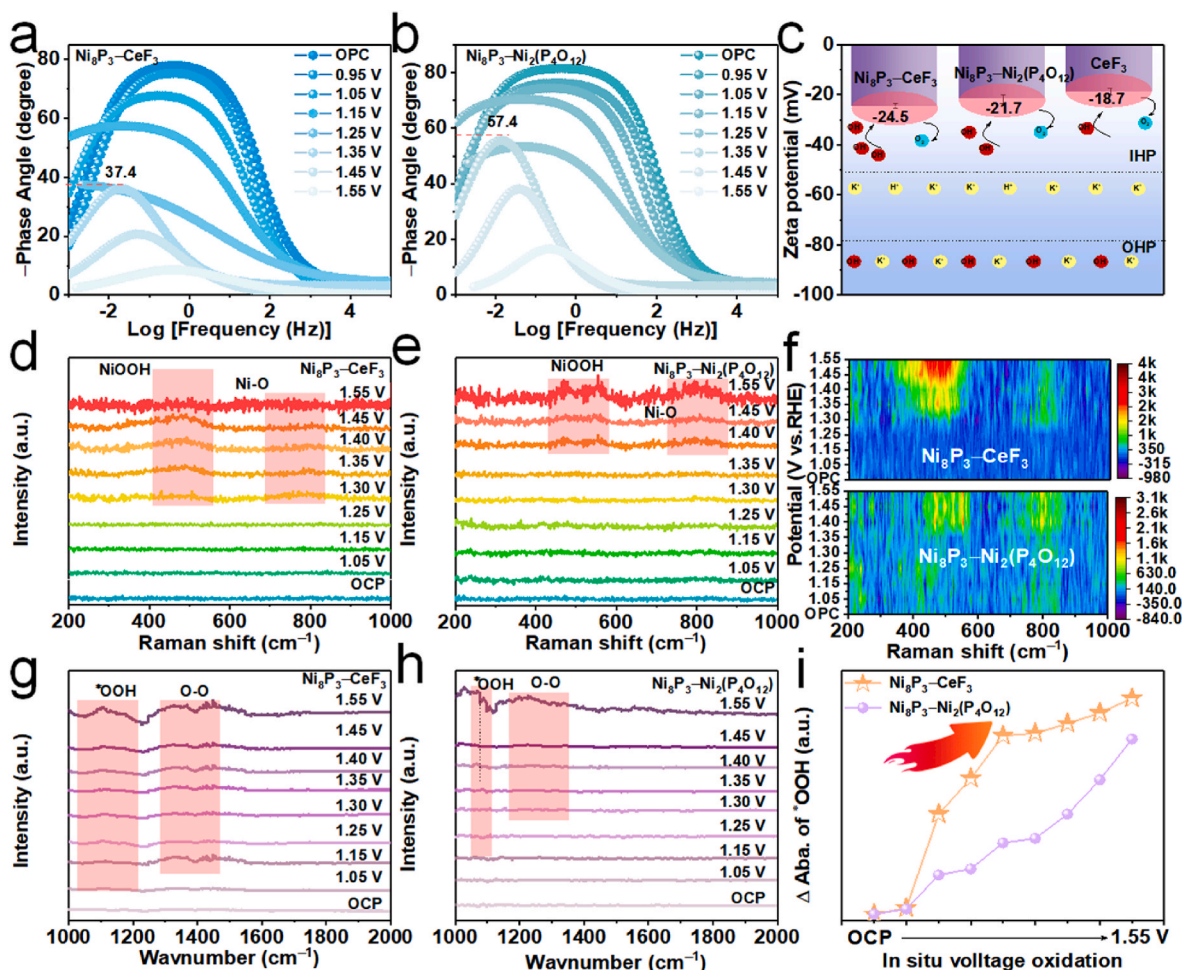


Fig. 5. Bode phase plots of (a) $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ and (b) $\text{Ni}_8\text{P}_3\text{-Ni}_2(\text{P}_4\text{O}_{12})$ at various potentials. (c) Zeta potentials of designed catalysts in KOH. Electrochemical in situ Raman spectra of (d) $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ and (e) $\text{Ni}_8\text{P}_3\text{-Ni}_2(\text{P}_4\text{O}_{12})$ in the potential range of 1.05–1.55 V (vs. RHE). (f) Corresponding contour plots of $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ and $\text{Ni}_8\text{P}_3\text{-Ni}_2(\text{P}_4\text{O}_{12})$. In-situ ATR FTIR spectra of (g) $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$, (h) $\text{Ni}_8\text{P}_3\text{-Ni}_2(\text{P}_4\text{O}_{12})$ and (i) Intensity differences of the infrared signals at $^*\text{OOH}$ as a function of potential for $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ and $\text{Ni}_8\text{P}_3\text{-Ni}_2(\text{P}_4\text{O}_{12})$ electrocatalysts.

efficient charge transfer at the catalyst/electrolyte interface during OER [43].

This enhanced interfacial behavior is likely attributed to asymmetric charge redistribution induced by CeF_3 , which facilitates catalyst reconstruction through two mechanisms: (1) modulation of the local reactive microenvironment to reduce OH^- accumulation and accelerate structural transformation kinetics, and (2) weakening of metal–oxygen bonds, thereby improving the oxidizability of active species under elevated potentials [44]. Zeta potential measurements further support this hypothesis. $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ exhibits the highest surface negativity (−24.5 mV) compared to CeF_3/NF (−18.7 mV) and $\text{Ni}_8\text{P}_3\text{-Ni}_2(\text{P}_4\text{O}_{12})/\text{NF}$ (−21.7 mV), indicating enhanced OH^- adsorption due to the synergistic $\text{Ni}_8\text{P}_3/\text{CeF}_3$ interaction (Fig. 5c). To monitor the catalyst's surface reconstruction during OER, in situ Raman spectroscopy was performed by increasing the potential from open-circuit potential (OCP) to 1.55 V (vs. RHE) in 0.1 V increments. As shown in Fig. 5d–f, distinct Raman peaks emerge for $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ starting at 1.30 V. A strong band at 545 cm^{-1} is assigned to the A_{1g} mode of Ni–O in NiOOH [45], confirming the in situ formation of NiOOH due to the oxidative transformation of exposed Ni–P species [46]. Another peak observed at $\sim 860\text{ cm}^{-1}$ corresponds to Ni–O bending vibrations typically found in metal oxides [47]. In contrast, $\text{Ni}_8\text{P}_3\text{-Ni}_2(\text{P}_4\text{O}_{12})/\text{NF}$ shows no observable phase transformation below 1.30 V, further highlighting the role of CeF_3 in accelerating NiOOH generation and surface activation.

To further probe the OER mechanism, in situ attenuated total

reflectance ATR-FTIR spectroscopy was conducted. As shown in Fig. 5g and h, two distinct absorption bands emerge with increasing applied potential: one at $\sim 1200\text{ cm}^{-1}$, attributed to an O–O intermediate, indicative of oxygenated surface species formation; and another at $\sim 1095\text{ cm}^{-1}$, corresponding to the $^*\text{OOH}$ intermediate [48]. Notably, $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ exhibits a substantially stronger $^*\text{OOH}$ signal than $\text{Ni}_8\text{P}_3\text{-Ni}_2(\text{P}_4\text{O}_{12})/\text{NF}$ (Fig. 5i), suggesting that CeF_3 incorporation promotes $^*\text{OOH}$ formation and thereby accelerates OER kinetics. Post-stability SEM (Fig. S9) images reveal that the hierarchical nano-flower morphology of $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ is well maintained after long-term operation, without obvious structural collapse, surface corrosion or particle aggregation, demonstrating excellent structural robustness. After a long-term stability test, HR-TEM analysis (Fig. S10) unambiguously confirms the in situ formation of crystalline NiOOH, identified by a d-spacing of 0.34 nm corresponding to the (003) plane. This phase is widely recognized as the true active species for the OER in nickel-based catalysts.

After confirming the electronic modulation effect of the CeF_3 heterointerface, we further compare $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ with representative bifunctional electrocatalysts reported in the literature (Table S3). Many reported catalysts exhibit satisfactory activity at 10 mA cm^{-2} but show a pronounced increase in overpotential at current densities $\geq 100\text{ mA cm}^{-2}$. In addition, most durability tests are conducted under moderate laboratory-scale current densities, while even recently reported rare-earth-oxide-modified phosphides and high-current-density

spinel oxides rarely demonstrate prolonged operation at 1000 mA cm^{-2} . It should also be noted that several studies employ concentrated alkaline electrolytes, making direct numerical comparisons inappropriate. Benefiting from its hierarchical nanoflower architecture and hetero-interfacial built-in electric field, $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ achieves an HER overpotential of 89 mV at 10 mA cm^{-2} and an OER overpotential of 310 mV at 100 mA cm^{-2} in 1 M KOH, while retaining 99.2% of its activity over 260 h and exhibiting negligible performance decay at 1000 mA cm^{-2} . Such a combination of high-current-density activity and ultra-long-term durability is uncommon among comparable electrocatalysts, as summarized by the catalyst comparison in Table S3. Distinct from conventional compositional/morphological tuning or rare-earth-oxide modification, this work demonstrates the potential of rare-earth-fluoride interfacial engineering for constructing robust, high-performance, self-supported water-splitting electrodes.

3.5. Overall water splitting

Electrochemical evaluations confirmed that $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ exhibits exceptional bifunctional activity for both the HER and OER in alkaline media. When employed as both the anode and cathode in a symmetric two-electrode configuration ($\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}^{(-)} || \text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}^{(+)}$), the water electrolyzer delivers impressive current densities ranging from 100 to 1000 mA cm^{-2} at cell voltages between 1.85 and 2.50 V (Fig. 6b), outperforming the benchmark $\text{Pt/C}^{(-)} || \text{RuO}_2^{(+)}$ system and most previously reported bifunctional electrocatalysts (Fig. 6c and Table S4). Furthermore, the system exhibits excellent long-term operational stability, retaining steady performance over 260 h at 100 mA cm^{-2} with negligible degradation (Fig. 6d). A parallel stability test at 1000 mA cm^{-2} was performed under the same duration; only slight current fluctuation was observed without obvious performance decay, further verifying the robust durability of this system and overcoming the inherent stability drawbacks of conventional non-precious-metal catalysts. Mechanistic insights and structural evolution during

electrocatalysis were elucidated through a series of advanced characterizations (Fig. 6e). The elevated Fermi level of CeF_3 promotes interfacial electron transfer to Ni_8P_3 , resulting in charge redistribution that enriches the electron density at Ni sites. This electron enrichment plays a pivotal role in stabilizing the NiOOH active phase during OER. For HER, kinetic analyses reveal that Ni sites preferentially adsorb and dissociate H_2O , while adjacent CeF_3 domains facilitate coupled proton-electron transfer, synergistically enhancing hydrogen evolution. The cooperative interaction between Ni_8P_3 and CeF_3 underpins the catalyst's high activity, low overpotentials, and robust stability in alkaline media. Integrated into renewable energy-powered setups such as solar-driven water splitting (Fig. 6f), the $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ catalyst demonstrates promise for scalable and sustainable hydrogen production. It meets industrial demands for efficient, low-cost, and eco-friendly electrolyzers. Benefiting from its robust structural stability and adaptability to variable current output, the catalyst is well suited to the intermittent and fluctuating power characteristics of renewable energy systems, demonstrating strong potential for integration with solar cells and future renewable energy-powered electrolysis technologies.

The exceptional performance of $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ can be attributed to a multifaceted design strategy: (i) In situ synthesis—A pH-etching-assisted method for Ni^{2+} release enables binder-free catalyst growth directly on the Ni foam substrate, thereby reducing interfacial resistance and improving conductivity. (ii) Structural engineering—The hierarchical nanoflower morphology offers high surface area and abundant catalytic sites, while also enhancing mass transport and gas release dynamics. (iii) Enhanced interfacial wettability—The superhydrophilic surface ensures rapid electrolyte penetration and efficient ion diffusion, particularly critical under high current density operation. (iv) Electronic modulation—The work function mismatch between Ni_8P_3 and CeF_3 generates a robust BEF, creating interfacial charge polarization that accelerates catalytic kinetics. (v) Energetic optimization—The interfacial synergy between Ni_8P_3 and CeF_3 effectively tunes the adsorption energies of key intermediates, reducing activation barriers for both HER and OER.

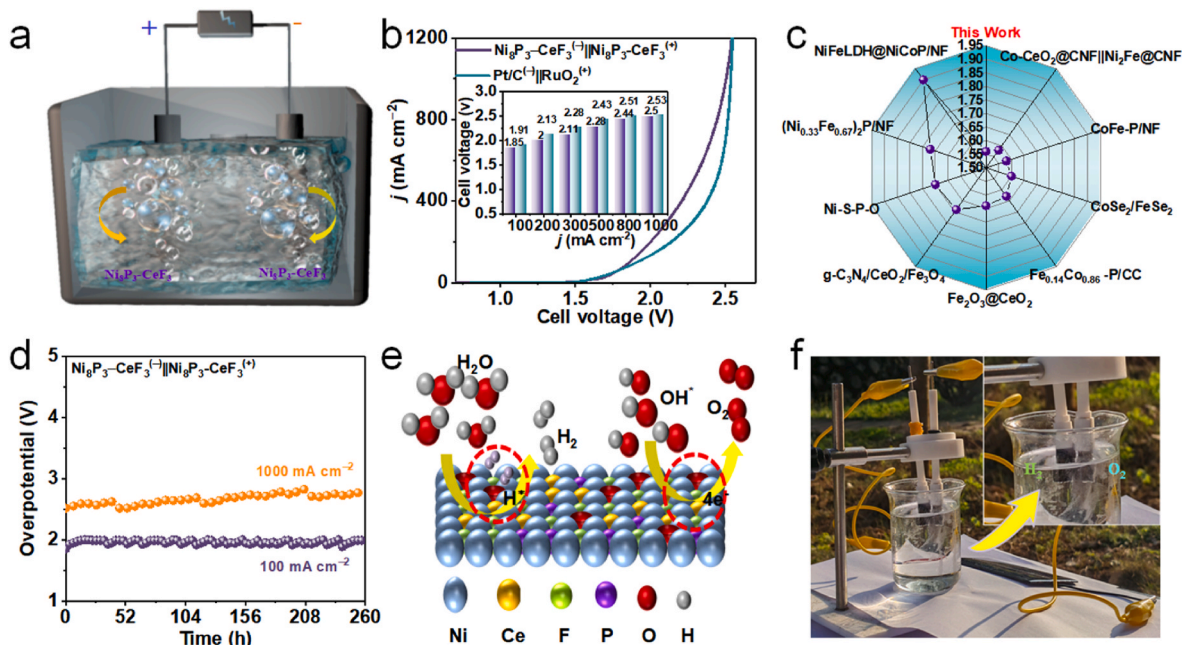


Fig. 6. (a) Schematic illustration of the two-electrode electrolyzer for overall water splitting. (b) LSV curves for overall water splitting using $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}^{(-)} || \text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}^{(+)}$ and $\text{Pt/C}^{(-)} || \text{RuO}_2^{(+)}$ in 1.0 M KOH. The inset shows a comparison of the required voltages at different current densities. (c) Comparison of the cell voltage at 10 mA cm^{-2} between $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}$ and recently reported catalysts. (All comparison data and corresponding literature references are summarized in Table S3 in the Supporting Information.) (d) Stability evaluation of $\text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}^{(-)} || \text{Ni}_8\text{P}_3\text{-CeF}_3/\text{NF}^{(+)}$ under a current density of 100 mA cm^{-2} and 1000 mA cm^{-2} for 260 h each in 1.0 M KOH. (e) Schematic illustration of the dynamic surface reconstruction process in a KOH electrolyte. (f) Actual operation diagram of hydrogen evolution systems powered by sunlight.

Together, these features enable Ni₈P₃-CeF₃/NF to serve as a highly efficient and durable bifunctional catalyst, advancing the development of next-generation alkaline water-splitting systems.

4. Conclusion

This work develops Ni₈P₃-CeF₃/NF as a high-performance bifunctional electrocatalyst for alkaline water electrolysis toward renewable energy utilization. Through in situ synthesis and CeF₃-modulated interfacial electronic regulation, the catalyst achieves low overpotentials ($\eta_{10} = 89$ mV for HER and $\eta_{100} = 310$ mV for OER), fast Tafel kinetics, and remarkable durability over 260 h at 100 mA cm⁻². In situ spectroscopy and electrochemical analyses confirm that the built-in electric field and optimized OH⁻ adsorption synergistically enhance catalytic activity and structural stability. The electrode delivers ultra-high current densities exceeding 1000 mA cm⁻² below 2.5 V with industrial-level operational stability, demonstrating strong potential for renewable energy-driven water splitting and sustainable green hydrogen production. Benefiting from its binder-free self-supported structure, Ni₈P₃-CeF₃/NF also exhibits low material cost and excellent scalability for practical deployment. Although direct testing under intermittent renewable power fluctuations has not yet been performed, its outstanding long-term operational stability strongly supports its potential applicability in solar-driven water splitting systems. Overall, this study presents a cost-effective non-noble metal electrocatalyst that is well aligned with the research focus and scope of *Renewable Energy*.

CRedit authorship contribution statement

Tingting Tang: Writing – original draft, Data curation, Conceptualization. **Zhendong Gao:** Methodology, Data curation. **Kuoteng Sun:** Investigation. **Chengcong Niu:** Formal analysis. **Chenxi Shang:** Investigation. **Jianniao Tian:** Writing – review & editing. **Jingya Guo:** Writing – review & editing. **Tayirjan Taylor Isimjan:** Writing – review & editing. **Xiulin Yang:** Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.renene.2026.126441>.

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