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Ni–P Nanoarray Scaffolds That Elevate Self-Supported Phosphides and Commercial Catalysts for Alkaline and Anion-Exchange-Membrane Water Electrolysis

Hyeonseok Lee¹ | Tai The Mai² | Wooseok Jeong¹ | Jin Young Kim³ | Yoonsu Park¹ | Yun Jae Hwang¹ | Boeun An¹ | Yeongbin Lee¹ | Gyuhyeon Kim¹ | Heesoo Jeong¹ | Yujeong Ahn¹ | Chanbi Kim¹ | Dong Hwan Wang^{1,3}  | Segeun Jang² | Don-Hyung Ha¹ 

¹School of Integrative Engineering, Chung-Ang University, Seoul, Republic of Korea | ²School of Mechanical Engineering, Kookmin University, Seoul, Republic of Korea | ³Department of Intelligent Semiconductor Engineering, Chung-Ang University, Seoul, Republic of Korea

Correspondence: Segeun Jang (sjang@kookmin.ac.kr) | Don-Hyung Ha (dhha@cau.ac.kr)

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ABSTRACT

Alkaline water electrolysis offers a cost-effective and robust route to green hydrogen production, but its practical deployment is hindered by sluggish hydrogen evolution reaction (HER) kinetics and electrode degradation. Herein, we report a self-supported hierarchical Co₃Mo₁-P/Ni-P/NF (NF: nickel foam) electrode fabricated by a two-step molten-salt method. Vertically aligned Ni-P nanoneedles are grown directly on NF, followed by deposition of a Co₃Mo₁-P catalytic overlayer. The resulting electrode requires only 45.9 mV at 10 mA cm⁻² and delivers outstanding high-current alkaline HER performance, outperforming previously reported transition-metal phosphide electrodes. This activity arises from synergistic Co-Mo chemistry, beneficial Ni-P/catalyst interfacial effects, and engineered surface topography that accelerates bubble release while maximizing active-site exposure. The Ni-P scaffold further enhances physical and chemical robustness, enabling stable water splitting for 200 h. Moreover, integrating commercial Pt/C with the Ni-P nanoarray increases the electrochemically active surface area by 4.52-fold and achieves 55.8 mV at 100 mA cm⁻², demonstrating the versatility of the scaffold. Single-cell anion-exchange membrane water electrolysis (AEMWE) further confirms that this hierarchical phosphide architecture translates intrinsic catalytic advantages into superior cell-level performance under practical membrane-electrode assembly conditions.

1 | Introduction

Nanostructural engineering is crucial for designing catalyst electrodes with high structural stability and large active surface areas [1–3]. During electrocatalysis, meticulously designed electrode architectures optimize mass transport, facilitate electron transfer, and ensure long-term stability under harsh operating conditions [4, 5]. Among various catalyst electrode designs, self-supported electrodes offer significant advantages over con-

ventional catalyst-coated electrodes by enabling precise control of nanoscale architectures, improving electrical contact, and enhancing structural stability [6, 7]. Because their fabrication does not require polymeric binders or carbon-based additives, interfacial resistance is minimized, and binder-induced delamination is avoided, resulting in higher electrical conductivity and greater mechanical robustness [8–10]. Conventional methods, such as solvothermal synthesis, electrodeposition, and vapor deposition, have been widely used to fabricate self-supported

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electrodes [11, 12]. Solvothermal synthesis is particularly effective for constructing controlled microstructures, such as pillar structures and two-dimensional architectures, on electrode surfaces [13–15]. However, the application of solvothermal synthesis is limited by prolonged reaction times, limited scalability, and suboptimal control over hierarchical architectures [16, 17]. To address these challenges, the molten-salt method can be used, a rapid and scalable synthesis route that yields materials with improved crystallinity [18, 19]. The high-temperature environment of molten salts facilitates rapid material formation and effectively mitigates phase separation issues that commonly occur during solvothermal synthesis when multiple elements with varying metal-ion solubility product constants (pK_{sp}) are incorporated [17, 20–22]. This effective elemental mixing enables the precise tuning of the electronic structure of multi-cation materials [23, 24]. Despite the absence of studies on self-supported electrodes fabricated using the molten salt method, its unique advantages indicate substantial potential for developing high-performance and stable self-supported electrodes [25].

Various materials—including phosphides, oxides, sulfides, nitrides, and metals—have been used as catalysts for the alkaline hydrogen evolution reaction (HER) [26–29]. Recent studies have also shown that composition-regulated non-noble-metal electrodes can undergo beneficial reconstruction into active oxyhydroxide phases during industrial water splitting, highlighting the importance of maintaining structural integrity under high-current operation [30]. Among noble-metal-free catalysts, transition metal phosphides (TMPs) are used extensively owing to their high electrical conductivity, excellent durability in alkaline electrolytes, and greater cost efficiency compared with Pt-based catalysts [31]. The incorporation of P atoms into the lattice of transition metals shifts the d-band center relative to the Fermi level [32, 33]. This modified electronic structure closely resembles that of Pt. Consequently, TMPs exhibit high catalytic activity in the HER [31]. In particular, Co–Mo phosphides exhibit a unique synergistic mechanism in alkaline HER [34]. Hydrogen intermediates (H^*) preferentially adsorb on Co sites, whereas hydroxyl species (OH^*) bind to adjacent Co–Mo interfacial sites [35]. This spatial separation of adsorption sites effectively lowers the activation barrier for the Volmer step ($H_2O \rightarrow H^+ + OH^-$), which is the rate-determining step in alkaline HER [36]. Furthermore, Mo modulates the surface electronic structure by weakening the hydrogen binding energy on Co, thereby tuning the free energy of hydrogen adsorption (ΔG_{H^*}) toward an optimal value that accelerates HER kinetics [37, 38].

Based on these considerations, this study reports the fabrication of a self-supported Co–Mo–P-based catalyst electrode via a two-step molten-salt-assisted method. Unlike conventional approaches that mainly deposit catalyst layers onto pre-existing conductive substrates, this strategy first converts the surface of Ni foam (NF) into a vertically aligned Ni–P nanoarray scaffold and subsequently uses this scaffold to direct the heterogeneous growth of a Co_3Mo_1P catalytic overlayer. This design simultaneously provides multi-cation phosphide chemistry, a conductive and oxidation-resistant Ni–P interface, and a hierarchical architecture with enlarged electrochemically active surface area (ECSA). This integrated structure is designed to combine the synergistic Co–Mo chemistry with the conductive Ni–P

scaffold, thereby improving interfacial charge transport, alkaline HER kinetics, and long-term durability. The objective of this study was to evaluate the electrocatalytic performance of the Co_3Mo_1P phosphide/Ni phosphide/NF (Co_3Mo_1P -P/Ni-P/NF) electrode in alkaline HER and compare it with commercial Pt/C at high current densities ($>150 \text{ mA cm}^{-2}$) and other reported NF-supported TMP electrodes. Furthermore, we examined the potential of molten-salt-route-derived Ni–P nanostructures to act as robust scaffolds for commercial catalysts, such as Pt/C and IrO_2 , and enhance their electrocatalytic activity and long-term durability compared with the same catalysts deposited on bare NF. To further assess the practical applicability of this electrode architecture under membrane-based electrolysis conditions, its performance was also evaluated in an anion exchange membrane water electrolyzer (AEMWE), where its superior electrochemical characteristics were also successfully demonstrated. This study establishes molten-salt-assisted synthesis as a general and scalable route for engineering high-performance and durable self-supported electrodes for the practical electrolysis of alkaline water.

Although numerous TMP-based catalysts have been reported for alkaline HER, most studies have focused on compositional optimization or nanostructuring of catalyst powders and conventional self-supported architectures. Constructing a conformal multi-cation phosphide layer on a three-dimensional conductive scaffold remains challenging because conventional solvothermal synthesis and electrodeposition often suffer from mismatched nucleation/growth kinetics, different metal-ion reactivities, and limited control over uniform phosphidation within porous substrates. In this context, a molten-salt-assisted route offers a distinct opportunity to couple multi-cation phosphide formation with direct scaffold engineering, enabling hierarchical self-supported electrodes that are difficult to access by conventional solution-based methods.

2 | Results and Discussion

The Co–Mo–P catalyst electrode was fabricated on Ni–P-modified NF (Ni–P/NF) via a two-step molten-salt-assisted method. Ni–P/NF served as a robust and conductive scaffold (Figure 1a). In the first step, a nanostructured Ni–P/NF was constructed by annealing a mixture of sodium hypophosphite monohydrate ($NaH_2PO_2 \cdot H_2O$) and pristine NF. This step ensured the precise engineering of the nanoscale electrode architecture (Figure 1b). During annealing, nanostructures gradually emerged on the NF surface. After 1 h, these nanostructures eventually formed vertically aligned needle-like arrays (Figure 1d), which uniformly covered the NF surface. This evolution is consistent with phosphorus-precursor seeding on Ni foam, followed by anisotropic crystallization of tetragonal $Ni_{12}P_5$. Facet-dependent interfacial energetics together with attachment-limited kinetics favor one-dimensional extension; in concert with defect-mediated nucleation on the substrate, this yields vertically aligned needle arrays [39, 40].

In the second step, a precursor ink containing Co and Mo was applied to the pre-synthesized Ni-P/NF substrate and dried (Figure 1c). The resulting composite was then annealed in the presence of additional $NaH_2PO_2 \cdot H_2O$ to yield a hierarchically

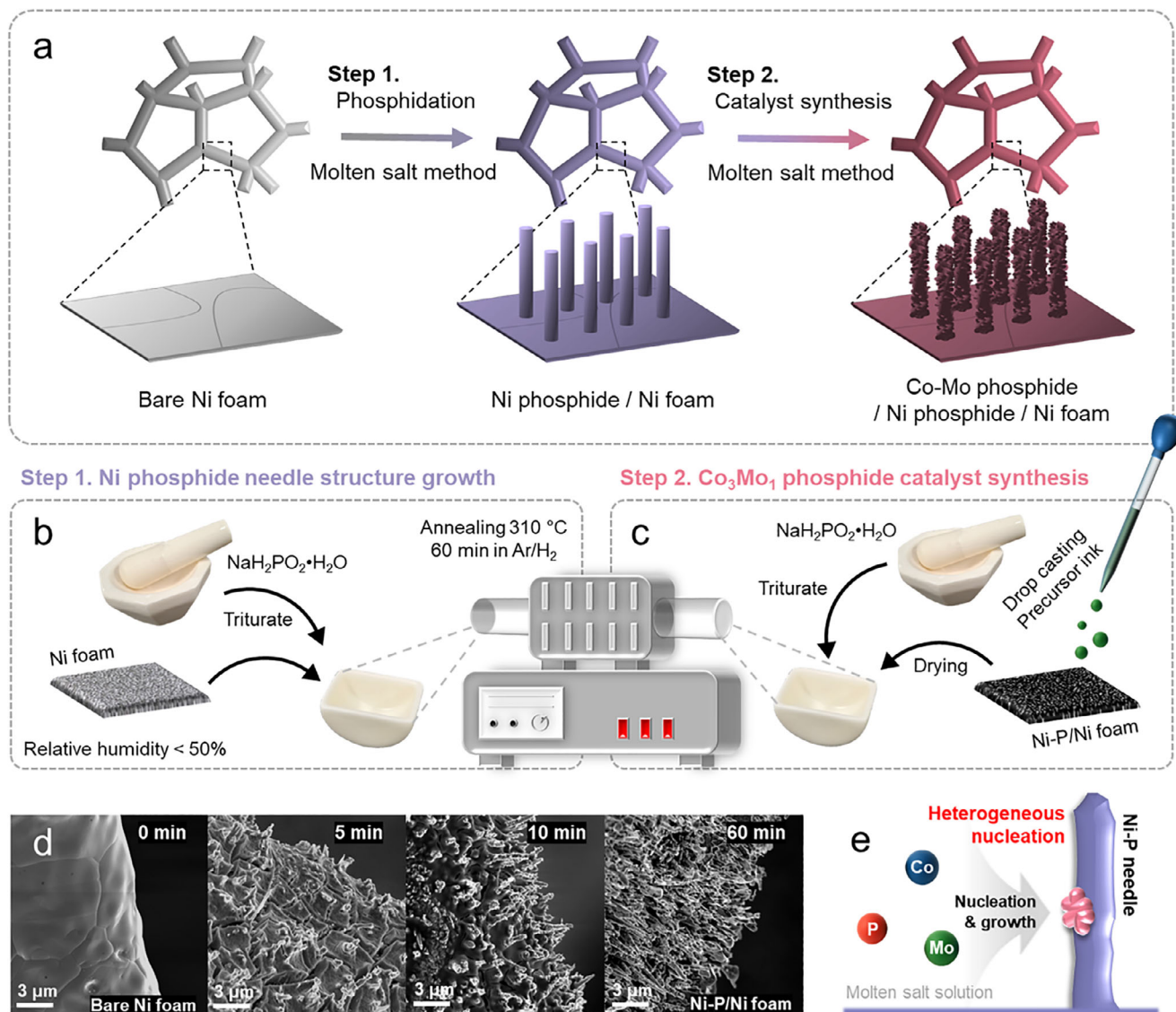


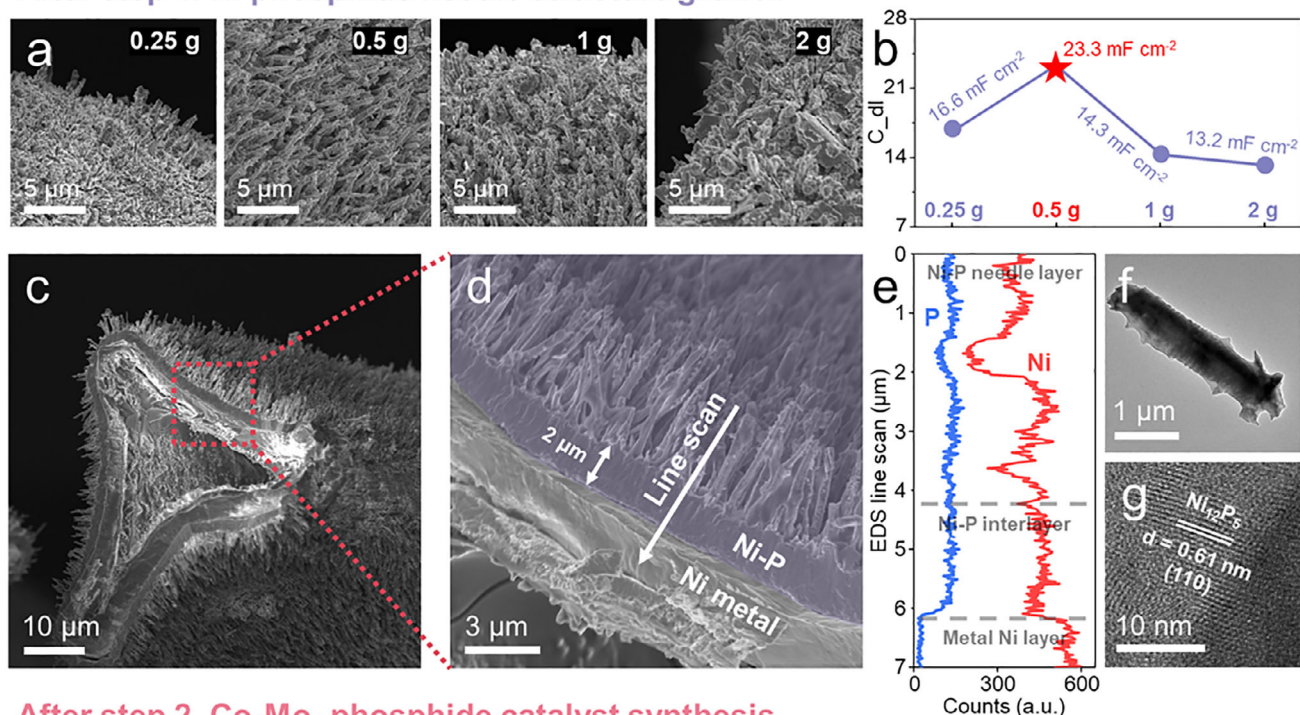
FIGURE 1 | (a) Schematic of the two-step molten-salt-assisted synthesis of $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ (NF: nickel foam). (b) Preparation of Ni-P/NF, in which vertically aligned Ni-P nanoneedle arrays were directly grown on NF (step 1). (c) Deposition of the $\text{Co}_3\text{Mo}_1\text{-P}$ catalyst layer on Ni-P/NF (step 2). (d) Time-resolved scanning electron microscopy (SEM) images showing the morphological evolution of Ni-P nanoneedle arrays. (e) Schematic of $\text{Co}_3\text{Mo}_1\text{-P}$ catalyst formation on Ni-P nanoneedles via the molten salt method.

structured Co-Mo-P/Ni-P/NF electrode. $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ transforms into a molten salt phase during annealing owing to its melting point of 310°C . This phase ionizes the Co and Mo precursor species and supplies P for phosphidation. The Ni-P layer on the NF provides a structural template that supports the nucleation of Co-Mo-P while its high surface energy further drives heterogeneous nucleation (Figure 1e). These conditions promoted the formation of nucleation sites directly on the Ni-P/NF surface. These nucleation sites subsequently evolved into self-supported catalysts with porous nanostructures. Detailed experimental procedures are described in the [Supporting Information](#).

The morphology and accessible surface area of the electrodes were regulated by tuning the P precursor loading. As shown in Figure 2a and Figure S1, a low P precursor loading (0.25 g) resulted in poorly defined Ni-P nanoneedle arrays, indicating insufficient

nucleation density of the P seeds on the NF. In contrast, excessive loading (2.0 g) led to overgrowth and coalescence, resulting in a coarse, irregular surface. A loading of 1.0 g produced partially agglomerated and less uniform features compared with a loading of 0.5 g, which yielded the most regular, vertically aligned nanoarray. Consistently, the electric double-layer capacitance (C_{dl}) (Figure 2b) was the highest at a P precursor loading of 0.5 g, indicating the largest ECSA and most favorable architecture for the subsequent fabrication of the catalyst electrode. Accordingly, 0.5 g was selected as the optimal P precursor loading for constructing the Ni-P/NF scaffold. The cross-sectional scanning electron microscopy (SEM) image of Ni-P/NF (Figure 2c) shows densely packed, vertically aligned needle-like structures with an average width of approximately $500\ \text{nm}$ and a length of approximately $4\ \mu\text{m}$. These three-dimensional nanostructures, which uniformly coated the entire NF surface, are expected to facilitate efficient hydrogen gas evolution and maximize

After step 1. Ni phosphide needle structure growth



After step 2. Co_3Mo_1 phosphide catalyst synthesis

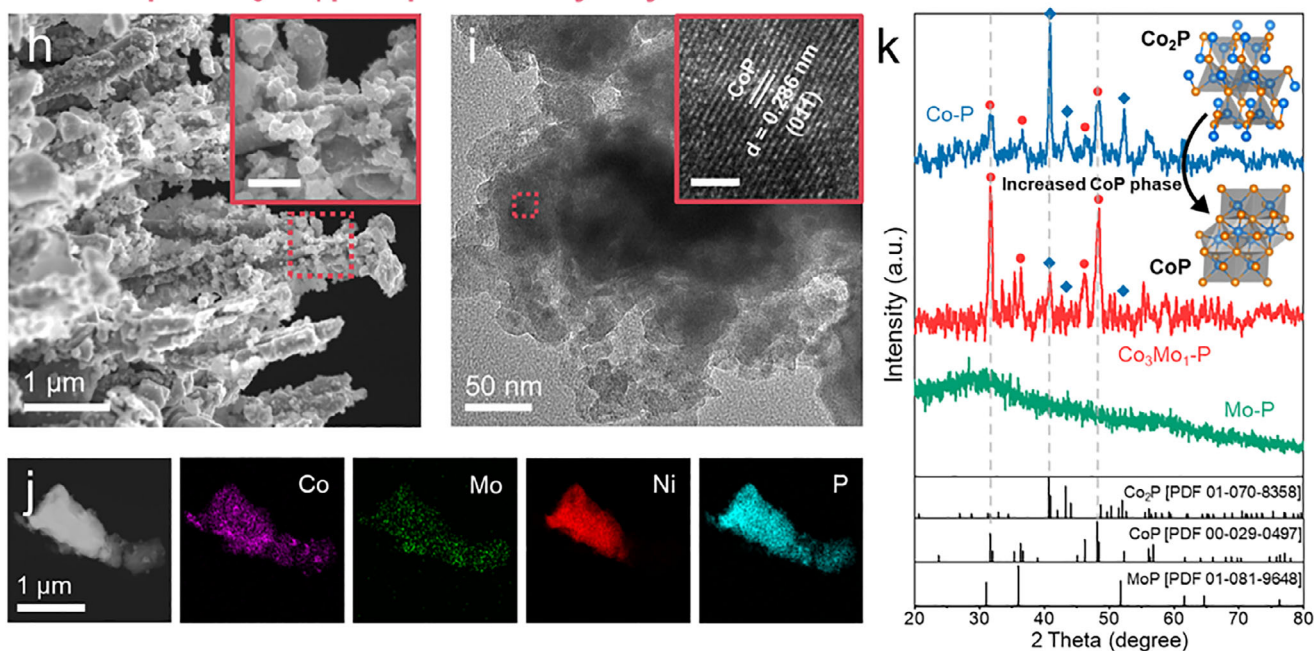


FIGURE 2 | (a) SEM images of Ni-P/NF with different P precursor loadings (0.25, 0.5, 1.0, or 2.0 g). (b) Electric double-layer capacitance (C_{dl}) of Ni-P/NF electrodes with different P precursor loading. (c,d) Cross-sectional SEM images of Ni-P/NF prepared using 0.5 g of P precursor. (e) Cross-sectional SEM–energy-dispersive X-ray spectroscopy (EDS) line scan of Ni-P/NF showing elemental distributions across the nanoneedle–NF interface. (f,g) High-resolution transmission electron microscopy (HRTEM) images of Ni–P nanoneedles. (h) SEM image of the Co_3Mo_1 -P/Ni-P/NF surface with a magnified view (inset, scale bar: 200 nm). (i) HRTEM image of Co_3Mo_1 -P nanocrystals with a magnified view (inset, scale bar: 2 nm). (j) Elemental maps of the hierarchical Co_3Mo_1 -P/Ni-P nanoarchitecture, as obtained from TEM–EDS analysis. (k) X-ray diffraction (XRD) patterns of Co_3Mo_1 -P, Co–P, and Mo–P catalysts.

active-site exposure for subsequent catalyst growth. A magnified view of the cross-section (Figure 2d) revealed the formation of a Ni-P phase not only along the vertical microcolumns but also as a conformal layer—approximately 2 μm thick—on the underlying Ni substrate. This passive Ni-P layer significantly enhances the

structural integrity and oxidation resistance of the electrode under alkaline electrochemical conditions.

SEM–energy-dispersive X-ray spectroscopy (EDS) line scan analysis (Figure 2e) confirmed the distinct compositional separation

between the NF and the overlying Ni-P layer. The needle-like Ni-P structures produced pronounced fluctuations in the EDS signal intensity owing to their sharp and irregular morphology. The X-ray diffraction (XRD) pattern of Ni-P/NF confirmed the coexistence of metallic Ni and various crystalline Ni-P phases. The observed diffraction peaks corresponded well with those of tetragonal Ni_{12}P_5 (PDF No. 03-065-4018), thereby validating the phase composition of the electrode (Figure S2). To further investigate the phase evolution of the Ni-P scaffold, XRD patterns were collected for samples synthesized at different annealing times (Figure S3). At short annealing times, the Ni-P/NF sample showed diffraction features assignable to Ni_2P , whereas longer annealing gradually promoted the formation of Ni_{12}P_5 as the dominant phase. This transition from Ni_2P to Ni_{12}P_5 indicates that the Ni-P phase can be tuned by the annealing duration. The observed phase evolution is attributed to prolonged heat treatment under the mildly reducing H_2/Ar atmosphere, which decreases the effective phosphorus chemical potential through partial loss of phosphorus-containing species and thus favors the formation of the more Ni-rich Ni_{12}P_5 phase. Transmission electron microscopy (TEM) confirmed the formation of well-defined columnar morphology of the Ni-P nanostructures (Figure 2f). High-resolution TEM (HRTEM) imaging revealed lattice fringes with an interplanar spacing of 0.61 nm, corresponding to the (110) crystallographic plane of the tetragonal Ni_{12}P_5 phase (Figure 2g). These observations provide direct structural evidence of phase purity and crystallinity at the nanoscale, consistent with the XRD results.

In the second step, the catalyst electrodes were synthesized on the Ni-P/NF substrate using mixtures of Co and Mo precursors at various molar ratios (Co: Mo = 4:6, 5:5, 6:4, 7:3, or 8:2) following the same procedure. These samples were evaluated for their performance in the HER to identify the optimal Co: Mo ratio (Figure S4). The electrode prepared with a Co: Mo precursor ratio of 6:4 exhibited the highest catalytic activity. Compositional analysis using SEM-EDS and X-ray photoelectron spectroscopy (XPS) confirmed an actual Co: Mo elemental ratio of approximately 3:1; therefore, this catalyst was designated $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$. The difference between the precursor ratio and the final catalyst composition can be attributed to the different incorporation efficiencies of Co and Mo during heterogeneous phosphidation on the Ni-P scaffold. SEM-EDS analysis of the residue collected after synthesis revealed a Mo-rich composition, with Co and Mo contents of 46.3 and 53.7 at%, respectively, when normalized to the total Co and Mo content (Figure S5). This Mo enrichment suggests that Co-containing species were more efficiently incorporated into the catalyst layer, whereas a fraction of Mo-containing species remained in the molten-salt-derived residue. Thus, the final Co-rich $\text{Co}_3\text{Mo}_1\text{-P}$ composition likely reflects preferential formation of Co-P-rich phases on the Ni-P nanoarray with partial Mo incorporation into the Co-P framework.

The SEM image of $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ (Figure 2h) shows that the original surface morphology of the Ni-P/NF scaffold was preserved. The catalyst nanoparticles were anchored onto individual Ni-P pillars, forming a hierarchical structure with a porous surface (Figure 2i and Figure S6). The HRTEM image further revealed the presence of a conformal, amorphous phosphate layer approximately 1.7 nm thick on the catalyst surface (Figure

S7). As previously discussed, the formation of these hierarchical architectures is attributed to heterogeneous nucleation on the thermodynamically stable Ni-P surface during phosphidation. This architecture enhances electron transport, structural robustness, and ECSA.

For comparison, the Co-P/Ni-P/NF and Mo-P/Ni-P/NF samples were synthesized under identical conditions. Both samples formed hierarchical architectures with uniformly distributed catalyst particles on the Ni-P pillars (Figure S8). The HRTEM images of the catalyst layers revealed that Mo-P/Ni-P/NF was amorphous, whereas Co-P/Ni-P/NF exhibited a crystalline Co-P phase (Figure S9). As shown in Figure S7, a comparison of $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ with Co-P/Ni-P/NF along the Co_2P (112) planes indicated a larger lattice d-spacing for $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$, which can be attributed to the incorporation of Mo into the Co_2P lattice and the resulting lattice expansion. Elemental mapping using SEM-EDS revealed the homogeneous distribution of Co, Mo, Ni, and P throughout the catalyst layer (Figure S10a-c). The TEM-EDS analysis of $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ confirmed that the $\text{Co}_3\text{Mo}_1\text{-P}$ was evenly deposited on the surface of the Ni-P columns, forming a conformal and well-dispersed catalytic layer (Figure 2j). The XRD pattern of $\text{Co}_3\text{Mo}_1\text{-P}$ revealed characteristic diffraction peaks corresponding to the orthorhombic Co_2P and CoP phases, confirming the coexistence of these two crystalline phases (Figure 2k). The prominent peak at 40.72° , corresponding to Co_2P (PDF No. 01-070-8358), and the additional peaks at 31.60° and 48.13° , corresponding to CoP (PDF No. 00-029-0497), indicate successful phosphidation and crystalline phase formation. Compared with the control Co-P sample, the XRD pattern of $\text{Co}_3\text{Mo}_1\text{-P}$ exhibited a more intense CoP peak, indicating that Mo incorporation subtly altered the phosphidation dynamics and favored CoP formation under the synthesis conditions. In contrast, the XRD pattern of Mo-P exhibited broad, low-intensity peaks consistent with the amorphous structure of MoP nanoparticles. These findings demonstrate that the $\text{Co}_3\text{Mo}_1\text{-P}$ phase retains a well-defined crystalline structure with compositional adjustment obtained via Mo incorporation, thereby providing a route to modulate the phase distribution and optimize the catalytic properties.

The electronic interactions between Co and Mo on the surface of the $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ catalyst were investigated using XPS. Compared with Co-P/Ni-P/NF, the Co 2p peak of $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ shifted by 0.13 eV toward negative binding energy (Figure 3a), indicating an increase in the electron density around the Co atoms [41, 42]. Although Mo has a higher electronegativity (2.16) than Co (1.88), this peak shift indicates that Co retains more electron density, likely because of the strong interaction between Mo and P [34]. The formation of robust Mo-P bonds weakened the covalent character of the Co-P bond and maintained a higher electron density for Co [43]. In contrast, the Mo 3d peaks of $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ shifted toward positive binding energy values compared with those of Mo-P/Ni-P/NF (Figure 3b), indicating a decrease in electron density on Mo, consistent with the redistribution of the intramolecular charge.

The P peaks shifted toward higher binding energy values with increasing Mo content, indicating that Mo incorporation altered the overall electronic environment of P (Figure 3c). This change in electron density enhances the interactions between the P atoms

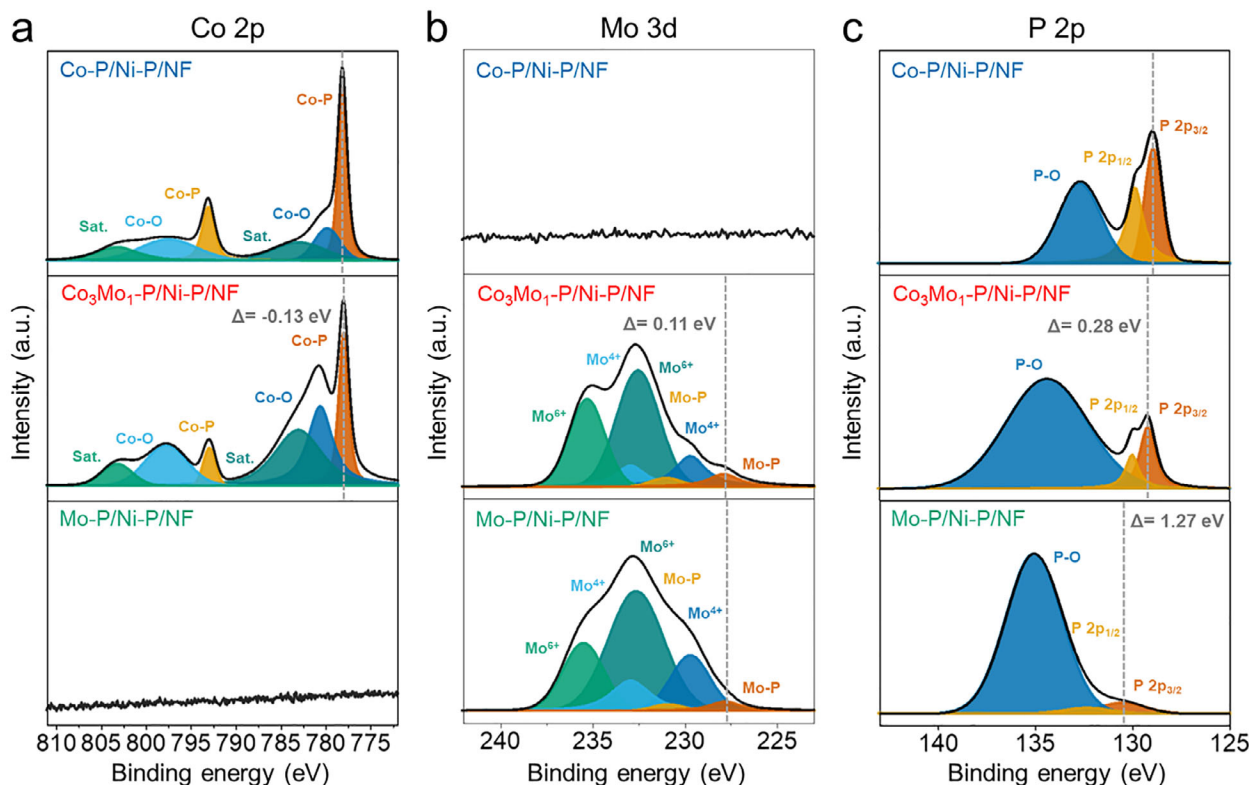


FIGURE 3 | (a–c) Background-corrected, peak-deconvoluted high-resolution X-ray photoelectron spectroscopy (XPS) spectra of Co-P/Ni-P/NF, $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$, and Mo-P/Ni-P/NF, respectively.

and oxygen species, resulting in a higher proportion of P–O bonding [44]. These Mo-induced modifications in the electronic environment of P govern the electrocatalytic performance of the material. This interpretation is also consistent with previous density functional theory (DFT) studies on Co–Mo–P and CoMo–P-based alkaline HER catalysts. Thenuwara et al. reported that Co–Mo centers in amorphous Co–Mo–P can serve as favorable water-dissociation sites, thereby accelerating the Volmer step in alkaline HER [35]. In addition, DFT calculations on CoMo–P/NF have shown that Mo incorporation promotes Co–Mo synergistic interactions and optimizes the Gibbs free energy of hydrogen adsorption/desorption [35, 45]. Therefore, the XPS-observed electronic redistribution in $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$, together with its lower charge-transfer resistance and improved ECSA-normalized HER activity, supports the role of Mo as an electronic modulator that facilitates alkaline HER kinetics.

HCl etching was further conducted to examine whether the P–O signal originated from superficial oxidation (Figure S11). After etching, Co–P, Mo–P, and phosphide P 2p signals remained clearly detectable, confirming the preservation of the underlying Co–Mo phosphide phase. The residual P–O component indicates that oxidized phosphorus species are present at the surface or near-surface region of the phosphide catalyst, rather than reflecting complete oxidation of the catalyst. Thus, $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ can be described as a phosphide-rich framework with a thin PO_x -containing surface layer.

Linear sweep voltammetry (LSV) analysis revealed that single-transition-metal-based catalyst electrodes exhibited limited HER

activity, whereas the bimetallic $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ electrode with an optimized Co: Mo ratio delivered the best performance (Figure 4a). The $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ electrode required overpotentials of 45.9, 113.5, and 154.8 mV to reach current densities of 10, 100, and 300 mA cm^{-2} , respectively. These overpotential values were significantly lower than those required for Co–P/Ni–P/NF (63.7, 140.7, and 198.3 mV), Mo–P/Ni–P/NF (160.3, 274.2, and 336.1 mV), and Ni–P/NF (134.1, 236.3, and 302.4 mV) to reach identical current densities (Figure 4b). Notably, $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ outperformed the commercial Pt/C/NF benchmark at current densities exceeding 150 mA cm^{-2} . The stepwise synthesis significantly enhanced the ECSA, as indicated by the C_{dl} values: NF (2.63 mF cm^{-2}), Ni–P/NF (23.3 mF cm^{-2}), and $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ (124.5 mF cm^{-2}) (Figure 4c). Compared with Co–P/Ni–P/NF (100.6 mF cm^{-2}) and Mo–P/Ni–P/NF (20.9 mF cm^{-2}), the $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ sample exhibited the largest ECSA, indicating that the incorporation of both Co and Mo enhanced the surface area and catalytic behavior. Among the tested TMP-based electrodes, $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ exhibited the highest intrinsic activity, as indicated by the ECSA-normalized polarization curves (Figure 4d), and the lowest charge-transfer resistance, as revealed by Nyquist analysis (Figure S12). The Tafel slope of $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ was 64.1 mV dec^{-1} , second only to that of Pt/C/NF (38.5 mV dec^{-1}), highlighting its favorable reaction kinetics (Figure 4e). Further benchmarking of $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ at current density of 10 and 100 mA cm^{-2} against reported NF-supported TMP catalysts is shown in Figure 4f. The detailed overpotential values and Tafel slopes for all samples are summarized in Table S1 [46–64]. Although several reported catalysts delivered competitive performance at 10 mA cm^{-2} , $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ maintained

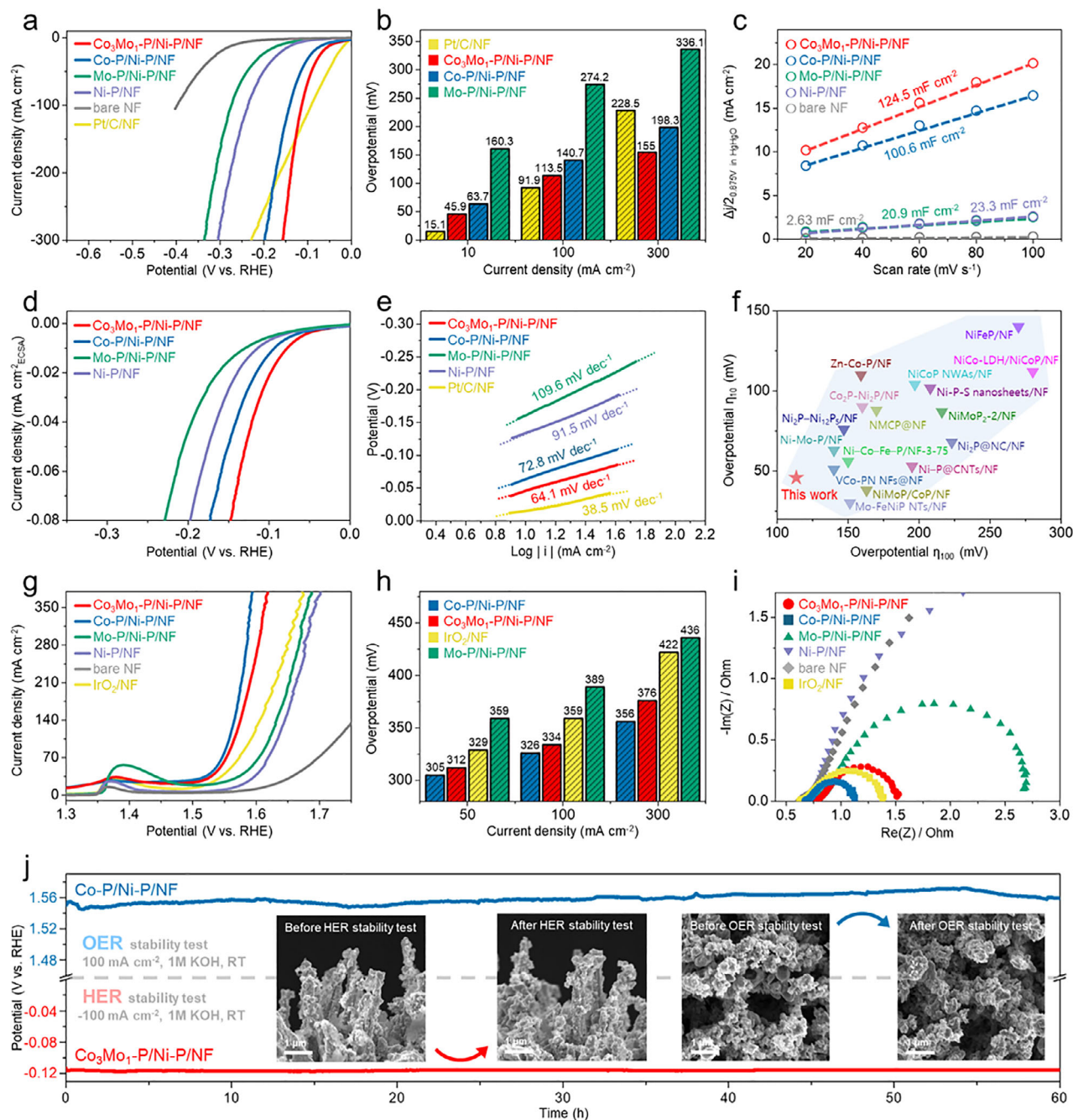


FIGURE 4 | (a) Linear sweep voltammetry (LSV) curves for the hydrogen evolution reaction (HER) over Co₃Mo₁-P/Ni-P/NF, Co-P/Ni-P/NF, Mo-P/Ni-P/NF, Ni-P/NF, bare NF, and Pt/C/NF. (b) Bar chart summarizing HER overpotentials (η) at 10, 100, and 300 mA cm⁻². (c) Electric double-layer capacitance (C_{dl}) extracted from scan-rate-dependent non-Faradaic cyclic voltammetry. (d) Electrochemically active surface area (ECSA)-normalized LSV curves for the HER. (e) Tafel slopes derived from polarization data. (f) Literature benchmark: Comparison of the η_{10} and η_{100} of recently reported transition-metal phosphide alkaline-HER electrodes, highlighting the superior performance of the electrode developed in this study. (g) LSV curves for the oxygen evolution reaction (OER) over Co₃Mo₁-P/Ni-P/NF, Co-P/Ni-P/NF, Mo-P/Ni-P/NF, Ni-P/NF, bare NF, and IrO₂/NF. (h) Bar chart of OER η at 10, 100, and 300 mA cm⁻². (i) Electrochemical impedance spectra (EIS) collected at the operating potentials (Nyquist plots). (j) Chronopotentiometric stability at 100 mA cm⁻² for 60 h: HER on Co₃Mo₁-P/Ni-P/NF and OER on Co-P/Ni-P/NF; SEM images of electrode surfaces before/after durability testing. (All measurements were conducted in 1.0 M KOH).

the lowest overpotential at 100 mA cm⁻², confirming its outstanding performance at industrially relevant current densities. Overall, these results demonstrate that the hierarchical Co₃Mo₁-P/Ni-P/NF not only has a larger ECSA compared with other NF-based catalysts but also exhibits intrinsically high HER activity.

In the LSV curves representing the oxygen evolution reaction (OER) activity, the Co-P/Ni-P/NF catalyst electrode outperformed all other tested electrodes (Figure 4g). Co-P/Ni-P/NF exhibited a low overpotential of 305 mV at a current density of 50 mA cm⁻², surpassing both IrO₂/NF (329 mV), a benchmark commercial catalyst, and Co₃Mo₁-P/Ni-P/NF (312 mV),

which previously demonstrated high HER activity (Figure 4h). Electrochemical impedance spectroscopy (EIS) further supported these findings (Figure 4i). The Nyquist plot of Co–P/Ni–P/NF displayed the smallest semicircle diameter, indicating the lowest charge-transfer resistance among the evaluated catalysts. To identify the actual OER-active species of Co–P/Ni–P/NF, Raman and XPS analyses were performed before and after OER operation (Figure S13). After OER, the Raman spectrum exhibited intensified broad bands in the 450–620 cm^{-1} region, assigned to Co–O/Co–OH vibrations associated with cobalt oxyhydroxide/oxide species, together with a Co–O-related vibration near 660–670 cm^{-1} . This spectral evolution indicates that the surface Co–P phase undergoes anodic reconstruction during OER, forming $\text{CoO}_x\text{H}_y/\text{CoOOH}$ -like species. Consistently, the Co 2p XPS spectrum after OER was dominated by Co–O components, whereas the Co–P contribution observed before OER was markedly suppressed (Figure S14a). In the P 2p region, the phosphide doublet disappeared after OER and was replaced by a dominant P–O signal, indicating the oxidation of surface phosphide species into phosphate-like species (Figure S14b). These results confirm that the high OER activity of Co–P/Ni–P/NF originates not from the pristine Co–P surface itself, but from the reconstructed cobalt oxyhydroxide/oxide surface layer formed under anodic OER conditions. The underlying Co–P/Ni–P framework likely serves as a conductive and structurally robust pre-catalyst that promotes the formation and stabilization of the active $\text{CoO}_x\text{H}_y/\text{CoOOH}$ -like layer.

Chronopotentiometric measurements conducted over 60 h at a current density of 100 mA cm^{-2} in 1.0 M KOH demonstrated the remarkable electrochemical durability of both $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ and Co-P/Ni-P/NF electrodes for the HER and OER, respectively (Figure 4j). In particular, $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ exhibited an initial overpotential of 113.3 mV, which increased marginally to 115.3 mV after 60 h of continuous operation, indicating its excellent long-term stability. Following long-term HER testing, XPS analysis revealed no significant shifts in the binding energies of the Co and Mo peaks. Furthermore, the area ratios of the Co 2p and Mo 3d peaks remained unchanged, indicating negligible catalyst degradation or elemental leaching during operation (Figure S15). The SEM images before and after long-term electrolysis confirmed the outstanding structural integrity of the $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ and Co-P/Ni-P/NF catalyst electrodes. The vertically aligned Ni–P columnar framework and porous catalyst morphology were preserved, reinforcing the robustness of the $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ and Co-P/Ni-P/NF architectures under harsh alkaline HER and OER conditions.

To investigate the effect of the hierarchical structure on the catalytic performance and durability of $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$, we fabricated a control electrode by directly synthesizing $\text{Co}_3\text{Mo}_1\text{-P}$ on bare NF. The cross-sectional SEM images of the $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ and $\text{Co}_3\text{Mo}_1\text{-P/NF}$ electrodes are shown in Figure 5a and b, respectively. The SEM image of the $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ sample (Figure 5a) shows distinct layered structures consisting of NF, a Ni–P interlayer, and a top $\text{Co}_3\text{Mo}_1\text{-P}$ catalytic layer. This hierarchical configuration enhances water electrolysis by providing large ECSA, chemical stability, and structural robustness.

Owing to the superior oxidation resistance of Ni–P under alkaline conditions compared with metallic Ni, the Ni–P interlayer

that completely encapsulated the NF served as an effective barrier against chemical corrosion. The underlying metallic NF, protected by the approximately 2- μm -thick Ni–P interlayer, remained unoxidized and provided a stable pathway for rapid electron transfer. In contrast, the SEM image of $\text{Co}_3\text{Mo}_1\text{-P/NF}$ (Figure 5b) shows that the catalyst was directly deposited onto the NF surface without an interlayer. The catalyst formed a rough and nonuniform layer with regions of minimal or no $\text{Co}_3\text{Mo}_1\text{-P}$ coverage. These low-coverage areas enabled the penetration of the electrolyte into the interface between $\text{Co}_3\text{Mo}_1\text{-P}$ and NF under alkaline HER, thereby promoting the surface oxidation of the NF and gas bubble formation at the interface. These effects weaken the physical contact between the layers and potentially compromise the catalytic performance.

Additional XPS analyses revealed that the Ni–P interlayer and nanoneedle architecture modified the surface structure and electronic properties of the catalyst, thereby improving its HER performance and long-term stability. Compared with $\text{Co}_3\text{Mo}_1\text{-P/NF}$, the Co–P peak in the Co 2p XPS spectrum of $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ appeared at a lower binding energy value, indicating a higher proportion of metallic or electron-rich Co–P species (Figure 5e) [65]. This shift indicates that the Ni–P interlayer enriched Co with electrons and facilitated charge delocalization, which stabilized the excited core–hole state during photoemission [66]. The Mo 3d XPS spectra revealed that the catalysts grown on Ni–P contained more oxidized $\text{Mo}^{4+}/\text{Mo}^{6+}$ species than those grown on bare NF, which exhibited intense signals at lower binding energy values (Figure 5f). This contrast likely stems from the diffusion of P from the Ni–P layer, forming an ultrathin PO_x surface layer; this process results in a surface dominated by Mo oxides when combined with Mo's oxophilicity and slow surface kinetics [67–69]. The Ni 2p XPS spectra of (Figure 5g) $\text{Co}_3\text{Mo}_1\text{-P/Ni-P/NF}$ exhibited a characteristic broad and weak Ni–P peak at 853.3 eV, whereas that of $\text{Co}_3\text{Mo}_1\text{-P/NF}$ exhibited a sharp Ni^0 peak at 852.9 eV, indicating that the metallic Ni was exposed because of incomplete catalyst coverage [70]. The P 2p XPS spectra revealed that Ni–P/NF exhibited both P^{3-} and PO_x peaks (phosphide and a surface cap), whereas the bare NF sample was predominantly phosphide-terminated (Figure 5h), consistent with the redistribution of the oxidation state of Mo shown in Figure 5f. Together, these XPS findings indicate that the catalyst grows conformally on Ni–P, forming a well-integrated interface due to effective seeding. This interfacial interaction between the underlayer and the catalyst (i) reduces contact resistance and improves core–hole screening [71, 72], (ii) stabilizes Co in a phosphide-rich electron-dense state ideal for H^* adsorption [73–77], and (iii) promotes the formation of $\text{PO}_x/\text{-OH}^-$ -bearing surfaces that facilitate water dissociation during the Volmer step [78, 79]. In contrast, catalyst growth on the bare NF is island-like, exposing Ni^0 regions, forming thinner oxide caps, and reducing interfacial conductivity. Although the surface Mo–P fraction appears lower on the Ni–P-grown catalysts, the combination of MoO_x/PO_x and Co–P/Ni–P forms a bifunctional interface: MoO_x/PO_x sites activate H_2O molecules, while Co–P/Ni–P regions efficiently adsorb and release H^* . Strong coupling with the Ni–P interlayer ensures rapid electron transport. These synergistic effects rationally account for the significantly lower overpotential and enhanced HER kinetics of the Ni–P-templated catalyst.

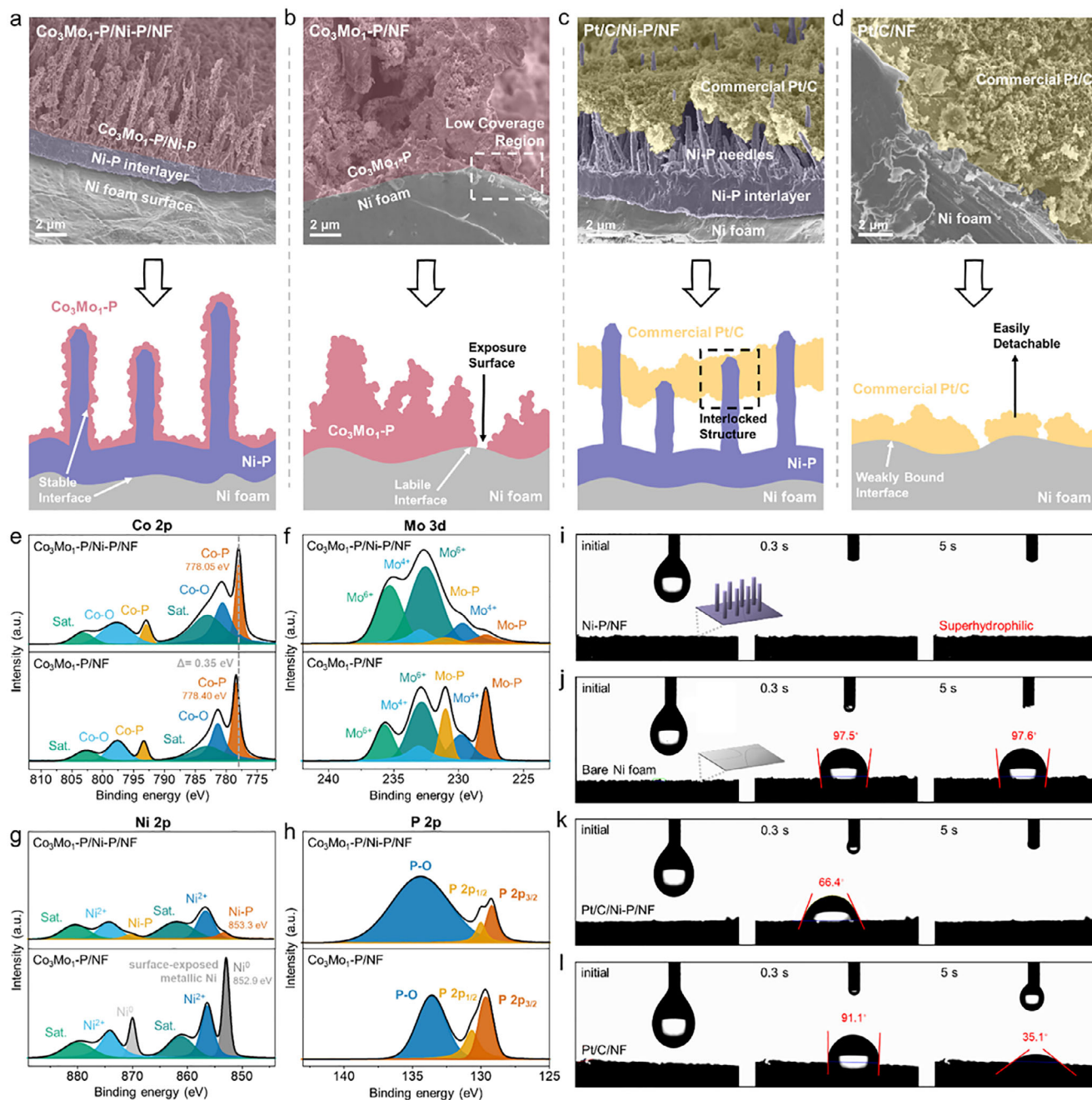


FIGURE 5 | (a–d) Cross-sectional SEM images and corresponding schematic cross-sections of Co₃Mo₁-P/Ni-P/NF, Co₃Mo₁-P/NF, Pt/C/Ni-P/NF, and Pt/C/NF, respectively. (e–h) High-resolution XPS spectra of Co₃Mo₁-P/Ni-P/NF and Co₃Mo₁-P/NF. (i–l) Time-resolved sessile-drop contact-angle images for Ni-P/NF, bare NF, Pt/C/Ni-P/NF, and Pt/C/NF, respectively.

A Pt/C/Ni-P/NF electrode was fabricated by depositing commercial Pt/C ink onto Ni-P/NF using the same procedure as for Pt/C/NF to further evaluate the suitability of Ni-P/NF as a versatile electrode platform for supporting commercial catalysts. The cross-sectional SEM image of Pt/C/Ni-P/NF (Figure 5c) reveals a four-layered architecture comprising NF, a Ni-P layer, Ni-P needle arrays, and a Pt/C catalytic layer. The surface SEM image shows that the commercial Pt/C catalyst is interlocked with the Ni-P needle structures, forming a robust composite network analogous to the reinforcement mechanism in rebar-reinforced concrete (Figure S16). This architecture effectively mitigates catalyst detachment during electrocatalytic operation. Nickel-

rich phosphides exhibit metallic conductivity [80]. Although direct bulk conductivity values for Ni₁₂P₅ are rarely reported, multiple studies show low charge-transfer resistance and high electronic transport in Ni₁₂P₅-containing electrodes [50, 81–83]. For reference, the related metallic phase Ni₂P shows a room-temperature resistivity of $\sim 30 \mu\Omega \text{ cm}$ ($\sigma \approx 3 \times 10^4 \text{ S cm}^{-1}$), underscoring the metallic nature of nickel phosphides [84]. This enhanced conductivity facilitates efficient charge transfer between the support and catalytic layer, thereby improving the performance of commercial catalysts. In contrast, the Pt/C/NF electrode features a sparsely dispersed Pt/C layer on a relatively flat Ni metal surface (Figure 5d). The weak bonding between Pt/C

and Ni metal and exposure of the bare Ni substrate render the catalyst susceptible to detachment and degradation. A similar interfacial structure and detachment tendency were observed when commercial IrO₂ catalyst ink was used (Figure S17).

We conducted static droplet contact-angle measurements using 1.0 M KOH under conditions representative of alkaline water electrolysis to gain deeper insight into the surface characteristics of the needle-like Ni–P nanostructured array. The term “initial” refers to the moment immediately before the droplet detaches from the syringe. As shown in Figure 5i, the water droplet dispersed so rapidly on the Ni–P/NF surface that it exceeded the temporal resolution of the high-speed camera. In contrast, the droplet on bare NF remained nearly static, maintaining a contact angle of approximately 97.5° over 5 s (Figure 5j). These results indicate that modifying the originally hydrophobic NF with Ni–P nanoneedle arrays induces a transition to a superhydrophilic surface.

This superhydrophilicity can be partly attributed to the spontaneous surface oxidation of the TMPs upon exposure to air, resulting in the formation of hydrophilic oxide layers. Notably, both Co₃Mo₁-P/Ni–P/NF and Co₃Mo₁-P/NF exhibited superhydrophilic behavior (Figure S18). This behavior may be due to Mo-induced lattice defects in the Co–P structure, which increase the surface energy and promote rapid wetting. The combination of a hydrophilic surface and vertically aligned nanoneedle architecture facilitates gas release under electrolysis conditions. The needle arrays generate a discontinuous triple-phase boundary between the electrode and gas bubbles, thereby reducing bubble adhesion and size and enhancing bubble detachment. The contribution of the nanoneedle array to bubble release is evidenced by chronopotentiometric measurements under high current densities, during which more pronounced potential fluctuations caused by bubble dynamics were observed for the Co₃Mo₁-P/NF electrode than those for Co₃Mo₁-P/Ni–P/NF (Figure S19). These findings indicate that the nanoneedle array significantly contributes to bubble release.

A slight reduction in the superhydrophilicity was observed (Figure 5k) when commercial Pt/C was deposited on the Ni–P/NF electrode. This reduction can be attributed to the physical coverage of the nanostructured surface by the Pt/C layer and the presence of the hydrophobic Nafion binder in the catalyst ink. Nevertheless, the Pt/C/NF electrode, which was fabricated by depositing Pt/C on bare NF, exhibited improved wettability compared with unmodified NF, likely due to the formation of partial nanostructures (Figure 5l). Despite the minor decrease in superhydrophilicity, the Pt/C/Ni–P/NF electrode retained rapid water absorption capability, indicating that the integration of commercial catalysts with Ni–P/NF preserves favorable surface wettability, which is beneficial for practical applications.

LSV analyses demonstrated that the catalyst electrodes with Ni–P nanostructures exhibited significantly enhanced HER and OER activities compared with those without the Ni–P layer, highlighting the beneficial role of the Ni–P framework in improving electrochemical performance (Figure 6a). Co₃Mo₁-P/Ni–P/NF achieved a significantly lower overpotential of 155 mV at a high current density of approximately 300 mA cm^{−2} in the HER, outperforming Co₃Mo₁-P/NF (225.9 mV). Similarly, Pt/C/Ni–P/NF

achieved an overpotential of 97.1 mV, which was lower than that of Pt/C/NF (228.5 mV). Enhanced performance was also observed in the OER: Co–P/Ni–P/NF (356 mV) and IrO₂/Ni–P/NF (389 mV) exhibited superior catalytic activity compared with Co–P/NF (381 mV) and IrO₂/NF (422 mV), respectively, at +300 mA cm^{−2}. These improvements are primarily attributed to the significantly larger ECSA provided by the Ni–P nanoneedle arrays. The ECSA of Ni–P/NF was 8.8 times larger than that of bare NF, and this enhancement persisted following catalyst deposition or integration with commercial catalysts (Figure 6b and Figure S12). Notably, Pt/C/Ni–P/NF, which was fabricated under identical conditions and differed only in the substrate, exhibited a 4.52-fold increase in ECSA compared with Pt/C/NF, highlighting the critical contribution of the nanostructured Ni–P base layer.

To further evaluate the overall water-splitting performance under alkaline conditions, we assembled two-electrode electrolyzer cells using the HER and OER electrodes as the cathodes and anodes, respectively. Four configurations were tested under identical conditions: Co₃Mo₁-P/Ni–P/NF||Co–P/Ni–P/NF, Pt/C/Ni–P/NF||IrO₂/Ni–P/NF, Co₃Mo₁-P/NF||Co–P/NF, and Pt/C/NF||IrO₂/NF. As shown in Figure 6c, the Ni–P-containing assemblies—Co₃Mo₁-P/Ni–P/NF||Co–P/Ni–P/NF and Pt/C/Ni–P/NF||IrO₂/Ni–P/NF—exhibited substantially lower cell voltages of 446 and 385 mV, respectively, at a current density of 100 mA cm^{−2}, compared with Co₃Mo₁-P/NF||Co–P/NF and Pt/C/NF||IrO₂/NF, which exhibited cell voltages of 563 and 524 mV, respectively. These results confirm that the Ni–P scaffold enhances the overall water-splitting performance. Notably, the non-noble-metal-based electrolyzer cell Co₃Mo₁-P/Ni–P/NF||Co–P/Ni–P/NF delivered performance comparable with that of the Pt/C/Ni–P/NF||IrO₂/Ni–P/NF cell at high current densities, indicating its potential as a viable alternative to noble-metal-based electrolyzers.

The long-term stability was assessed under alkaline conditions (1.0 M KOH) at 100 mA cm² (Figure 6d). The Co₃Mo₁-P/Ni–P/NF||Co–P/Ni–P/NF cell exhibited excellent durability, with a minimal increase of 7 mV in overpotential after 200 h of continuous operation. Comparative analysis of the Co₃Mo₁-P catalyst after initial HER operation and after the durability test showed that its characteristic three-dimensional porous architecture was well preserved (Figure S20). In contrast, the Co₃Mo₁-P/NF||Co–P/NF cell exhibited an increase of 28 mV in overpotential within 75 h, indicating lower stability. The performance of commercial catalyst-based cells degraded over the first 10 h, which subsequently stabilized. This behavior can be attributed to the partial physical detachment of the catalyst particles and the hydration or reorganization of the Nafion binder. Notably, the Pt/C/Ni–P/NF||IrO₂/Ni–P/NF cell exhibited a threefold smaller overpotential shift than the Pt/C/NF||IrO₂/NF cell. This improvement is likely due to the formation of a mechanically robust interlocked architecture between the Ni–P nanostructures and the overlying catalyst layer, which mitigates catalyst detachment. The SEM images of the post-stability-tested electrodes (Figure 6e–g) further confirmed the physical degradation of the catalyst layer on the substrates without the Ni–P structure. In the absence of Ni–P, interfacial adhesion between the catalyst layer and the substrate was insufficient, and extensive delamination of the catalyst layer after HER operation was observed (Figure S21). Collectively,

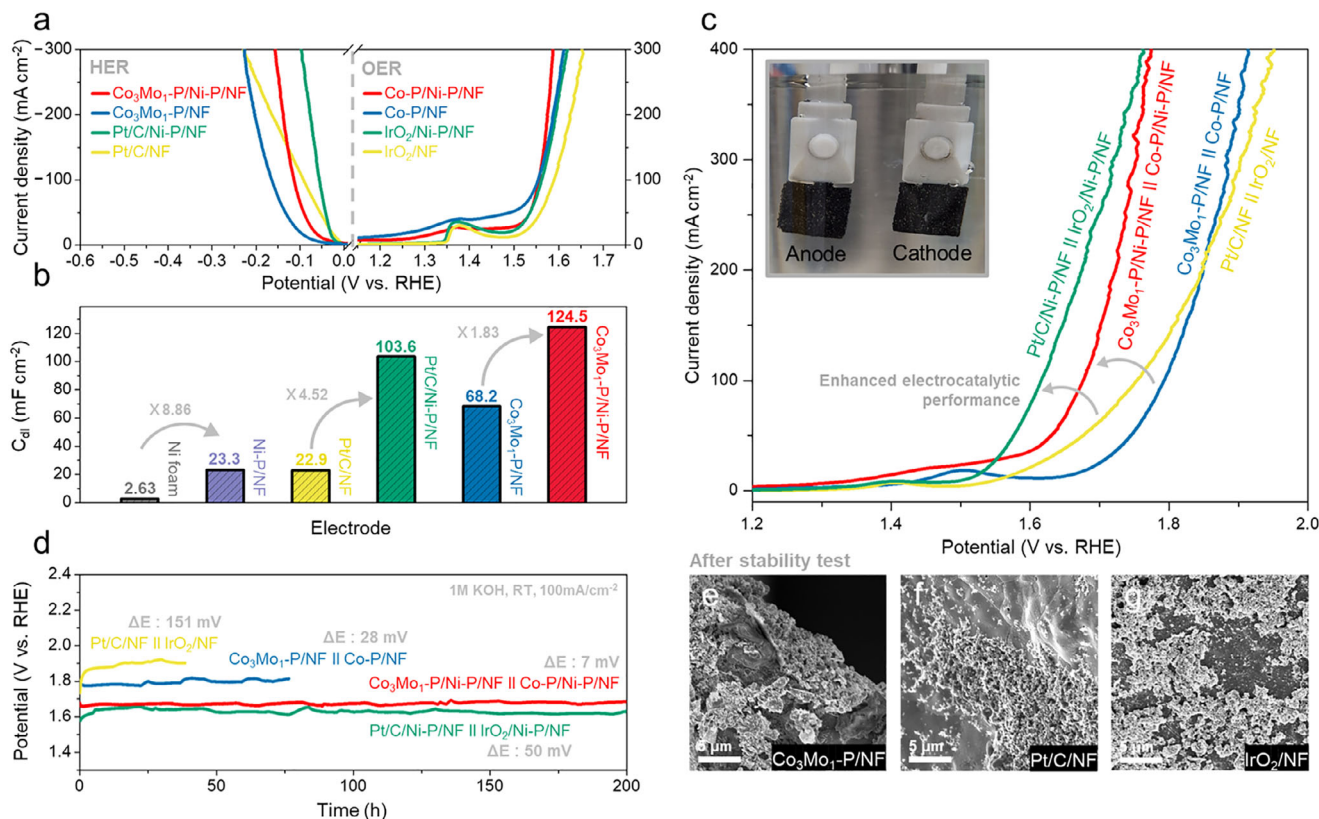


FIGURE 6 | (a) LSV curves for HER in 1.0 M KOH using Co₃Mo₁-P/Ni-P/NF, Co₃Mo₁-P/NF, Pt/C/Ni-P/NF, and Pt/C/NF, and LSV curves for OER using Co-P/Ni-P/NF, Co-P/NF, IrO₂-Ni-P/NF, and IrO₂/NF. (b) Bar chart of C_{dl} values for Co₃Mo₁-P/Ni-P/NF, Co₃Mo₁-P/NF, Pt/C/Ni-P/NF, Pt/C/NF, Ni-P/NF, and bare NF. (c) Overall water-splitting LSV curves for two-electrode configurations: Co₃Mo₁-P/Ni-P/NF || Co-P/Ni-P/NF, Pt/C/Ni-P/NF || IrO₂-Ni-P/NF, Co₃Mo₁-P/NF || Co-P/NF, and Pt/C/NF || IrO₂/NF. (d) Chronopotentiometric stability at 100 mA cm⁻² for 200 h for the same two-electrode pairs. (e–g) SEM images of Co₃Mo₁-P/NF, Pt/C/NF, and IrO₂/NF surfaces after long-term stability testing.

these findings highlight the excellent performance and feasibility of molten salt-derived TMP electrodes for alkaline water splitting. Moreover, substrate modification with hierarchical nanostructures enhances the activity and durability of commercial catalysts. This approach is compatible with existing electrode fabrication workflows, indicating its potential for industrial scalability and implementation.

From an economic perspective, the advantage of Co₃Mo₁-P/Ni-P/NF mainly arises from replacing Pt-dominated HER catalyst layers with Co, Mo, Ni, and P-based components while forming a binder-free self-supported electrode architecture. Although the molten-salt route involves thermal treatment, it directly converts the Ni substrate into a conductive Ni-P scaffold and enables catalyst growth on the same current collector, reducing reliance on noble-metal catalysts and separate catalyst-ink layers. Moreover, the mechanically anchored structure suppresses catalyst detachment during long-term operation, suggesting potential benefits in electrode lifetime and replacement cost.

The scalability and mechanical integrity of the Ni-P scaffold were further examined using larger-area Ni foam and Ni felt substrates (Figures S22 and S23). Uniform Ni-P nanoarray coverage was achieved on a 5 cm² Ni foam substrate using 1.5 g of NaH₂PO₄·H₂O as the P source, indicating that the P-source loading should be optimized according to electrode area and substrate geometry rather than simply scaled linearly from smaller electrodes. For the

5 cm² Ni felt substrate, the P-source loading strongly affected the surface morphology: excessive loading of 2.0 g produced dense and partially coarsened surface coverage, whereas 0.75 g yielded a more open and well-developed three-dimensional Ni-P architecture. Importantly, both Ni-P/Ni foam and Ni-P/Ni felt retained macroscopic flexibility after molten-salt-assisted phosphidation without brittle fracture when bent to angles greater than 60° (Figure S24). These results confirm that the optimized molten-salt treatment preserves sufficient mechanical integrity of the Ni-based substrates. Accordingly, the optimized Ni-P/Ni felt was used as the electrode platform for the AEMWE measurements.

To adapt the molten-salt-assisted electrode architecture to AEMWE operation, CoMo-P/Ni-P/Ni felt was synthesized using a two-step process analogous to that used for Ni foam. SEM images showed that the Ni felt fibers were uniformly covered with porous CoMo-P catalyst layers while retaining the open fibrous network of the substrate (Figure S25). SEM-EDS analysis confirmed a Co: Mo atomic ratio of approximately 3:1, consistent with the optimized CoMo-P composition on Ni foam. In addition, Pt/C deposited on Ni-P/Ni felt exhibited more uniform coverage than Pt/C deposited on bare Ni felt under identical loading conditions (Figures S26 and S27). The improved catalyst distribution is attributed to the enhanced wettability and nanostructured surface of the Ni-P scaffold, which promote homogeneous ink spreading and mechanical interlocking with the Pt/C layer. These results support the superior AEMWE performance of

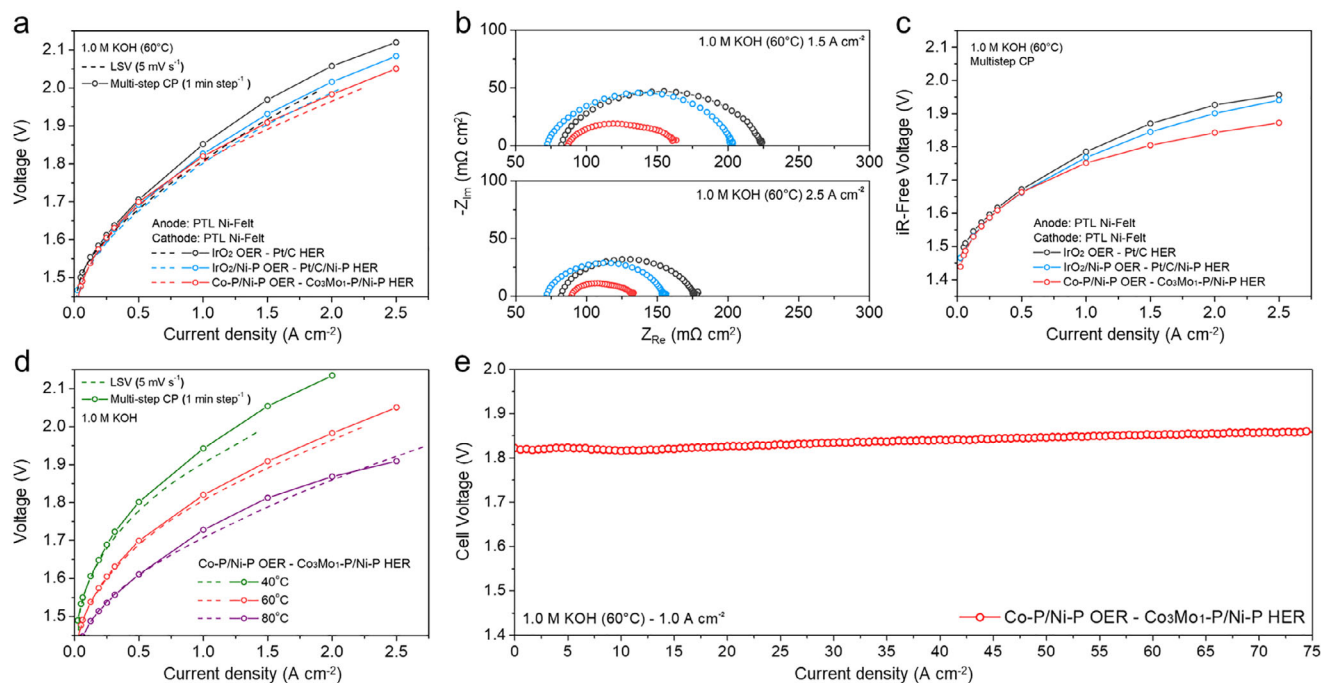


FIGURE 7 | AEMWE single-cell performance of phosphide-based self-supported electrodes. (a) LSV (5 mV s^{-1} , dashed) and multi-step chronopotentiometry (1 min step^{-1} , symbols) polarization curves of AEMWE single cells with different anode/cathode catalyst configurations ($\text{IrO}_2||\text{Pt/C}$, $\text{IrO}_2/\text{Ni-P}||\text{Pt/C/Ni-P}$, and $\text{Co-P/Ni-P}||\text{Co}_3\text{Mo}_1\text{-P/Ni-P}$) measured at 60°C . (b) EIS spectra measured at 1.5 and 2.5 A cm^{-2} . (c) IR-free polarization curves. (d) Temperature-dependent polarization performance of the $\text{Co-P/Ni-P}||\text{Co}_3\text{Mo}_1\text{-P/Ni-P}$ single cell at 40°C , 60°C , and 80°C . (e) Durability test of the $\text{Co-P/Ni-P}||\text{Co}_3\text{Mo}_1\text{-P/Ni-P}$ single cell at 1 A cm^{-2} and 60°C for 75 h .

the molten-salt-derived self-supported electrode and the Ni-P-supported commercial catalyst electrode shown in Figure 7.

To examine whether the performance trends observed in the half-cell measurements are retained under practical membrane-electrode operation, AEMWE single-cell performance was evaluated using three different anode/cathode catalyst configurations: $\text{IrO}_2||\text{Pt/C}$, $\text{IrO}_2/\text{Ni-P}||\text{Pt/C/Ni-P}$, and $\text{Co-P/Ni-P}||\text{Co}_3\text{Mo}_1\text{-P/Ni-P}$. All single-cell measurements were conducted at 60°C using polarization measurements obtained by linear sweep voltammetry (5 mV s^{-1}) and multi-step chronopotentiometric holding (1 min at each current density). As shown in Figure 7a, the polarization curves exhibit a clear performance trend of $\text{IrO}_2||\text{Pt/C} < \text{IrO}_2/\text{Ni-P}||\text{Pt/C/Ni-P} < \text{Co-P/Ni-P}||\text{Co}_3\text{Mo}_1\text{-P/Ni-P}$, which is consistent with the general trend observed in the half-cell measurements. The performance enhancement from $\text{IrO}_2||\text{Pt/C}$ to $\text{IrO}_2/\text{Ni-P}||\text{Pt/C/Ni-P}$ suggests that the Ni-P nanostructured scaffold improves electrode interfacial characteristics and catalyst utilization even under membrane-based single-cell operation. More importantly, the superior performance of $\text{Co-P/Ni-P}||\text{Co}_3\text{Mo}_1\text{-P/Ni-P}$ demonstrates that the synergistic catalytic benefits of Co-Mo phosphide chemistry, combined with the self-supported hierarchical electrode architecture, are effectively translated and retained under practical AEMWE operating conditions. Electrochemical impedance spectroscopy (EIS) performed at 1.5 and 2.5 A cm^{-2} (Figure 7b) further supports this trend. In the high-current-density region, $\text{Co-P/Ni-P}||\text{Co}_3\text{Mo}_1\text{-P/Ni-P}$ exhibited the smallest charge-transfer resistance, indicating accelerated electrode kinetics under practical operating conditions. This favorable behavior

is likely attributed to the hierarchical nanostructured electrode architecture, which facilitates rapid gas-bubble release, maintains effective active-site accessibility, and alleviates mass-transport limitations during high-current operation. Interestingly, despite exhibiting the best overall performance, $\text{Co-P/Ni-P}||\text{Co}_3\text{Mo}_1\text{-P/Ni-P}$ showed the highest high-frequency resistance (HFR), whereas $\text{IrO}_2/\text{Ni-P}||\text{Pt/C/Ni-P}$ exhibited the lowest HFR, as shown in Figure 7b and Figure S28. Specifically, at 0.5 A cm^{-2} , the HFR values were 71.51 , 67.52 , and $59.63 \text{ m}\Omega \text{ cm}^2$ for $\text{Co-P/Ni-P}||\text{Co}_3\text{Mo}_1\text{-P/Ni-P}$, $\text{IrO}_2||\text{Pt/C}$, and $\text{IrO}_2/\text{Ni-P}||\text{Pt/C/Ni-P}$, respectively. The relatively higher HFR of the $\text{Co-P/Ni-P}||\text{Co}_3\text{Mo}_1\text{-P/Ni-P}$ cell may be associated with differences in electrode architecture, including the use of a self-supported carbon-support-free phosphide cathode instead of a conventional Pt/C-based catalyst layer, as well as differences in catalyst layer composition and interfacial/contact resistance compared with the IrO_2 -based systems. Nevertheless, the $\text{Co-P/Ni-P}||\text{Co}_3\text{Mo}_1\text{-P/Ni-P}$ cell still delivered the best performance, indicating that its superior kinetic and mass-transport characteristics more than compensate for the increased ohmic contribution under practical operating conditions. This interpretation is further supported by the IR-free polarization curves shown in Figure 7c, where the superior performance of $\text{Co-P/Ni-P}||\text{Co}_3\text{Mo}_1\text{-P/Ni-P}$ becomes even more pronounced after HFR compensation.

To further investigate the effect of operating temperature on AEMWE performance, the optimized $\text{Co-P/Ni-P}||\text{Co}_3\text{Mo}_1\text{-P/Ni-P}$ cell was evaluated under temperature-dependent operating conditions. As shown in Figure 7d, at 2 A cm^{-2} , the cell voltages were 2.13 , 1.98 , and 1.87 V at 40°C , 60°C , and 80°C ,

respectively, demonstrating substantial performance improvement with increasing temperature. The corresponding EIS spectra (Figure S29a), HFR spectra (Figure S29b), and overpotential breakdown analysis (Figure S29c) provide further insight into the origin of this behavior. Notably, the overpotential breakdown analysis reveals that increasing temperature significantly reduces both kinetic and ohmic overpotentials, whereas the mass-transport overpotential remains relatively unchanged, suggesting that mass-transport limitations were less sensitive to temperature under the tested conditions. These results indicate that elevated operating temperature enables more effective utilization of the developed self-supported electrode architecture by improving reaction kinetics and ionic transport within the cell. Finally, the durability of the Co–P/Ni–P||Co₃Mo₁-P/Ni–P cell was evaluated at 60°C under a constant current density of 1 A cm^{−2} for 75 h (Figure 7e). The initial cell voltage was 1.822 V, consistent with the multi-step chronopotentiometric polarization data, indicating stable initial operation without any abrupt voltage increase during the initial operation. After 75 h of continuous operation, the cell voltage increased only slightly to 1.858 V, demonstrating excellent operational stability. Further supporting this result, the polarization curves measured before and after durability testing in Figure S30 show negligible performance degradation, while the EIS spectra measured at 0.25 and 0.5 A cm^{−2} remain nearly unchanged. These results confirm the stable operation of the developed Co–Mo phosphide-based self-supported electrode architecture under practical AEMWE single-cell conditions.

3 | Conclusions

The two-step molten salt-assisted synthesis strategy developed in this study enabled the fabrication of self-supported electrocatalyst electrodes. This method enabled the formation of a vertically aligned Ni–P nanoneedle array on NF, followed by the controlled growth of a Co₃Mo₁-P catalytic overlayer without compromising structural integrity. The nanostructured Ni–P scaffold physically anchored the catalyst particles, thereby preventing their detachment during operation. Additionally, the Ni–P layer provided strong oxidation resistance and metallic conductivity, simultaneously contributing to structural stability and efficient electron transport. The resulting Co₃Mo₁-P/Ni–P/NF electrode exhibited an exceptionally low overpotential of 113.5 mV at 100 mA cm^{−2}, outperforming previously reported TMP-based electrodes under identical conditions.

The optimized Co: Mo ratio not only modulated the surface electronic structure to enhance the catalytic activity but also expanded the ECSA. Furthermore, the vertically aligned nanoneedle architecture maximized accessible active sites and facilitated rapid hydrogen bubble release, ensuring stable operation under high current densities.

Beyond its intrinsic performance, the nanostructured Ni–P array also functioned as a versatile support for commercial catalysts. The integration of commercial catalysts, such as Pt/C and IrO₂, onto the Ni–P/NF scaffold—an approach rarely explored—significantly improved both catalytic activity and durability. In particular, Pt/C loaded onto the nanostructured support achieved a 4.52-fold increase in ECSA and an impressively low overpotential of 55.8 mV at 100 mA cm^{−2} compared with Pt/C deposited

on bare NF. This mechanically interlocked electrode structure effectively suppressed catalyst detachment and preserved long-term stability. Furthermore, the practical applicability of the developed self-supported electrode architecture was validated in an AEMWE single cell under membrane-based electrolysis conditions, where the synergistic Co–Mo phosphide chemistry and Ni–P nanoarray-enabled architecture translated into superior cell-level performance and stable operation under practical operating conditions.

These results emphasize the importance of precise nanostructural design for high-performance and durable electrocatalysts. They also highlight the potential of molten-salt-based synthetic strategy as a scalable route for engineering robust, conductive, and industrially viable electrode platforms for alkaline water electrolysis.

Author Contributions

Hyeonseok Lee: Investigation, Formal analysis, Conceptualization, Writing – original draft, Methodology. **Tai The Mai:** Investigation, Data curation, Formal analysis, Validation. **Wooseok Jeong:** Formal analysis, Validation. **Jin Young Kim:** Data curation, Formal analysis. **Yoonsu Park:** Formal analysis, Investigation. **Yun Jae Hwang:** Investigation, Validation. **Boeun An:** Investigation. **Yeongbin Lee & Gyuhyeon Kim:** Visualization. **Heesoo Jeong & Yujeong Ahn:** Validation. **Chanbi Kim:** Data curation. **Dong Hwan Wang:** Supervision. **Segeun Jang:** Methodology, Validation, Supervision, Writing – review & editing. **Don-Hyung Ha:** Funding acquisition, Validation, Supervision, Writing – review & editing.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

1. B. Yang and Z. Xiang, “Nanostructure Engineering of Cathode Layers in Proton Exchange Membrane Fuel Cells: From Catalysts to Membrane Electrode Assembly,” *ACS Nano* 18 (2024): 11598–11630, <https://doi.org/10.1021/acsnano.4c01113>.
2. Y. Qin, Z. Li, Y. Duan, J. Guo, M. Zhao, and Z. Tang, “Nanostructural Engineering of Metal-Organic Frameworks: Construction Strategies and Catalytic Applications,” *Matter* 5 (2022): 3260–3310, <https://doi.org/10.1016/j.matt.2022.07.014>.
3. W. Xu, Y. Bai, and Y. Yin, “Surface Engineering of Nanostructured Energy Materials,” *Advanced Materials* 30 (2018): 1802091.

4. W. Jeong, H. Lee, Y. J. Hwang, et al., "Solution Processing for Colloidal Nanoparticle Thin Film: From Fundamentals to Applications," *Advances in Colloid and Interface Science* 342 (2025): 103538, <https://doi.org/10.1016/j.cis.2025.103538>.
5. Z. Zhou, Z. Jin, and N. Tsubaki, "Synergistic Effects Between Pd Single Atoms and Nanoscopic Pd Atom Clusters: Facilitating Formation of Pd-N Charge Channels and Strong Internal Electric Fields for Large-Scale Photocatalytic Hydrogen Evolution," *Nano Energy* 146 (2025): 111533, <https://doi.org/10.1016/j.nanoen.2025.111533>.
6. Y. Park, B. An, H. Kim, et al., "Ionomer-Free Co-Ru Based Electrode for Efficient Proton Exchange Membrane Water Electrolysis via Synergistic Catalysis," *Chemical Engineering Journal* 511 (2025): 161979, <https://doi.org/10.1016/j.cej.2025.161979>.
7. S. Jun, J.-W. Lee, S.-C. Kim, S. J. Oh, and S. Jeong, "Unveiling the Ligand-Mediated Phase Engineering Mechanism in Two-Dimensional Transition Metal Chalcogenides Through Coordination Geometry Control," *Journal of Materials Chemistry A* 12 (2024): 7522–7527, <https://doi.org/10.1039/D4TA00326H>.
8. E. Enkhbayar, A. Gaur, J. U. Jang, et al., "Self-Supported Electrocatalyst for Seawater Splitting," *ChemElectroChem* 11 (2024): 202300835.
9. H. Xiong, R. Zhuang, B. Cheng, et al., "Self-Supported Metallic Alkaline Hydrogen Evolution Electrocatalysts Tolerant for Ampere-Level Current Densities," *Advanced Energy Materials* 15 (2025): 2404077, <https://doi.org/10.1002/aenm.202404077>.
10. E. Zhang and W. Song, "Review—Self-Supporting Electrocatalysts for HER in Alkaline Water Electrolysis," *Journal of The Electrochemical Society* 171 (2024): 052503, <https://doi.org/10.1149/1945-7111/ad4c0d>.
11. H. Sun, B. Yao, Y. Han, et al., "Multi-Interface Engineering of Self-Supported Nickel/Yttrium Oxide Electrode Enables Kinetically Accelerated and Ultra-Stable Alkaline Hydrogen Evolution at Industrial-Level Current Density," *Advanced Energy Materials* 14 (2024): 2303563, <https://doi.org/10.1002/aenm.202303563>.
12. M. A. Gaikwad, V. V. Burungale, D. B. Malavekar, et al., "Self-Supported Fe-Based Nanostructured Electrocatalysts for Water Splitting and Selective Oxidation Reactions: Past, Present, and Future," *Advanced Energy Materials* 14 (2024): 2303730, <https://doi.org/10.1002/aenm.202303730>.
13. R. Xue, R. Deng, Y. Li, M. Gao, J. Wang, and Q. Zhang, "Deep Eutectic Solvent-Induced Controllable Synthesis of Bifunctional Ni-Fe-P Catalysts for Electrochemical Water Splitting," *Green Chemical Engineering* 6 (2025): 93–101, <https://doi.org/10.1016/j.gce.2024.04.002>.
14. H. Wang, H. Jiang, C. Gao, et al., "Self Supported FeS/Fe₅Ni₄S₈ Heterostructure Catalyst for Efficient Water Splitting," *Chemical Engineering Journal* 501 (2024): 157738.
15. S. A. Abdelfattah, M. M. Omran, A. Mohamed, A. M. Matloob, and O. E. Mahmoud, "In-Situ Preparation of NiCo-LDH/NF Electrode for Green Hydrogen Production Through Alkaline Water Electrolysis," *Materials Chemistry and Physics* 332 (2025): 130097, <https://doi.org/10.1016/j.matchemphys.2024.130097>.
16. J. Hu, Z. Huang, and Y. Liu, "Beyond Solvothermal: Alternative Synthetic Methods for Covalent Organic Frameworks," *Angewandte Chemie International Edition* 62 (2023): 202306999, <https://doi.org/10.1002/anie.202306999>.
17. X. Yu, B. Wang, C. Wang, et al., "2D High-Entropy Hydrotalcites," *Small* 17 (2021): 2103412, <https://doi.org/10.1002/smll.202103412>.
18. S. K. Gupta and Y. Mao, "Recent Developments on Molten Salt Synthesis of Inorganic Nanomaterials: A Review," *The Journal of Physical Chemistry C* 125 (2021): 6508–6533, <https://doi.org/10.1021/acs.jpcc.0c10981>.
19. Y. Jiang, T. Fu, J. Liu, J. Zhao, B. Li, and Z. Chen, "Molten Salt Synthesis of Carbon-Supported Pt–Rare Earth Metal Nanoalloy Catalysts for Oxygen Reduction Reaction," *RSC Advances* 12 (2022): 4805–4812, <https://doi.org/10.1039/D1RA09400A>.
20. H. Lee, H. Jeong, W. Jeong, et al., "Wet Chemistry Methods for Synthesizing High-Entropy Nanoparticles: A Review of the Synthesis Strategies and Various Applications," *Korean Journal of Chemical Engineering* 41 (2024): 3371–3393, <https://doi.org/10.1007/s11814-024-00249-4>.
21. S. K. Nemani, M. Torkamanzadeh, B. C. Wyatt, V. Presser, and B. Anasori, "Functional Two-Dimensional High-Entropy Materials," *Communications Materials* 4 (2023): 16, <https://doi.org/10.1038/s43246-023-00341-y>.
22. N. K. Mahdy, M. El-Sayed, S. E.-D. Al-Mofty, et al., "Toward Scaling up the Production of Metal Oxide Nanoparticles for Application on Washable Antimicrobial Cotton Fabrics," *ACS Omega* 7 (2022): 38942–38956, <https://doi.org/10.1021/acsomega.2c04692>.
23. W. Jeong, Y.-K. Hong, H. Kim, et al., "Colloidal-Nanoparticle-Derived Nickel/Ferric Oxide Heterointerfaces for Promoting the Alkaline Oxygen Evolution Reaction," *Journal of Materials Chemistry A* 13 (2025): 16469–16480, <https://doi.org/10.1039/D4TA09280E>.
24. Y. Chen, Z. Lai, X. Zhang, et al., "Phase Engineering of Nanomaterials," *Nature Reviews Chemistry* 4 (2020): 243–256, <https://doi.org/10.1038/s41570-020-0173-4>.
25. S. Li, J. Song, Y. Che, S. Jiao, J. He, and B. Yang, "Advances in Molten Salt Synthesis of Non-Oxide Materials," *Energy & Environmental Materials* 6 (2023): 12339, <https://doi.org/10.1002/eem2.12339>.
26. H. Tüysüz, "Alkaline Water Electrolysis for Green Hydrogen Production," *Accounts of Chemical Research* 57 (2024): 558–567.
27. I. M. Perović, S. D. Mitrović, S. M. Brković, and I. A. Pašti, "Advances in Nickel-Based Catalysts for Alkaline Water Electrolysis: Comprehensive Review of Current Research Direction for HER and OER Applications," *Chemical Record* 25 (2025): 202500049.
28. Y. Sun, M. Qi, X. Tan, et al., "Gram-Scale Synthesis of N-NiMo/MoO₂ Heterostructures to Boost Hydrogen Evolution in Low-Alkalinity Anion Exchange Membrane Water Electrolysis," *Nano Energy* 146 (2025): 111489, <https://doi.org/10.1016/j.nanoen.2025.111489>.
29. B. Guo, W. Li, H. Chen, et al., "Single-Atom Ru Anchored on Co₃S₄ Nanowires Enabling Ampere-Level Water Splitting for Multi-scenarios Green Energy-To-Hydrogen Systems," *Nano Energy* 138 (2025): 110881, <https://doi.org/10.1016/j.nanoen.2025.110881>.
30. R. Ren, J. Wang, Y. Xie, et al., "Fe-Doping Accelerates the Reconstruction Kinetics of Metal-Organic Frameworks Toward Active Amorphous Oxyhydroxide Enabling Industrial Water Splitting," *Applied Catalysis B: Environment and Energy* 388 (2026): 126543, <https://doi.org/10.1016/j.apcatb.2026.126543>.
31. Y. Lee, W. Jeong, Y. J. Hwang, et al., "Basics, Developments, and Strategies of Transition Metal Phosphides Toward Electrocatalytic Water Splitting: Beyond Noble Metal Catalysts," *Journal of Materials Chemistry A* 12 (2024): 28574–28594, <https://doi.org/10.1039/D4TA04455J>.
32. H. Lei, Y. Zhou, Z. Huangfu, et al., "Noble Metal Nanoparticles Anchored on Transition Metal Phosphides for Effective pH-Universal Hydrogen Evolution," *Advanced Science* 12 (2025): 2504462, <https://doi.org/10.1002/adv.202504462>.
33. X. Lv, T. Wang, W. Zhang, and Y. Wang, "Modulation Strategies for Improving Electrocatalytic Performance of Transition Metal Phosphides," *Chemcatchem* 16 (2024): 202400872, <https://doi.org/10.1002/cctc.202400872>.
34. H. Wang, C. Niu, W. Liu, and S. Tao, "D-Electron Tuned CoMoP for Enhance 5-Hydroxymethylfurfural Oxidation and HER," *Applied Catalysis B: Environmental* 340 (2024): 123249.
35. A. C. Thenuwara, L. Dheer, N. H. Attanayake, Q. Yan, U. V. Waghmare, and D. R. Strongin, "Co-Mo-P Based Electrocatalyst for Superior Reactivity in the Alkaline Hydrogen Evolution Reaction," *Chemcatchem* 10 (2018): 4832–4837, <https://doi.org/10.1002/cctc.201801389>.
36. L. Zhao, Y. Zhang, Z. Zhao, et al., "Steering Elementary Steps towards Efficient Alkaline Hydrogen Evolution via Size-Dependent

- Ni/NiO Nanoscale Heterosurfaces,” *National Science Review* 7 (2020): 27–36, <https://doi.org/10.1093/nsr/nwz145>.
37. L. Peng, M. Liao, X. Zheng, et al., “Accelerated alkaline hydrogen evolution on $M(OH)_x/M-MoPO_x$ ($M = Ni, Co, Fe, Mn$) Electrocatalysts by Coupling Water Dissociation and Hydrogen Ad-Desorption Steps,” *Chemical Science* 11 (2020): 2487–2493.
38. T. Dey, A. Rajput, G. Jhaa, et al., “Rapid Electronic Transport Channel of Co-P With Mo in a Heterostructure Embedded With P, N Dual Doped Porous Carbon for Electrocatalytic Oxygen and Hydrogen Evolution,” *ChemNanoMat* 10 (2024): 202400089, <https://doi.org/10.1002/cnma.202400089>.
39. C. Sun and D. Xue, “Crystal Growth: An Anisotropic Mass Transfer Process at the Interface,” *Physical Chemistry Chemical Physics* 19 (2017): 12407–12413, <https://doi.org/10.1039/C7CP01112A>.
40. X. Zhou, H. Gao, Y. Wang, Z. Liu, J. Lin, and Y. Ding, “P Vacancies-Enriched 3D Hierarchical Reduced Cobalt Phosphide as a Precursor Template for Defect Engineering for Efficient Water Oxidation,” *Journal of Materials Chemistry A* 6 (2018): 14939–14948, <https://doi.org/10.1039/C8TA03784A>.
41. Y. Wang, Y. Wang, J. Bai, and W.-M. Lau, “Trace Amount of NiP_2 Cooperative CoMoP Nanosheets Inducing Efficient Hydrogen Evolution,” *ACS Omega* 6 (2021): 33057–33066, <https://doi.org/10.1021/acsomega.1c05206>.
42. Y. Lian, H. Sun, X. Wang, et al., “Carved Nanoframes of Cobalt–Iron Bimetal Phosphide as a Bifunctional Electrocatalyst for Efficient Overall Water Splitting,” *Chemical Science* 10 (2019): 464–474, <https://doi.org/10.1039/C8SC03877E>.
43. A. P. Grosvenor, R. G. Cavell, and A. Mar, “Next-Nearest Neighbour Contributions to $P\ 2p_{3/2}$ X-Ray Photoelectron Binding Energy Shifts of Mixed Transition-Metal Phosphides $M_{1-x}M'_xP$ With the MnP -Type Structure,” *Journal of Solid State Chemistry* 180 (2007): 2702–2712, <https://doi.org/10.1016/j.jssc.2007.07.027>.
44. X. Wang, L. Yang, C. Xing, et al., “MOF-Derived Ultrathin Cobalt Molybdenum Phosphide Nanosheets for Efficient Electrochemical Overall Water Splitting,” *Nanomaterials* 12 (2022): 1098, <https://doi.org/10.3390/nano12071098>.
45. D. Guo, L. Wen, T. Wang, and X. Li, “Electrodeposition Synthesis of Cobalt-Molybdenum Bimetallic Phosphide on Nickel Foam for Efficient Water Splitting,” *Journal of Colloid and Interface Science* 659 (2024): 707–717, <https://doi.org/10.1016/j.jcis.2023.09.173>.
46. X. Wang, J. Zhou, W. Cui, et al., “Electron Manipulation and Surface Reconstruction of Bimetallic Iron–Nickel Phosphide Nanotubes for Enhanced Alkaline Water Electrolysis,” *Advanced Science* 11 (2024): 2401207, <https://doi.org/10.1002/advs.202401207>.
47. A. Toghræi, T. Shahrabi, and G. B. Darband, “Electrodeposition of Self-Supported Ni–Mo–P Film on Ni Foam as an Affordable and High-Performance Electrocatalyst Toward Hydrogen Evolution Reaction,” *Electrochimica Acta* 335 (2020): 135643, <https://doi.org/10.1016/j.electacta.2020.135643>.
48. L. Zhang, J. Peng, Y. Yuan, W. Zhang, and K. Peng, “Bifunctional Heterostructure NiCo-layered Double Hydroxide Nanosheets/NiCoP Nanotubes/Ni Foam for Overall Water Splitting,” *Applied Surface Science* 557 (2021): 149831, <https://doi.org/10.1016/j.apsusc.2021.149831>.
49. X. Luo, L. Wang, W. Sun, et al., “One-Step Electrodeposition of NiMoP/NF as an Efficient and Cost-Effective Cathodic Electrocatalyst for Alkaline Water Electrolysis,” *Industrial & Engineering Chemistry Research* 62 (2023): 10454–10466, <https://doi.org/10.1021/acs.iecr.3c00803>.
50. Z. Wang, S. Wang, L. Ma, et al., “Water-Induced Formation of $Ni_2P-Ni_{12}P_5$ Interfaces With Superior Electrocatalytic Activity Toward Hydrogen Evolution Reaction,” *Small* 17 (2021): 2006770, <https://doi.org/10.1002/smll.202006770>.
51. Q. Han, H. Wu, F. Li, et al., “Self-Standing Hierarchical Porous Nickel-Iron Phosphide/Nickel Foam for Long-Term Overall Water Splitting,” *Catalysts* 13 (2023): 1242, <https://doi.org/10.3390/catal13091242>.
52. H. Zhang, H. Jiang, Y. Hu, H. Jiang, and C. Li, “Integrated Ni–P–S Nanosheets Array as Superior Electrocatalysts for Hydrogen Generation,” *Green Energy & Environment* 2 (2017): 112–118, <https://doi.org/10.1016/j.gee.2016.12.004>.
53. Y. Song, Q. Wang, X. Liu, et al., “Nickel Foam-Loaded Zn/Co Bimetallic Phosphide as an Efficient Bifunctional Electrolytic Water Catalyst,” *Catalysis Letters* 154 (2024): 5101–5109, <https://doi.org/10.1007/s10562-024-04718-7>.
54. J. Wang, J. Yang, F. Huang, et al., “Porous Tremella-Like NiMoP/CoP Network Electrodes as an Efficient Electrocatalyst,” *Physical Chemistry Chemical Physics* 26 (2024): 11667–11675, <https://doi.org/10.1039/D3CP04423H>.
55. Y. Yang, R. Zou, J. Gan, et al., “Integrating Electrocatalytic Seawater Splitting and Biomass Upgrading via Bifunctional Nickel Cobalt Phosphide Nanorods,” *Green Chemistry* 25 (2023): 4104–4112, <https://doi.org/10.1039/D3GC00684K>.
56. Z.-P. Lv, D.-H. Zhang, M.-L. Zang, S.-L. Li, J.-L. He, and J.-X. Song, “Boosting Alkaline Hydrogen Evolution via Spontaneous Built-In Electric Field,” *Rare Metals* 43 (2024): 5848–5859, <https://doi.org/10.1007/s12598-024-02859-7>.
57. S. Song, A. Song, L. Bai, et al., “Hierarchical Design of Homologous NiCoP/NF From Layered Double Hydroxides as a Long-Term Stable Electrocatalyst for Hydrogen Evolution,” *Catalysts* 13 (2023): 1232, <https://doi.org/10.3390/catal13091232>.
58. B. Deng, L. Zhou, Z. Jiang, and Z.-J. Jiang, “High Catalytic Performance of Nickel Foam Supported Co_2P-Ni_2P for Overall Water Splitting and Its Structural Evolutions During Hydrogen/Oxygen Evolution Reactions in Alkaline Solutions,” *Journal of Catalysis* 373 (2019): 81–92, <https://doi.org/10.1016/j.jcat.2019.03.038>.
59. K. Wang, Y. Si, Z. Lv, et al., “Efficient and Stable Ni–Co–Fe–P Nanosheet Arrays on Ni Foam for Alkaline and Neutral Hydrogen Evolution,” *International Journal of Hydrogen Energy* 45 (2020): 2504–2512, <https://doi.org/10.1016/j.ijhydene.2019.11.154>.
60. S. Sirisomboonchai, N. Kitiphatpiboon, M. Chen, et al., “Multi-Hierarchical Porous Mn-Doped CoP Catalyst on Nickel Phosphide Foam for Hydrogen Evolution Reaction,” *ACS Applied Energy Materials* 5 (2021): 149–158, <https://doi.org/10.1021/acsaem.1c02650>.
61. B. Lu, Y. Wang, W. Li, et al., “Ni–P Alloy@Carbon Nanotubes Immobilized on the Framework of Ni Foam as a 3D Hierarchical Porous Self-Supporting Electrode for Hydrogen Evolution Reaction,” *International Journal of Hydrogen Energy* 46 (2021): 23245–23253, <https://doi.org/10.1016/j.ijhydene.2021.04.139>.
62. J. Li, G. Wei, Y. Zhu, et al., “Hierarchical NiCoP Nanocone Arrays Supported on Ni Foam as an Efficient and Stable Bifunctional Electrocatalyst for Overall Water Splitting,” *Journal of Materials Chemistry A* 5 (2017): 14828–14837, <https://doi.org/10.1039/C7TA03947F>.
63. X.-W. Lv, Z.-P. Hu, L. Chen, J.-T. Ren, Y.-P. Liu, and Z.-Y. Yuan, “Organic–Inorganic Metal Phosphonate-Derived Nitrogen-Doped Core–Shell Ni_2P Nanoparticles Supported on Ni Foam for Efficient Hydrogen Evolution Reaction at All pH Values,” *ACS Sustainable Chemistry & Engineering* 7 (2019): 12770–12778, <https://doi.org/10.1021/acssuschemeng.9b01355>.
64. M. R. Kandel, U. N. Pan, D. R. Paudel, P. P. Dhakal, N. H. Kim, and J. H. Lee, “Hybridized Bimetallic Phosphides of Ni–Mo, Co–Mo, and Co–Ni in a Single Ultrathin-3D-Nanosheets for Efficient HER and OER in Alkaline Media,” *Composites Part B: Engineering* 239 (2022): 109992, <https://doi.org/10.1016/j.compositesb.2022.109992>.
65. T. C. Taucher, O. T. Hofmann, and E. Zojer, “Final-State Simulations of Core-Level Binding Energies at Metal-organic Hybrid Interfaces: Artifacts Caused by Spurious Collective Electrostatic Effects,” *ACS Omega* 5 (2020): 25868–25881, <https://doi.org/10.1021/acsomega.0c03209>.
66. G. Liu, F. Hou, X. Wang, and B. Fang, “Stainless Steel-Supported Amorphous Nickel Phosphide/Nickel as an Electrocatalyst for Hydrogen

- Evolution Reaction,” *Nanomaterials* 12 (2022): 3328, <https://doi.org/10.3390/nano12193328>.
67. C. Pan, W. Li, and S. Jiang, “Study on the XPS-ESCA of Aluminum Phosphide Products,” *International Journal of Molecular Sciences* 6 (2005): 198–202, <https://doi.org/10.3390/i6030198>.
68. Y. Zhu, M. Klingenhof, C. Gao, et al., “Facilitating Alkaline Hydrogen Evolution Reaction on the Hetero-interfaced Ru/RuO₂ Through Pt Single Atoms Doping,” *Nature Communications* 15 (2024): 1447, <https://doi.org/10.1038/s41467-024-45654-9>.
69. M. C. Oliveira and A. B. do Rego, “The Effect of the Hypophosphite Ion Oxidation on the Ni Surface Electrode—An XPS Study,” *Journal of Alloys and Compounds* 425 (2006): 64–68, <https://doi.org/10.1016/j.jallcom.2005.11.092>.
70. A. P. Grosvenor, M. C. Biesinger, R. S. C. Smart, and N. S. McIntyre, “New Interpretations of XPS Spectra of Nickel Metal and Oxides,” *Surface Science* 600 (2006): 1771–1779, <https://doi.org/10.1016/j.susc.2006.01.041>.
71. K. Edamoto, Y. Nakadai, H. Inomata, K. Ozawa, and S. Otani, “Soft X-Ray Photoelectron Spectroscopy Study of Ni₂P (0001),” *Solid State Communications* 148 (2008): 135–138, <https://doi.org/10.1016/j.ssc.2008.07.037>.
72. Y. Shi, Y. Xu, S. Zhuo, J. Zhang, and B. Zhang, “Ni₂P Nanosheets/Ni Foam Composite Electrode for Long-Lived and pH-Tolerable Electrochemical Hydrogen Generation,” *ACS Applied Materials & Interfaces* 7 (2015): 2376–2384, <https://doi.org/10.1021/am5069547>.
73. X. Cao, Y. Tan, H. Zheng, J. Hu, X. Chen, and Z. Chen, “Effect of Cobalt Phosphide (CoP) Vacancies on Its Hydrogen Evolution Activity via Water Splitting: A Theoretical Study,” *Physical Chemistry Chemical Physics* 24 (2022): 4644–4652, <https://doi.org/10.1039/D1CP05739A>.
74. D.-Y. Kuo, E. Nishiwaki, R. A. Rivera-Maldonado, and B. M. Cossairt, “The Role of Hydrogen Adsorption Site Diversity in Catalysis on Transition-Metal Phosphide Surfaces,” *ACS Catalysis* 13 (2022): 287–295.
75. N. A. Arnosti, V. Wyss, and M. F. Delley, “Controlled Surface Modification of Cobalt Phosphide With Sulfur Tunes Hydrogenation Catalysis,” *Journal of the American Chemical Society* 145 (2023): 23556–23567, <https://doi.org/10.1021/jacs.3c07312>.
76. H. H. Do, “Recent Progress and Perspectives of Co₃O₄-Based Electrocatalysts for Oxygen Evolution Reaction,” *Transactions on Electrical and Electronic Materials* 26 (2025): 667–678.
77. S. Naeem, “Electrodeposited Cobalt Hydroxide Thin Films: A Comprehensive Investigation From Synthesis to Advanced Electrochemical Behavior for High-Performance Energy Storage,” *Transactions on Electrical and Electronic Materials* 25 (2024): 589–599, <https://doi.org/10.1007/s42341-024-00542-3>.
78. M. Luo, J. Yang, X. Li, M. Eguchi, Y. Yamauchi, and Z.-L. Wang, “Insights Into Alloy/Oxide or Hydroxide Interfaces in Ni–Mo-Based Electrocatalysts for Hydrogen Evolution Under Alkaline Conditions,” *Chemical Science* 14 (2023): 3400–3414, <https://doi.org/10.1039/D2SC06298D>.
79. T. Kim, K.-R. Yeo, H. Kim, J. Lee, and S.-K. Kim, “Impact of Phosphide–Phosphate Ratio on NiCoP Catalysts for Hydrogen Evolution in Anion Exchange Membrane Water Electrolysis,” *International Journal of Energy Research* 2025 (2025): 6685212, <https://doi.org/10.1155/er/6685212>.
80. I. Shirovani, E. Takahashi, N. Mukai, et al., “Electrical Conductivity of Nickel Phosphides,” *Japanese Journal of Applied Physics* 32 (1993): 294, <https://doi.org/10.7567/JJAPS.32S3.294>.
81. S. Duan and R. Wang, “Au/Ni₂P₅ Core/Shell Nanocrystals From Bimetallic Heterostructures: In Situ Synthesis, Evolution and Supercapacitor Properties,” *NPG Asia Materials* 6 (2014): e122–e122, <https://doi.org/10.1038/am.2014.65>.
82. S. Ghosh, S. R. Kadam, S. Kolatkar, et al., “W Doping in Ni₂P₅ as a Platform to Enhance Overall Electrochemical Water Splitting,” *ACS Applied Materials & Interfaces* 14 (2021): 581–589, <https://doi.org/10.1021/acsami.1c16755>.
83. J. Chang, S. Li, G. Li, J. Ge, C. Liu, and W. Xing, “Monocrystalline Ni₁₂P₅ Hollow Spheres With Ultrahigh Specific Surface Areas as Advanced Electrocatalysts for the Hydrogen Evolution Reaction,” *Journal of Materials Chemistry A* 4 (2016): 9755–9759, <https://doi.org/10.1039/C6TA03481K>.
84. X. K. Wei, G. Bihlmayer, X. Zhou, et al., “Discovery of Real-Space Topological Ferroelectricity in Metallic Transition Metal Phosphides,” *Advanced Materials* 32 (2020): 2003479.

Supporting Information

Additional supporting information can be found online in the Supporting Information section.

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