

Interfacial water regulation in Co/FeP heterojunction enables high-rate nitrate-to-ammonia electroreduction and Zn-NO₃⁻ battery

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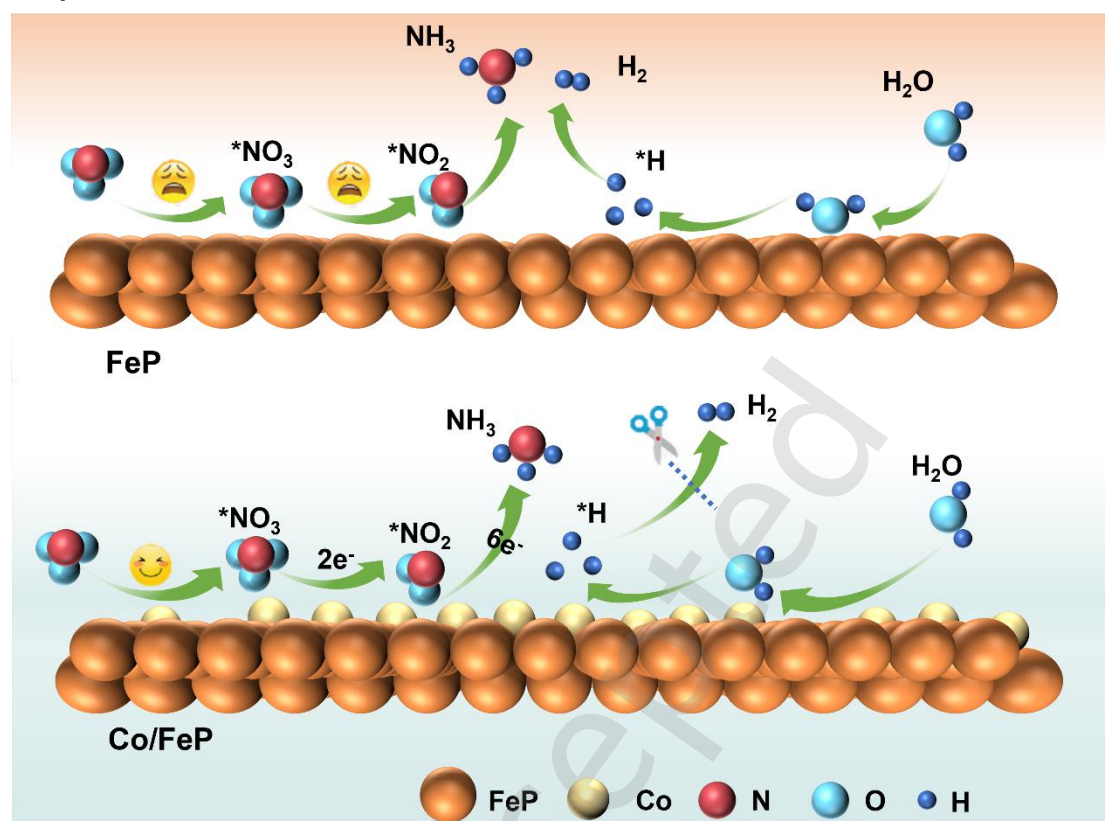
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Graphical Abstract:



Schematic illustration of the interfacial water regulation mechanism for nitrate electroreduction to ammonia. On pristine FeP (top), excessive water dissociation generates abundant *H that preferentially combines into H_2 via the hydrogen evolution reaction (HER), leading to poor nitrate reduction efficiency. In contrast, Co-doped FeP modulates the interfacial water structure, suppressing HER (scissors symbol) and enabling selective *H participation in the 8-electron reduction pathway ($\text{NO}_3^- \rightarrow \text{*NO}_3 \rightarrow \text{*NO}_2 \rightarrow \text{NH}_3$), thereby achieving high-efficiency ammonia synthesis.

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ABSTRACT : Electrocatalytic nitrate reduction (e-NO₃⁻ RR) offers a sustainable route for nitrate (NO₃⁻) removal from aqueous environments while concurrently producing ammonia (NH₃); however, its practical implementation is hindered by insufficient surface-adsorbed atomic hydrogen (*H) and the undesirable accumulation of nitrite (NO₂⁻). For this purpose, we report a heterojunction tandem catalyst comprising cobalt (Co) nanosheets anchored on iron (Fe) phosphide (Co/FeP/CC) nanorods. This bifunctional electrocatalytic system achieves a Faradaic efficiency (FE) of 98.23% for NH₃ synthesis at -0.4 V vs. RHE, with a corresponding production rate of 31.6 mg·h⁻¹·cm⁻². Moreover, it exhibits exceptional electrochemical stability, retaining over 97% of its initial FE after 100 h of continuous operation. *In situ* studies and DFT calculations reveal that the Co/FeP interface promotes NO₃⁻ activation on Co sites and *H supply on FeP sites, while interfacial charge transfer from Co to FeP optimizes the energetics of hydrogenation, thereby enabling efficient tandem catalysis. Based on the above design, we integrated the catalyst into a Zn-NO₃⁻ battery, enabling concurrent NH₃ synthesis and electricity generation, with a peak power density of 6.29 mW·cm⁻². A practical, scalable strategy for engineering efficient tandem electrocatalysts and advancing integrated energy-environment systems is provided by this work.

Keywords: interfacial electronic coupling, heterojunction, tandem catalyst, adsorbed atomic hydrogen (*H), nitrate reduction.

1. Introduction

Ammonia (NH₃) is extensively employed in modern agriculture and industrial applications; owing to its high hydrogen content (17.75 wt%), it is widely regarded as a promising hydrogen-rich energy carrier[1-4]. However, the conventional Haber-Bosch process for NH₃ synthesis operates under stringent conditions (high temperature and high pressure), accounts for approximately 2% of global annual energy consumption, and generates 1.9 tons of carbon dioxide per ton of NH₃ produced[5-7]. The electrochemical nitrate reduction reaction (e-NO₃⁻ RR), powered by renewable energy, has attracted considerable attention owing to its potential for sustainable NH₃ synthesis[8-10]. However, the e-NO₃⁻ RR is fundamentally a complex multi-step reduction process involving the transfer of eight electrons and nine protons: $\text{NO}_3^- + 6\text{H}_2\text{O} + 8\text{e}^- \rightarrow \text{NH}_3 + 9\text{OH}^-$ ($E^0 = 0.69 \text{ V vs. RHE, pH} = 14$)[11-13]. In the reaction pathway, the key intermediate *NO₂ readily desorbs from the electrode surface into the electrolyte, where it accumulates as nitrite (NO₂⁻), thereby directly compromising NH₃ selectivity[14-16]. Moreover, for all intermediates in the multi-step e-NO₃⁻ RR, their adsorption energies show a linear scaling relationship. Consequently, a single active site is unable to concurrently tune the adsorption affinities of all reaction intermediates, revealing an inherent drawback of single-site catalysts for the e-NO₃⁻ RR[17, 18]. Inspired by the microbial denitrification pathway, NO₃⁻ to NH₃ can be conceptually divided into two sequential steps: an initial two electrons reduction (NO₃⁻ → NO₂⁻) followed by a subsequent six-electron reduction (NO₂⁻ → NH₃)[19, 20]. Based on this strategy, researchers have developed spatially separated tandem catalysts for the e-NO₃⁻ RR, wherein two adjacent yet functionally complementary active phases are rationally engineered: the initial 2e⁻ reduction proceeds efficiently at one site, while the subsequent 6e⁻

reduction is selectively relayed to the other active phase. These two sequential processes impose distinct functional requirements on the catalytic sites: the former must efficiently activate NO_3^- and selectively produce NO_2^- , whereas the latter must supply sufficient active hydrogen to enable the deep hydrogenation of NO_2^- . Therefore, a thorough grasp of these distinct catalytic mechanisms is crucial for the rational selection and construction of tandem catalysts.

Metallic cobalt (Co) possesses an unfilled 3d subshell (electron configuration: $3d^74s^2$), with its d-band center situated near the Fermi level; consequently, it exhibits moderate adsorption affinity toward oxygen-containing anions such as NO_3^- [21-23]. This distinctive electronic configuration endows cobalt with moderate NO_3^- activation capability. On one hand, it facilitates efficient cleavage of the N-O bond in NO_3^- , enabling its selective reduction to NO_2^- with high $2e^-$ reduction selectivity. On the other hand, the d-band electronic structure of Co is thermodynamically and kinetically unfavorable for water dissociation[24], its capacity to generate $^*\text{H}$ is relatively low, thereby impeding the subsequent deep hydrogenation steps necessary for the complete reduction of NO_2^- to NH_3 . Therefore, Co is commonly employed to catalyze the initial two electrons reduction step ($\text{NO}_3^- \rightarrow \text{NO}_2^-$), but it cannot mediate the complete eight-electron reduction process independently. Fe-based catalysts also exhibit notable advantages in the $e\text{-NO}_3^-$ RR. Beyond their low cost and earth-abundant availability, Fe-based materials possess a highly tunable electronic structure, enabling precise optimization of catalytic performance through compositional modulation or interfacial engineering[25-27], it indicates that as a core component of an efficient catalytic system, it has great potential. However, the capacity of isolated Fe sites to generate adsorbed $^*\text{H}$ via water dissociation is inherently limited, rendering them insufficient to drive the subsequent deep

hydrogenation steps independently[28, 29], this limitation restricts its applicability in highly selective NH_3 synthesis. To address this issue, researchers have demonstrated that incorporating nonmetallic elements to form compounds can effectively modulate water activation behavior. Specifically, the FeP active phase, fabricated via phosphorization treatment, demonstrates exceptional capability for water dissociation[14, 30]. FeP significantly lowers the reaction energy barrier of the Volmer step ($\text{H}_2\text{O} + \text{e}^- \rightarrow \text{*H} + \text{OH}^-$), thereby enabling efficient and sustained generation of adsorbed *H . This strategy enhancing the performance of iron-based electrocatalysts through precise regulation of proton-coupled electron transfer (PCET) kinetics provides a critical foundation for optimizing the *H step in the e-NO_3^- RR pathway. Further research reveals that phosphorus (P) atoms in FeP not only contribute to the formation of active sites but also serve as electron-transfer bridges, thereby fundamentally modulating the kinetics of catalytic reactions[14, 31]. The electronegativity of P is relatively strong, which can attract electrons from the adjacent Fe atoms, forming a localized polarization distribution, thereby synergistically enhancing the overall reduction efficiency and selectivity. Compared with Fe, the advantages of FeP in promoting water dissociation and *H supply make it an ideal active phase for the subsequent 6e^- hydrogenation step in tandem catalysis.

In this study, a Co/FeP/CC heterostructure catalyst was fabricated using carbon cloth as the conductive substrate. Within this architecture, FeP nanorods function as the active phase for the six-electron reduction of $\text{NO}_2^- \rightarrow \text{NH}_3$, and the surfaces of these FeP nanorods are uniformly decorated with electrodeposited Co nanosheets, which serve as catalytic centers for the 2e^- conversion of NO_3^- into NO_2^- . Electrochemical measurements reveal that the Co/FeP/CC catalyst delivers a FE of 98.23% for electrochemical NH_3 synthesis at -0.4 V vs. RHE , an excellent NH_3

generation rate of $31.6 \text{ mg} \cdot \text{h}^{-1} \cdot \text{cm}^{-2}$. Furthermore, the FE remains consistently above 97% after a 100 h stability test. Through comparative experiments involving Co/CC and FeP/CC complemented by *in situ* characterization techniques, the tandem catalytic mechanism of Co/FeP/CC was unambiguously confirmed and elucidated: Co sites selectively catalyze the transformation from NO_3^- to NO_2^- , while FeP sites facilitate water dissociation to generate $^*\text{H}$ species and interfacial electron coupling at the heterojunction facilitates the formation of weakly hydrogen bonded interfacial water molecules, which subsequently drive the $^*\text{H}$ and further transformation from NO_2^- to NH_3 . Moreover, the Zn- NO_3^- battery fabricated using Co/FeP/CC as the cathode delivered a maximal power density of $6.29 \text{ mW} \cdot \text{cm}^{-2}$. This work offers new insights into the rational design of electrocatalysts for the NO_3^- reduction reaction to NH_3 .

2. Experimental section

2.1. Material synthesis

2.1.1. The synthesis of FeOOH/CC

Dissolve 2.165 g of ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and 6.8 g of potassium nitrate (KNO_3) in a mixed solvent consisting of 240 μL of hydrochloric acid (HCl), 24 mL of deionized water and 56 mL of acetonitrile (CH_3CN). The obtained solution was transferred into a stainless steel autoclave (100 mL) lined with polytetrafluoroethylene. The pretreated carbon cloth was submerged into the solution, after which the autoclave was closed and heated at 120°C for 4 h. Once the reaction finished, the autoclave was left to cool naturally to ambient temperature. Subsequently, the carbon cloth was retrieved and rinsed sequentially with deionized water and absolute ethanol. Finally, it was dried in a vacuum drying oven at 60°C . Thus, the FeOOH precursor material loaded on the carbon cloth (FeOOH/CC) was obtained.

2.1.2. The synthesis of FeP/CC

Take 1.2 g of sodium hypophosphite monohydrate ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$) and place it in a porcelain boat. Put the boat in the upstream area of the tube furnace, and then place the pre-prepared FeOOH/CC sample in the downstream area, maintaining a distance of approximately 15 cm from the phosphorus source. The sample was heated to 350 °C at a rate of 2 °C/min in an Ar atmosphere (flow rate approximately 25 mL/min), maintained at this temperature for 120 min, and then naturally cooled to room temperature to obtain FeP/CC.

2.1.3. The synthesis of Co/FeP/CC

The original FeP/CC catalyst with a geometric area of 2.0 cm × 0.5 cm was used as the working electrode. The electroplating solution was prepared by dissolving 0.0594 g of cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) in 25 mL of deionized water. Electrodeposition was performed using a conventional three-electrode configuration, employing an Ag/AgCl reference electrode and a platinum sheet as the counter electrode. The working electrode was polarized for 120 s, 240 s and 360 s respectively at a constant potential of -1.4 V (vs. Ag/AgCl). After the electrodeposition was completed, the obtained electrodes were successively washed thoroughly with deionized water and ethanol, and then dried in a vacuum at 60 °C for 30 min. According to different deposition times, the final obtained catalysts were respectively labeled as Co/FeP/CC-120, Co/FeP/CC-240 and Co/FeP/CC-360, among which Co/FeP/CC-240 was denoted as Co/FeP/CC.

2.1.4. The synthesis of Co/CC

The synthesis procedure is analogous to that of Co/FeP/CC, except that carbon cloth is employed as the working electrode; all other experimental conditions remain unchanged.

Detailed in the Supporting Information are the materials, chemicals, physical characterization methods, electrochemical measurements, and product analysis procedures.

3. Results and discussion

3.1. Characterization of electrocatalysts

In this study, a one-step hydrothermal method was employed to in-situ grow uniformly distributed FeOOH nanorod arrays on carbon cloth as precursors. After phosphidation treatment, metal Co was electrochemically deposited on the surface of the obtained FeP nanorods by chronoamperometric. The loading amount of metal Co was controllably constructed by regulating the deposition time (120 s, 240 s and 360 s) (**Figure 1a**). To further identify the optimal catalytic material, the initial electrocatalytic performance of the samples prepared with varying electrodeposition times in the $e\text{-NO}_3^-$ RR was evaluated via LSV (**Figure S1**). The results revealed that Co/FeP/CC demonstrated superior electrocatalytic reduction performance and was therefore selected as the primary focus for subsequent investigations. The catalyst morphology was characterized using Transmission Electron Microscope (TEM) and Scanning Electron Microscope (SEM). Metallic Co presents a flaky structure on carbon cloth (CC) (**Figure S2**), while FeP catalyst on CC shows a rod-like morphology (**Figure S3**). Co/FeP/CC, on the other hand, features a layer of nanosheets coated on the rods (**Figure S4**), which is conducive to increasing the electrochemically active specific surface area. TEM images (**Figure 1b** and **Figure S5**) further reveal the composite architecture of Co/FeP/CC, wherein uniformly distributed Co nanosheets are anchored on the surface of FeP nanorods. The high resolution transmission electron microscopy (HRTEM) image (**Figure 1c**) shows clear lattice fringes. Among them, the lattice fringes with spacings of 0.273 nm, 0.242 nm

and 0.188 nm correspond to the (011), (111) and (211) crystal planes of FeP, respectively. Meanwhile, the lattice fringes with spacings of 0.204 nm and 0.191 nm can be attributed to the (002) and (101) crystal planes of metallic Co. The observed lattice fringes are in excellent agreement with the corresponding crystallographic planes of FeP/CC and Co/CC (**Figure S6**), confirming the successful fabrication of the Co/FeP/CC heterostructure. The corresponding X-ray spectroscopy (EDS) elemental distribution maps (**Figure 1d**) reveal uniform spatial distribution of Co, Fe, and P across the nanorod region. The EDS elemental mapping results for Co/CC and FeP/CC are shown in **Figures S7 and S8**. Inductively coupled plasma optical emission spectroscopy (ICP-OES) quantitative analysis (**Table 1**) reveals Fe/P atomic ratios of 1.53:1 and 1.56:1 for FeP/CC and Co/FeP/CC, respectively, both exceeding the theoretical stoichiometric ratio of FeP (1:1). This deviation is likely attributed to incomplete phosphorization of the FeOOH precursor, resulting in residual amorphous iron oxide/hydroxide species within the samples. Furthermore, the areal Co loading in Co/FeP/CC is determined to be 1.58 mg cm⁻², confirming the effective deposition of Co onto the FeP surface (**Table 2**).

Contact angle measurements (**Figure 1e**) revealed good hydrophilicity for all catalysts, with contact angles of 50.66° (CC), 8.36° (Co/CC), 0° (FeP/CC), and 10.5° (Co/FeP/CC). Such favorable wettability facilitates electrolyte permeation and interfacial mass transfer, thereby enhancing catalytic performance.

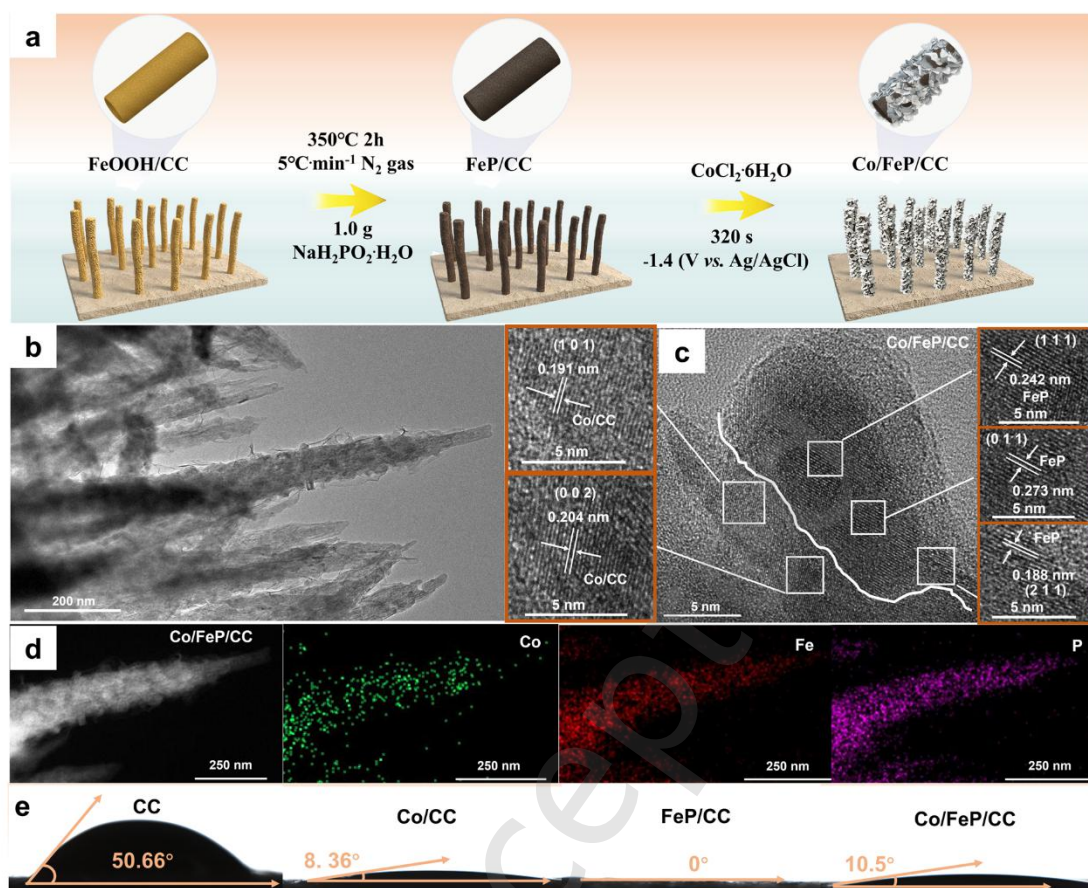


Figure 1. (a) Schematic diagram depicting the synthetic route. TEM images of: (b) Co/FeP/CC (c) HRTEM image of Co/FeP/CC. (d) EDS elemental distribution maps for Fe 、 Co and P in Co/FeP/CC. (e) Wettability of different catalysts.

The phase structures of Co/FeP/CC and the reference samples FeP/CC and Co/CC were characterized by X-ray diffraction (XRD). **Figure 2a** reveals that both Co/FeP/CC and FeP/CC exhibit distinct diffraction peaks at $2\theta \approx 32.75^\circ$, 37.15° , and 48.31° , belonging to the (011), (111), and (211) lattice planes of orthorhombic FeP. The diffraction peaks observed at $2\theta \approx 44.76^\circ$ and 47.57° for the Co/FeP/CC and Co/CC samples are assigned to the (002) and (101) crystallographic planes of metallic cobalt, respectively. These diffraction features align well with the reference patterns for FeP (PDF#71-2262) and Co (PDF#05-0727), which confirms the successful fabrication of the target catalyst [14, 32]. The chemical states and electronic structures of the synthesized samples were characterized by X-ray photoelectron spectroscopy

(XPS). The analysis results of the spectra of the Co/CC, FeP/CC and Co/FeP/CC catalysts indicated that the Co, Fe and P elements were present in the corresponding samples' spectra (**Figure S9**). In the high-resolution P $2p$ spectrum (**Figure 2b**), two prominent doublets are observed. The peaks at approximately 129.5 eV and 130.3 eV are assigned to Fe-P bonds, confirming the presence of the FeP primary structure. Meanwhile, the higher binding energy peak at ~ 133.5 eV corresponds to P-O bonds, which arises from the slight oxidation of phosphorus on the material surface, forming a thin phosphate layer. This is a common phenomenon after the sample is exposed to air[33-35]. The characteristic peaks observed at 710.2 eV, 724.3 eV, 712.8 eV, and 726.2 eV are assigned to $\text{Fe}^{2+} 2p_{3/2}$, $\text{Fe}^{2+} 2p_{1/2}$, $\text{Fe}^{3+} 2p_{3/2}$, and $\text{Fe}^{3+} 2p_{1/2}$, respectively. In comparison with pure FeP (**Figure 2c**), the additional peak at 707.2 eV suggests an Fe oxidation state intermediate between 0 and +2, consistent with the presence of Fe-P covalent bonding. Moreover, the Fe $2p$ peaks in Co/FeP/CC exhibit a pronounced positive shift of +0.53 eV relative to those in pure FeP[36, 37]. The observation of Co in the metallic state (778.1 eV) suggests a modification of the electronic environment surrounding the iron atoms likely arising from the strongly polar covalent character of the FeP bond and the interfacial electronic coupling between Co and FeP. More importantly, in this composite system, the P $2p$ binding energy exhibits a significant negative shift of -0.2 eV (**Figure 2c**), the binding energy of the metallic-state Co $2p$ peak (**Figure 2d**) exhibits a shift of +0.07 eV[38-41]. This directly confirms the net electron transfer from iron sites to phosphorus sites at the Co/FeP interface, as well as the electron transfer from Co to FeP. The main factors controlling the above-mentioned charge redistribution include the electronegativity difference of the Fe-P bond and the interfacial electronic coupling effect, rather than merely depending on the atomic electronegativity of the metal components

themselves.[42-44]. The electron transfer channel established at the Co/FeP/CC heterointerface can reconfigure the electronic structure of Co. although XPS data indicate that Co behaves as an electron donor under static conditions, the structural stability of Co during the catalytic reaction process mainly stems from the electronic coupling synergy at the heterointerface rather than solely depending on the increase or decrease of electron density. The FeP sites generated via this approach, in concert with the structurally robust cobalt sites, the adsorption step and the activation step of the reactants are regarded as a coupled whole for coordinated optimization, thereby facilitating the subsequent catalytic reduction. Interfacial electronic coupling between FeP and Co stabilizes the metallic state of Co, leading to enhanced catalytic performance of the material.

The Fe K-edge XANES spectra (**Figure 2e**) show that the absorption edge of Co/FeP/CC lies between those of Fe foil and Fe₃O₄, indicating an average Fe valence state between 0 and +3[34]. Compared with pristine FeP, the edge exhibits a slight positive shift, suggesting electron depletion at the Fe sites upon heterojunction formation, consistent with the positive shift of the Fe 2p peak (+0.53 eV) in the XPS spectra and confirming electron transfer from Fe to the Co/FeP interface. The Fe K-edge FT-EXAFS spectra (**Figure 2f**) show peaks at ~1.8-2.0 Å and ~2.8-3.0 Å, assigned to Fe-O from incompletely phosphidized FeOOH and Fe-Fe scattering, respectively; the slightly shifted Fe-P peak position indicates that the interfacial interaction with Co alters the local coordination environment of Fe. The Co K-edge XANES spectra (**Figure 2g**) show an absorption edge between Co foil and Co₃O₄, closer to the former, confirming the coexistence of metallic Co (Co⁰) and minor oxidized Co species, with metallic Co as the dominant phase[45]. The Co K-edge FT-EXAFS spectra (**Figure 2h**) display a prominent Co-Co peak at ~2.1-2.2 Å, with

no detectable Co-P or Co-Fe signals, providing direct atomic-level evidence for a Co/FeP heterojunction interface rather than a doped/alloyed phase, consistent with the XRD and HRTEM results. Furthermore, the Fe K-edge WT-EXAFS (**Figure 2i and Figure S10**) identifies Fe-P and Fe-Fe coordination at $k \approx 4.5$ and $\approx 7.0 \text{ \AA}^{-1}$, respectively, while the Co K-edge WT-EXAFS (**Figure S11**) shows a single maximum at $k \approx 7.5 \text{ \AA}^{-1}$, characteristic of Co-Co metallic coordination. These results conclusively confirm that Co/FeP/CC consists of metallic Co nanosheets deposited on FeP nanorods, forming a heterojunction interface rather than an alloyed or doped structure.

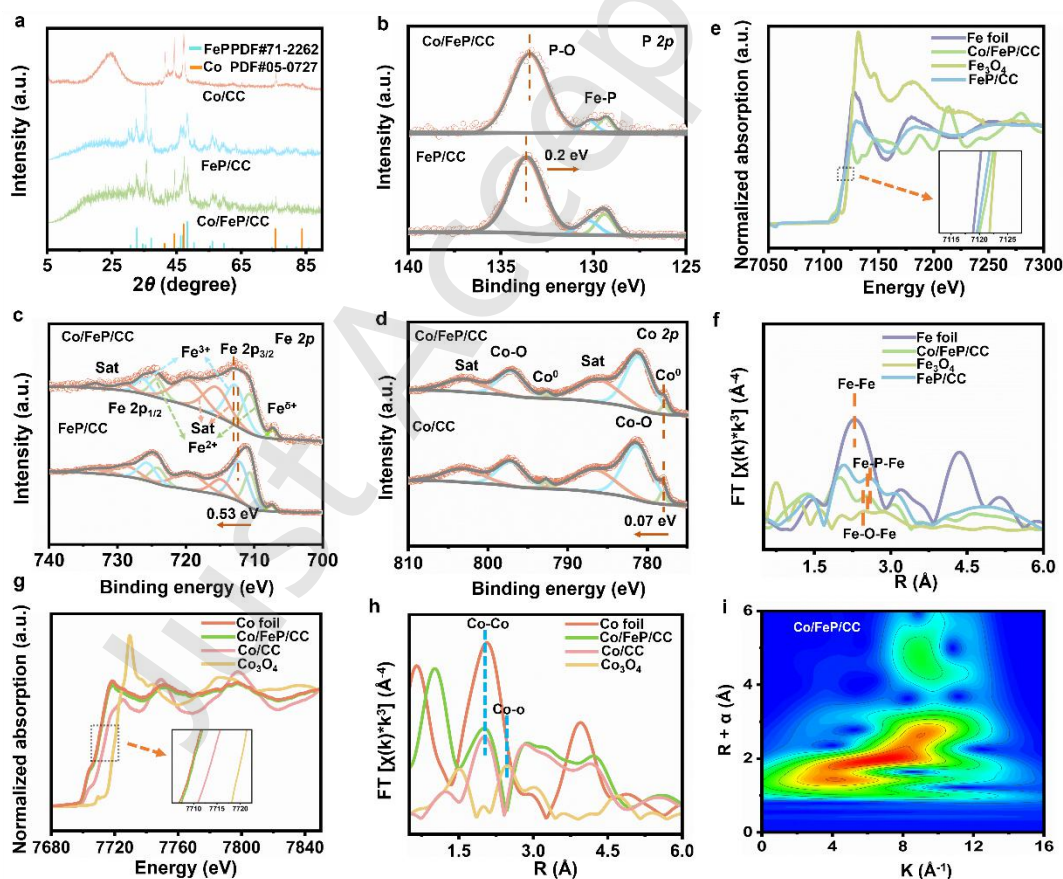


Figure 2. (a) XRD patterns of different catalysts. Measured XPS signals from (b) P 2p, (c) Fe 2p, and (d) Co 2p. (e) Fe K-edge XANES spectra. (f) k^3 -weighted Fe K-edge FT-EXAFs spectra. (g) Co K-edge XANES spectra. (h) k^3 -weighted Co K-edge FT-EXAFs spectra. (i) WT of k^3 -weighted Fe K-edge of Co/FeP/CC.

3.2. Co/FeP Electrocatalytic NO_3^- RR Performance

Initial screening of e-NO_3^- RR activity for each catalyst was performed via LSV, and the results are presented in **Figure 3a**. The iR drops were negligible (<7 mV, $<3\%$ of overpotential) for all catalysts, and the LSV data are presented without iR correction. By comparing the LSV curves of Co/CC, FeP/CC, and Co/FeP/CC in electrolytes containing NO_3^- versus NO_3^- free (blank) electrolyte, we observe that the current density for all three catalysts is markedly higher in the presence of NO_3^- . This pronounced enhancement unambiguously confirms their catalytic activity toward the e-NO_3^- RR. Among them, Co/FeP/CC exhibited the most pronounced increase in current density with increasingly negative applied potential, demonstrating superior catalytic activity for the e-NO_3^- RR. FeP/CC showed the smallest current density increase, which is primarily ascribed to its relatively limited capability to reduce NO_3^- to NO_2^- . Notably, compared with both Co/CC and FeP/CC, Co/FeP/CC displayed a more positive onset potential for e-NO_3^- RR, indicating that incorporation of the Co component facilitates the activation of NO_3^- reduction. However, in the more negative potential region, the current density of Co/CC increases at a reduced rate likely attributable to the accumulation of the reaction intermediate NO_2^- on the electrode surface, resulting from its insufficient consumption kinetics and subsequent inhibition of the overall electrochemical reaction. The electrochemically active surface area (ECSA) of the catalyst was determined from the double-layer capacitance (C_{dl}). As shown in **Figure S12**, compared with Co/CC and FeP/CC, Co/FeP/CC exhibits a significantly higher C_{dl} . Nitrogen adsorption-desorption measurements (**Figures S13 and Table 3**) reveal that Co/FeP/CC exhibits a markedly enhanced porous structure: its Brunauer-Emmett-Teller (BET) specific surface area is $22.0246 \text{ m}^2 \text{ g}^{-1}$, 1.69 times that of pristine FeP/CC ($13.0303 \text{ m}^2 \text{ g}^{-1}$), and its total pore volume

increases from $0.021 \text{ cm}^3 \text{ g}^{-1}$ to $0.039 \text{ cm}^3 \text{ g}^{-1}$. Pore size distribution analysis confirms the predominantly mesoporous nature of both catalysts, indicating that it exposes more active sites to participate in the e-NO_3^- RR process, which is conducive to improving the efficiency of NH_3 synthesis. The e-NO_3^- RR performance at different potentials was further investigated by multi-potential step chronoamperometric (i-t) (**Figure S14**), and the reduction products NH_3 and the by-products NO_2^- and hydrazine (N_2H_4) within the potential range of 0 V to -0.7 V were quantitatively analyzed by ultraviolet-visible spectrophotometry (**Figures S15 and S16**). The results reveal that the FE of Co/FeP/CC exhibits a volcano shaped dependence on applied potential, initially increasing and then decreasing with progressive cathodic polarization. A maximum FE of 98.23% is achieved at -0.4 V vs. RHE, NH_3 rate of $31.6 \text{ mg} \cdot \text{h}^{-1} \cdot \text{cm}^{-2}$. Further cathodic polarization to -0.6 V vs. RHE leads to the highest observed NH_3 rate of $39.56 \text{ mg} \cdot \text{h}^{-1} \cdot \text{cm}^{-2}$. Under identical potential conditions, the catalytic performance of Co/FeP/CC was markedly superior to that of Co/CC and FeP/CC (**Figures 3b and 3c, Figure S17**), and outperformed most previously reported catalysts (**Figure 3d and Table S4**). By analyzing the potential-dependent variation of FE for different products, the catalytic reaction behavior can be more thoroughly elucidated. As shown in **Figure S18**, no by-product N_2H_4 was detected on any of the catalysts at all tested potentials. It is noteworthy that Co/FeP/CC consistently exhibits superior $\text{FE}(\text{NH}_3)$ across the entire applied potential range, outperforming both FeP/CC and Co/CC. This enhanced performance underscores its superior selectivity, specifically, its ability to effectively suppress competing side reactions, including the accumulation of unconverted NO_2^- and H_2 evolution via the HER. At all applied potentials, the $\text{FE}(\text{NO}_2^-)$ for NO_2^- reduction over Co/CC consistently exceeded that over Co/FeP/CC, indicating that FeP incorporation

promotes the further electrochemical conversion of NO_2^- (**Figure S19**), in addition, the $\text{FE}(\text{NO}_2^-)$ of FeP/CC is higher than that of Co/FeP/CC, suggesting that the Co sites exhibit a stronger catalytic capability for the reduction of NO_3^- to NO_2^- . Based on the above results, the tandem catalytic mechanism between Co and FeP in Co/FeP/CC effectively synergizes their respective advantages: Co sites selectively catalyze the reduction of NO_3^- to NO_2^- , while FeP rapidly consumes the generated NO_2^- intermediate. This cooperative action mitigates NO_2^- accumulation on Co/CC and suppresses the competing HER on FeP/CC at high applied potentials.

Isotope labeling experiments unambiguously identified and confirmed the nitrogen source of the ammonia ($\text{NH}_4^+/\text{NH}_3$) product. **Figure 3e** presents the ^1H NMR spectra of the electrolyte collected following NO_3^- RR tests employing either $^{15}\text{NO}_3^-$ or $^{14}\text{NO}_3^-$ as the nitrogen source. The characteristic doublet of $^{15}\text{NH}_4^+$ ($\delta = 6.85$ and 7.04 ppm) and the characteristic triplet of $^{14}\text{NH}_4^+$ ($\delta = 6.83, 6.96$, and 7.09 ppm) were clearly resolved in the spectrum, with maleic acid (MAC) serving as the internal standard. The possibility of NH_3 contamination from external sources was eliminated by control experiments (**Figure S20**), confirming that the sole origin of all NH_3 detected in the electrolyte is the e- NO_3^- RR. **Figure 3f** monitors how the surface concentrations of NO_3^- , NO_2^- , and NH_3 vary over time on Co/FeP/CC at -0.4 V vs. RHE. NO_3^- decreases continuously until it is almost completely consumed. At the same time, NH_3 accumulates steadily. By contrast, the intermediate NO_2^- exhibits a rise-and-fall behavior: its concentration first increases, reaches a maximum, and then gradually decreases below the detection limit. This is primarily attributed to the excessively low NO_3^- concentration in the later stages of the reaction, which results in incomplete utilization of adsorbed $^*\text{H}$ on the electrode surface and thereby favors the competing HER. Despite this limitation, the NO_3^- removal efficiency reached

98.7% within just 9 h of reaction, underscoring the material's exceptional potential for treating NO_3^- contaminated wastewater. Further nitrogen mass balance analysis revealed that, after 9 h of reaction, nearly all nitrate nitrogen (NO_3^- -N) in the system was selectively converted to NH_3 nitrogen (NH_3 -N) (**Table S5**), no nitrogen-containing byproducts were detected.

To systematically assess the electrochemical stability of Co/FeP/CC, we performed a long term chronoamperometric (i-t) measurement at a constant potential of -0.4 V vs. RHE. During 100 h of continuous electrolysis, the current density of the Co/FeP/CC catalyst remained stable (**Figure 3g and Figure S21**). Quasi-*in situ* XRD (**Figure S22**) revealed that the diffraction peaks of FeP and Co exhibited no shift, broadening, or emergence of new peaks, confirming the absence of phase transitions in the bulk structure. Meanwhile, neither the Faradaic efficiency (FE) nor the yield of ammonia showed a significant decrease (**Figure 3h**). ICP-OES analysis determined dissolved Co and Fe concentrations in the electrolyte to be merely 0.046 and 0.213 mg L^{-1} (**Table S6**). Furthermore, post-reaction XPS analysis of Co/FeP/CC confirmed the persistence of metallic Co, consistent with our earlier characterization results (**Figure S23**). Full spectrum scanning confirmed that Co/FeP/CC showed no significant changes before and after the reaction (**Figure S24**). Respectively, indicating negligible element leaching. Collectively, these results from structural, activity, and stability perspectives demonstrate the excellent stability of the Co/FeP/CC catalyst under the reaction conditions. To further validate the feasibility of direct fertilizer synthesis using this system, we integrated the e- NO_3^- RR with an argon-stripping-acid absorption process (**Figure 3i**). Following prolonged electrolysis, the electrolyte was sparged with argon gas to liberate generated NH_3 , which was subsequently captured by a dilute hydrochloric acid solution. The resulting NH_4Cl

containing absorption solution was then evaporated to dryness and crystallized to yield high-purity NH_4Cl solid. The XRD pattern reveals that all observed diffraction peaks are in excellent agreement with the reference pattern for NH_4Cl (PDF#07-0007) (**Figure 3j**). This finding confirms the technical feasibility of the catalyst for the direct conversion of model NO_3^- electrolytes into high value solid-phase products.

To verify that the enhanced performance of Co/FeP/CC originates from the interfacial synergy rather than the simple coexistence of Co and FeP, we conducted a control experiment with a physical mixture of Co/CC and FeP/CC (see Supporting Information). The physical mixture delivered an FE of only 93.83% and an NH_3 yield rate of $25.48 \text{ mg h}^{-1} \text{ cm}^{-2}$ (**Figure S25**), substantially lower than those of the Co/FeP/CC heterojunction. This comparison unequivocally demonstrates that intimate interfacial contact between Co and FeP is indispensable for the observed tandem catalytic enhancement.

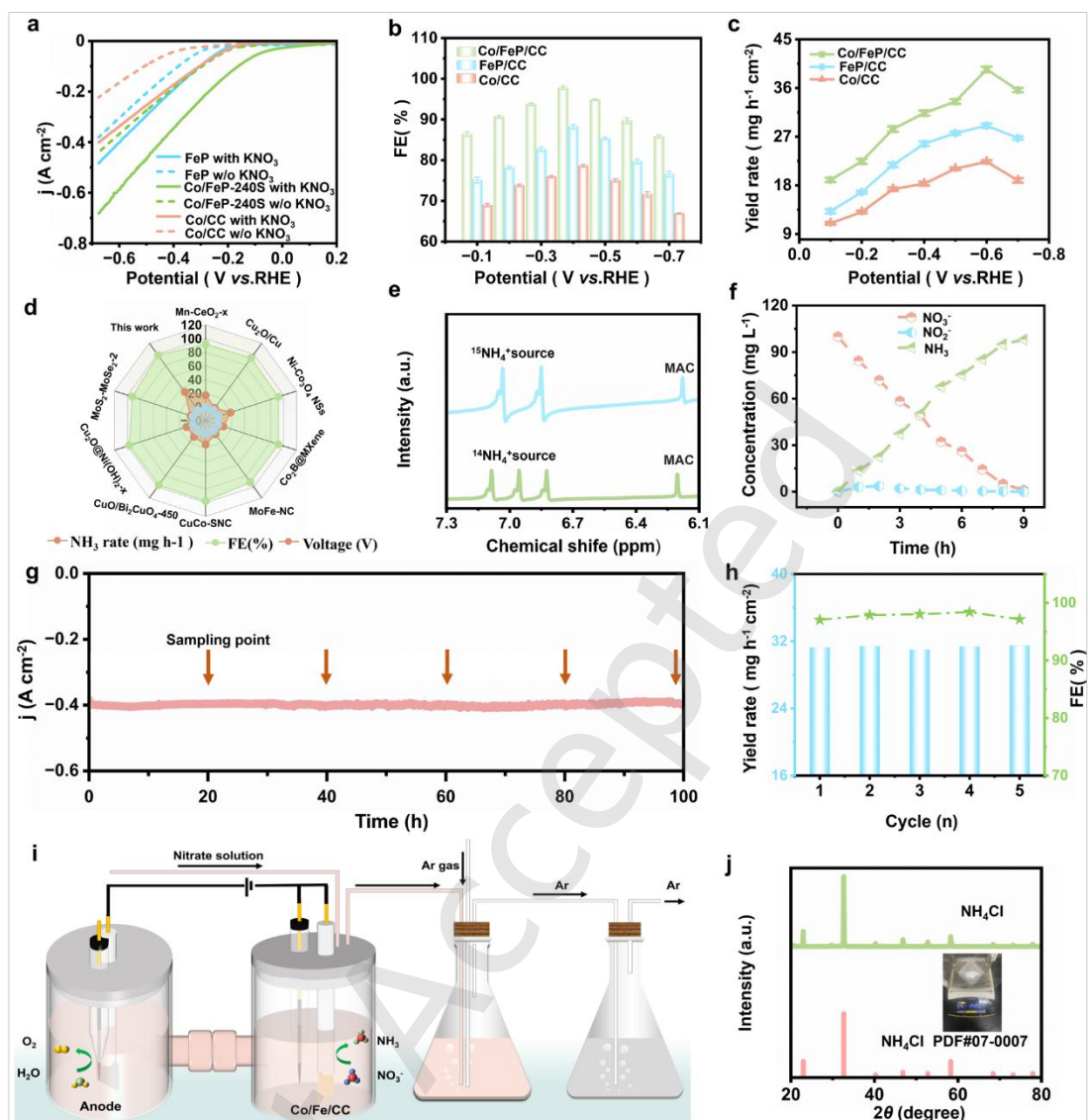


Figure 3. (a) LSV of different catalysts. (b) NH_3 FE and (c) yields of electrocatalysts at different potentials. (d) Comprehensive comparison of NH_3 yield rate, FE, and corresponding potential for electrocatalytic nitrate reduction to ammonia reported in the literature. (e) ^1H NMR spectra obtained on Co/FeP/CC using electrolytes containing $^{15}\text{NO}_3^-$ and $^{14}\text{NO}_3^-$. (f) The Co/FeP/CC electrode was subjected to chronopotentiometric testing at a constant potential of -0.4 V vs. RHE , while the time-dependent variations in the electrolyte concentrations of NO_3^- -N, NH_3 -N, and NO_2^- -N were simultaneously monitored. (g) Current density of Co/FeP/CC during stability testing at -0.4 V vs. RHE . (h) The F and NH_3 production rate of Co/FeP/CC recorded during the stability test. (i) Schematic illustration of nitrate conversion from wastewater to high-value ammonium chloride. (j) XRD pattern of the NH_4Cl product.

3.3. Mechanistic analysis

To elucidate the kinetic roles of Co and FeP in the sequential electrochemical reduction steps $\text{NO}_3^- \rightarrow \text{NO}_2^-$ and $\text{NO}_2^- \rightarrow \text{NH}_3$, this study compares the overpotentials required for three catalysts to achieve a current density of $-50 \text{ mA}\cdot\text{cm}^{-2}$ in $0.1 \text{ mol}\cdot\text{L}^{-1} \text{ NO}_3^-$ and NO_2^- electrolytes, respectively[46]. The results demonstrate that, in the NO_3^- solution, Co/FeP/CC exhibits a comparatively more positive reduction potential (**Figure 4a**), outperforming FeP/CC, indicating that formation of the Co/FeP/CC heterojunction facilitates both the adsorption and e- NO_3^- RR, arising from the synergistic contribution of Co sites for NO_3^- activation and FeP sites for water dissociation. In the step involving the reduction of NO_2^- to NH_3 , In the step involving the reduction of NO_2^- to NH_3 , the required overpotential for Co/FeP/CC is significantly lowered than Co/CC (**Figure 4b**), indicating that FeP facilitates the subsequent deoxygenation and *H steps of NO_2^- (**Figure S26 and Figure S27**). Notably, Co/FeP/CC exhibits the lowest overpotential among all tested catalysts in both electrolyte systems, underscoring its superior activity toward the e- NO_3^- RR. The above results demonstrate that Co/FeP/CC functions as a tandem catalyst, synergistically leveraging the complementary catalytic advantages of Co and FeP to achieve highly efficient e- NO_3^- RR performance.

In order to clarify the specific function of *H in the catalytic system, the hydrogen adsorption/desorption behavior of various catalysts was first characterized in this study via CV.[45, 47] As illustrated in **Figure 4c**, the peak area associated with adsorbed *H on the Co/FeP/CC catalyst is markedly larger than those observed for the individual Co/CC and FeP/CC catalysts, The incorporation of FeP significantly promotes the generation of *H. In addition, during the e- NO_3^- RR in a NO_3^- -containing system, the surface coverage of *H on Co/FeP/CC decreased markedly (**Figure 4d**), confirming that the electrogenerated active hydrogen species

efficiently participate in the hydrogenation of NO_3^- and its reaction intermediates. Collectively, the dynamic behavior of $^*\text{H}$ in terms of both consumption and utilization during catalysis is clarified by these results. To directly verify the generation of adsorbed $^*\text{H}$ and its involvement in the catalytic mechanism, we employed electron paramagnetic resonance (EPR) spectroscopy with 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the spin trap to detect the $^*\text{H}$ signal in the reaction system[48-50]. As shown in **Figure 4e**, under without NO_3^- conditions, the $^*\text{H}$ signal intensity associated with the Co/FeP/CC catalyst is markedly higher than those of Co/CC and FeP/CC, confirming its superior capability for water dissociation and $^*\text{H}$ generation. It is noteworthy that upon addition of NO_3^- to the system (**Figure 4f**), the $^*\text{H}$ signals of all catalysts diminished to varying extents. Notably, the $^*\text{H}$ signal of Co/FeP/CC exhibited the most pronounced attenuation nearly disappearing altogether. This observation suggests that $^*\text{H}$ species generated under reaction conditions are rapidly scavenged and consumed by NO_3^- and its reduction intermediates, thereby directly participating in subsequent hydrogenation steps. The above results collectively demonstrate that Co/FeP/CC construction not only enhances the intrinsic $^*\text{H}$ generation capability of the catalyst but also facilitates the rapid consumption and utilization of $^*\text{H}$ at neighboring active sites. This synergistic effect drives the tandem hydrogenation process in the e- NO_3^- RR, thereby significantly improving both NH_3 synthesis efficiency and overall catalytic performance.

To investigate interfacial electrochemical processes, *in situ* EIS was conducted at various potentials (**Figure S28 and tables S7 and S8**). Co/FeP/CC exhibited the lowest charge-transfer resistance, indicating superior e- NO_3^- RR kinetics. Bode phase analysis revealed that the peak magnitude reflects interfacial charge-transfer kinetics(**Figures 4g-i**), while its characteristic frequency corresponds to specific steps

such as water dissociation. In the absence of NO_3^- , a pronounced low-frequency peak indicated vigorous water dissociation to generate $^*\text{H}$. Upon NO_3^- introduction, this peak attenuated and shifted to higher frequencies, suggesting that $^*\text{H}$ species were rapidly consumed by nitrate and its reduction intermediates for e-NO_3^- RR hydrogenation steps, thereby suppressing $^*\text{H}$ dimerization and the competing HER. Notably, the overall low phase angle in the NO_3^- containing system indicates efficient charge-transfer utilization toward e-NO_3^- RR rather than interfacial accumulation or HER, significantly enhancing reaction kinetics. This confirms the Co/FeP/CC advantage in promoting $^*\text{H}$ generation and its efficient utilization.

It has been reported that Fourier transform infrared (FTIR) spectroscopy can probe the O-H stretching vibration mode ($3000\text{-}3600\text{ cm}^{-1}$), which is highly sensitive to the microenvironment of interfacial water and governs the kinetics of proton transfer[51-53]. Spectral analysis reveals that the spectral resolution resolves three distinct water species: strongly hydrogen-bonded, tetrahedrally coordinated water (S- H_2O); weakly hydrogen-bonded, bidentate water (W- H_2O); and cation-associated free water (F- H_2O)(**Figures 4j-l and Figure S29**). The incorporation of FeP markedly enhanced the F- H_2O ratio at the catalyst interface. These interfacial water molecules exhibit weakened hydrogen bonding and structural disorder, rendering their O-H bonds more labile and thereby facilitating higher electrochemical dissociation activity. In comparison with the Co/CC and FeP/CC control samples(**Figures 4j and 4k**), the Co/FeP/CC catalyst consistently exhibited the highest F- H_2O ratio across all tested potentials(**Figures 4l**). Furthermore, as the negative value of the applied potential gradually increases, the F- H_2O signal becomes increasingly stronger. This indicates that under the influence of the electric field, the electron coupling at the heterojunction interface optimizes the structure of interfacial water and can also stably

maintain the arrangement of water molecules that is favorable for efficient proton transfer.

The FeP substrate itself exhibits exceptional water dissociation activity, enabling efficient and sustained generation of adsorbed $^*\text{H}$ by significantly lowering the energy barrier of the Volmer step ($\text{H}_2\text{O} + \text{e}^- \rightarrow ^*\text{H} + \text{OH}^-$). In the tandem catalytic process, metallic Co sites selectively adsorb and activate nitrate ($\text{NO}_3^- \rightarrow \text{NO}_2^-$), whereas FeP primarily facilitates water dissociation to supply $^*\text{H}$. This division of labor establishes a clear spatial and functional synergy between the two active components. Specifically, electrons are transferred from Co to FeP/the Co-FeP interface; FeP promotes water dissociation to produce $^*\text{H}$, which then migrates to Co sites to participate in NO_2^- hydrogenation.

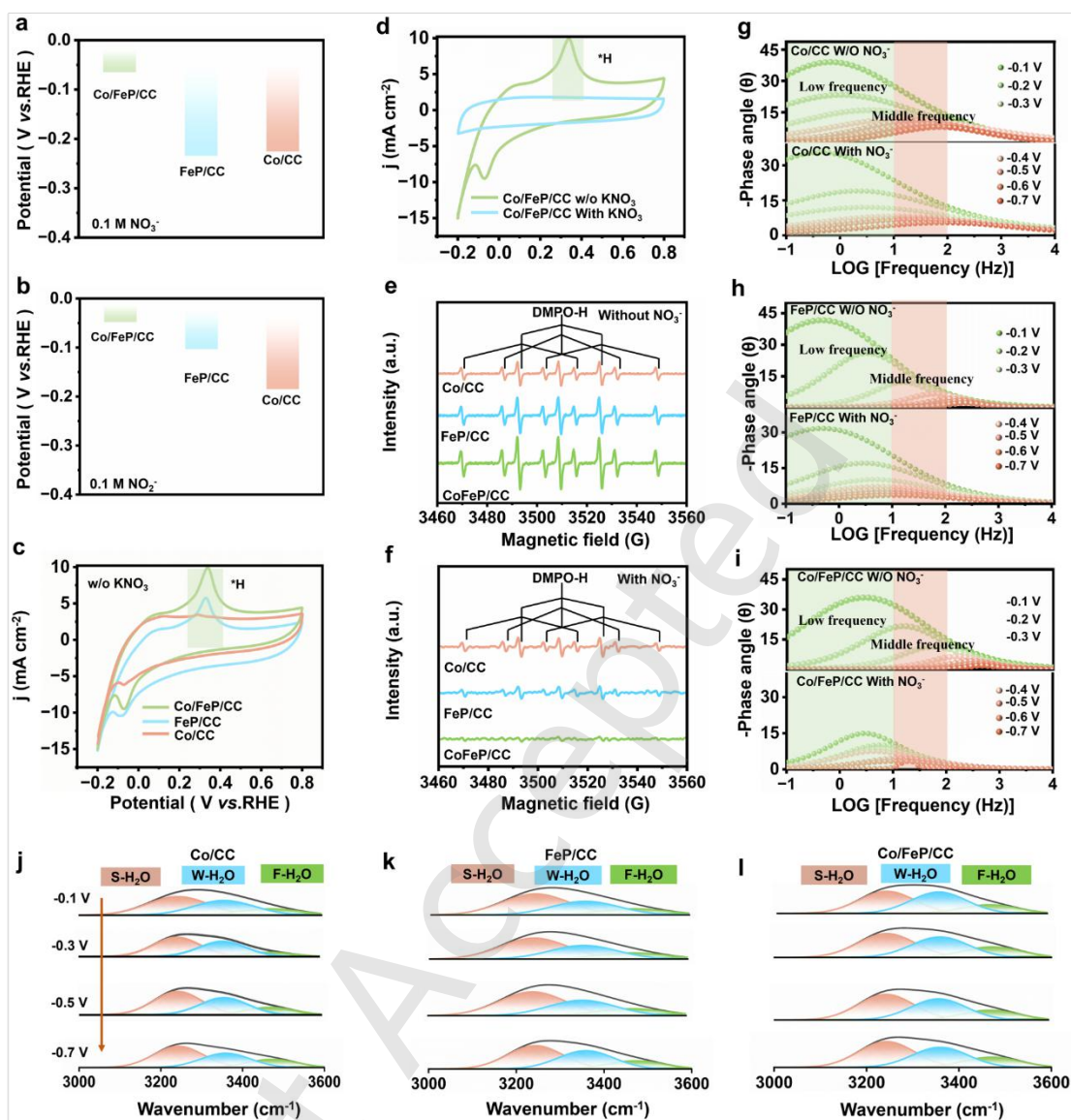


Figure 4. (a) The potential measured by LSV at a current density of $-50 \text{ mA} \cdot \text{cm}^{-2}$ in a $0.1 \text{ mol} \cdot \text{L}^{-1} \text{NO}_3^-$ solution and (b) the corresponding potential in a NO_2^- solution. (c) Cyclic voltammetry curves measured in the electrolyte without NO_3^- . (d) Cyclic voltammetry curves of Co/FeP/CC in the presence and absence of NO_3^- . (e) The EPR spectrum measured in 1.0 mol/L KOH solution. (f) The EPR spectrum measured in $1.0 \text{ mol/L KOH} + 0.1 \text{ mol/L KNO}_3$ solution. (g-i) The Bode phase plots of Co/CC, FeP/CC and Co/FeP/CC at different potentials. (j-l) Peak-fitting analysis of the *in situ* FTIR spectrum revealed three distinct O-H stretching vibration modes.

To elucidate the catalytic mechanism of the catalyst in the electrochemical e- NO_3^- RR, we employed *in situ* FTIR to monitor the reaction process in real time. The analytical results indicate that positive peaks correspond to the formation of

reaction intermediates or products, whereas negative peaks reflect the consumption of reactants. Infrared absorption bands characteristic of $^*\text{NO}_x^-$, H_2O , and $^*\text{NH}_x$ species were observed on the catalyst surface (**Figures 5a-c**). Specifically, the positive absorption band at 1104 cm^{-1} is assigned to the formation of the $^*\text{NH}_2$ intermediate; The band at 1248 cm^{-1} is assigned to the generation of $^*\text{NO}_2^-$ species, while the negative band at 1374 cm^{-1} originates from the depletion of NO_3^- ; and the bands at 1462 cm^{-1} and 3719 cm^{-1} are assigned to the formation of $^*\text{NH}_3$ and $^*\text{NH}$ species, respectively[54-56]. Additionally, the bands observed at 1628 cm^{-1} and 3285 cm^{-1} are assigned to water dissociation, which generates the requisite active $^*\text{H}$ species for the e-NO_3^- RR[35, 57]. On the FeP/CC surface, virtually no characteristic signal attributable to $^*\text{NO}_2^-$ was observed, indicating rapid consumption and subsequent hydrogenation of the generated $^*\text{NO}_2^-$ intermediate to $^*\text{NH}_3$. In contrast, Co/CC consistently exhibited a distinct adsorption peak corresponding to $^*\text{NO}_2^-$ within the tested potential window (**Figure 5b**), reflecting both the accumulation of this intermediate on the catalyst surface and the kinetic inhibition of its further conversion. Interestingly, in the Co/FeP/CC composite system, the $^*\text{NO}_2^-$ species rapidly disappeared within a short time, indicating that cobalt incorporation effectively promoted the reduction of $^*\text{NO}_2^-$ to NH_3 (**Figure 5c**). This conclusion was further corroborated by electrochemical nitrite reduction (e-NO_2^- RR) performance measurements. Both FeP/CC and Co/FeP/CC demonstrate excellent e-NO_2^- RR, whereas Co/CC alone exhibits significantly lower activity consistent with the aforementioned adsorption transformation behavior of key reaction intermediates. **Figures 5(d-f)** present the *in situ* Raman spectra of Co/CC, FeP/CC, and Co/FeP/CC, respectively, recorded under applied potentials ranging from -0.1 to -0.7 V vs. RHE. As shown in **Figure 5d**, the characteristic peaks located at 689.4, 1048.3 and 1590.2

cm^{-1} can be attributed to $^*\text{NO}_2^-$, $^*\text{NO}_3^-$ and $^*\text{NH}_3$ species, respectively[58, 59]. By comparing **Figures 5e and 5f**, it can be seen that the accumulation intensity of the $^*\text{NO}_2^-$ intermediate on the Co/CC surface is significantly higher than that on FeP/CC and Co/FeP/CC, indicating that the Co site has a stronger catalytic ability for the initial conversion step of $\text{NO}_3^- \rightarrow \text{NO}_2^-$. As the applied potential is shifted negatively, the intensity of the $^*\text{NH}_3$ characteristic peak exhibits a distinct trend-first increasing and then decreasing. The initial increase can be attributed to the rapid hydrogenation of the pre-formed $^*\text{NO}_2^-$, the subsequent decrease, however, reflects a diminishing $^*\text{H}$ coverage, which impedes the sustained reduction of $^*\text{NO}_2^-$ intermediates to $^*\text{NH}_3$. In addition, the characteristic peak observed at 1140.8 cm^{-1} in the spectrum is assigned to the Fe-P bond vibration[33], confirming the stable incorporation of the FeP phase into the composite catalyst. In contrast, the characteristic peak intensity of $^*\text{NO}_2^-$ on the surfaces of FeP/CC and Co/FeP/CC is comparatively weak and decays rapidly indicating that the FeP component effectively promotes the subsequent hydrogenation of the $^*\text{NO}_2^-$ intermediate. This advantage is especially pronounced for the Co/FeP/CC composite catalyst. The underlying mechanism stems from the strong interfacial electron coupling at the Co/FeP heterojunction, which effectively facilitates water dissociation at the interface, thereby supplying a more abundant source of adsorbed $^*\text{H}$ and significantly accelerating the kinetics of $^*\text{NO}_2^-$ reduction to $^*\text{NH}_3$. This inference is further supported by infrared spectroscopy analysis. Overall, the above results shed light on a significant synergistic catalytic mechanism underpinning the enhanced performance of the Co/FeP/CC composite catalyst: Co sites efficiently generate the $^*\text{NO}_2^-$ intermediate, whereas the FeP component leverages the interfacial interaction to accelerate the subsequent hydrogenation-reduction step. Such a relay synergism markedly boosts the overall

catalytic activity and the selectivity for the e- NO_3^- RR.

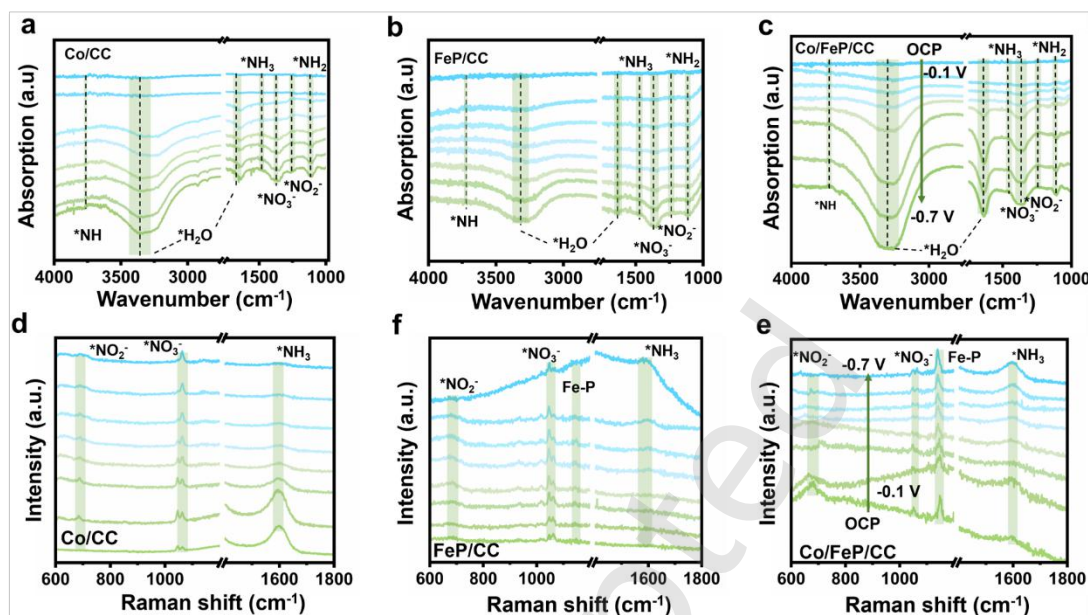


Figure 5. (a-c) *In situ* FTIR spectra of Co/CC, FeP/CC, and Co/FeP/CC recorded at potentials ranging from -0.1 to -0.7 V vs. RHE. (d-e) *In situ* Raman spectra of Co/CC, FeP/CC, and Co/FeP/CC recorded at potentials ranging from -0.1 to -0.7 V vs. RHE.

To further elucidate the synergistic catalytic mechanism of the Co/FeP heterointerface, DFT calculations were performed. The conversion of NO_3^- to NO_2^- requires free-energy inputs of 0.855 and 0.601 eV on FeP and Co (**Figure 6a**), respectively, whereas this process becomes slightly exergonic at the Co/FeP interface, indicating that the heterointerface significantly facilitates the initial activation of NO_3^- . Water adsorption is strong on the FeP surface but relatively weak on the Co surface, indicating that H_2O preferentially adsorbs at FeP sites (**Figure 6b**). However, water dissociation on FeP involves a highly endothermic energy barrier, whereas it is exothermic on Co, suggesting that Co is thermodynamically more favorable for O-H bond cleavage. Based on these calculations, we propose a synergistic mechanism in which H_2O first adsorbs on FeP and then migrates to the Co/FeP heterointerface for dissociation. The generated active *H subsequently spills over onto Co sites and participates locally in the hydrogenation of NO_3^- -reduction intermediates, thereby enabling efficient tandem catalysis. Charge density difference (CDD) analysis reveals electron transfer from Co to FeP upon interface formation, thereby modulating the electronic structure and adsorption behavior of Co sites (**Figures 6c-d**). In addition, HNO_2

spontaneously dissociates into $\ast\text{OH}$ and $\ast\text{NO}$ during structural optimization on both Co and the Co/FeP interface, further demonstrating the capability of Co-related sites to activate nitrite species. These results collectively support a tandem catalytic mechanism in which different sites at the Co/FeP interface cooperatively participate in NO_3^- activation, water activation, and subsequent reduction.

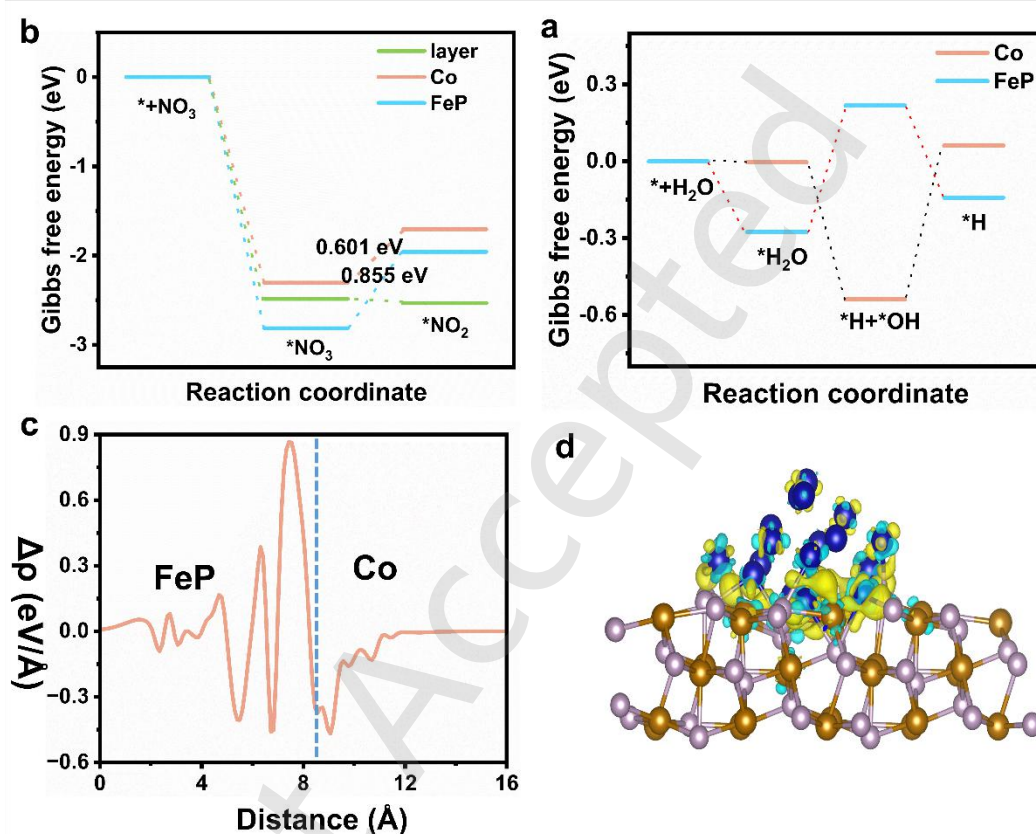


Figure 6. (a) Calculated adsorption free energies of NO_3^- to NO_2^- on Co, FeP, and Co/FeP interface. (b) Calculated free-energy profiles for water dissociation on Co and FeP surfaces. (c-d) The planar average charge density difference of Co/FeP/CC along the Z-axis.

3.4 Zinc- NO_3^- Battery Performance

Based on the outstanding performance of the Co/FeP/CC composite material in the e- NO_3^- RR, we further designed and successfully assembled a Zn- NO_3^- battery system. This device selected Co/FeP/CC as the cathode material, metallic zinc as the anode, and introduced Nafion 117 membrane as the separator to systematically

evaluate its feasibility of simultaneously producing NH_3 and providing power in practical scenarios (**Figure 7a**). The OCP test results (**Figure 7b**) reveal that the battery delivered a stable open-circuit voltage of approximately 1.32 V (vs. Zn/Zn^{2+}) over the entire 3600 s measurement period. The peak power density, determined from the power density curve (**Figure 7c**), was $6.29 \text{ mW}\cdot\text{cm}^{-2}$. Further discharge performance studies revealed that the $\text{Zn}-\text{NO}_3^-$ battery employing this composite cathode delivered a stable discharge plateau across a range of current densities, with the discharge current density markedly increasing as the cathode polarization potential decreased (**Figure 7d**). FE evaluation demonstrated that NH_3 synthesis achieved a maximum FE of 97.54% at a current density of $15 \text{ mA}\cdot\text{cm}^{-2}$ (**Figure 7e**). Practicality tests revealed that the battery could continuously power commercial electronic timers and successfully complete 13 consecutive 100 min cycles of stable operation, simultaneously achieving ultra-long charge–discharge cycling at a constant current density of 60 mA cm^{-2} (**Figure 7f and Figure S30**). These experimental results conclusively demonstrate that the as-constructed Co/FeP/CC-based $\text{Zn}-\text{NO}_3^-$ battery simultaneously enables efficient NH_3 synthesis and stable electrical energy output, thereby exhibiting outstanding operational performance and cycling stability.

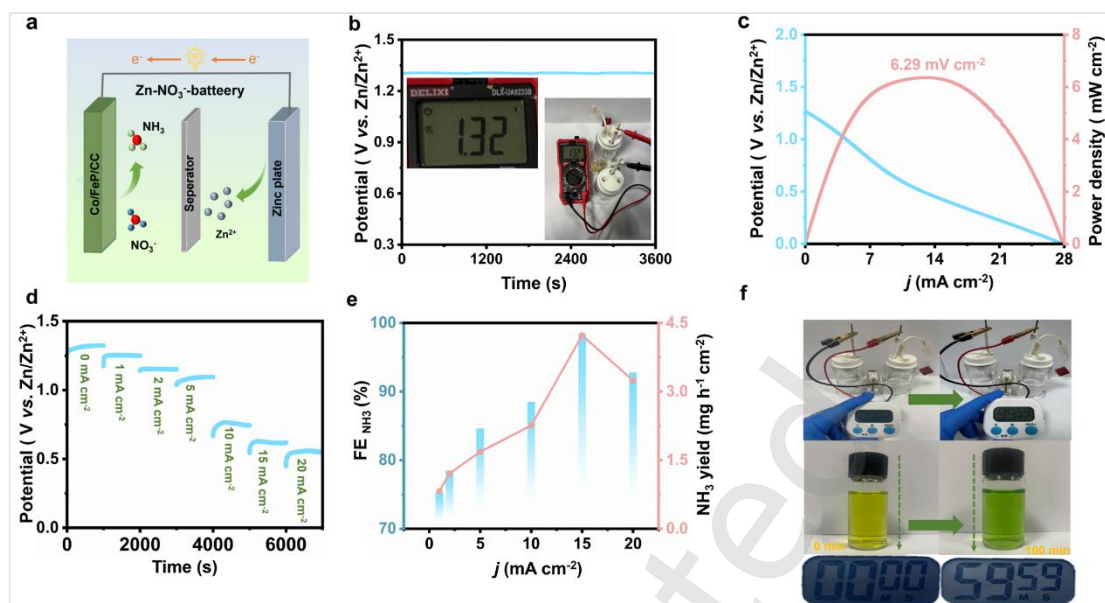


Figure 7. (a) Schematic illustration of the Zn-NO₃⁻ battery configuration. (b) Open-circuit potential of the Zn-NO₃⁻ battery employing Co/FeP/CC as the cathode catalyst. (c) Discharge voltage profiles of the Zn-NO₃⁻ battery and the corresponding power density evolution; (d) Galvanostatic discharge curves recorded at various current densities. (e) NH₃ production rate and the associated FE of the Zn-NO₃⁻ battery as a function of current density. (f) Digital photograph demonstrating continuous operation of an electronic timer powered by the battery for 100 min.

4. Conclusion

The Co/FeP/CC catalyst exhibits outstanding performance in the e-NO₃⁻ RR for NH₃ production. The improvement arises from the combined contribution of interfacial synergy and structure/loading optimization, among which interfacial electronic coupling plays a key role in *H supply and NO₂⁻ hydrogenation. In this heterostructure, metallic Co is responsible for rapidly reducing NO₃⁻ to NO₂⁻. In contrast, FeP optimizes water molecule dissociation at the interface through electronic coupling at the Co/FeP heterojunction, thereby enabling continuous generation of hydrogen radicals, facilitating the deep hydrogenation of NO₂⁻ to NH₃ and effectively preventing the accumulation of the intermediate NO₂⁻. The Co/FeP/CC catalyst delivers a high FE of 98.23% and a NH₃ production rate of 31.6 mg·h⁻¹·cm⁻² at -0.4 V

vs. RHE, significantly outperforming Co/CC and FeP/CC. Meanwhile, the removal rate of NO_3^- by this catalyst reached as high as 98.7% within 9 h. To further verify its potential for practical application, a Zn- NO_3^- battery assembled based on this material achieved a peak power density of $6.29 \text{ mW}\cdot\text{cm}^{-2}$. This study not only provides a feasible solution for designing highly efficient tandem nitrate electroreduction catalysts but also opens up new avenues for constructing integrated electrocatalytic systems (such as the integration of energy output and pollutant treatment).

CRedit authorship contribution statement

Shiyi Liu: Writing—original draft, Methodology. **Jun Ma:** Writing—review & editing, Supervision, Funding support. **Shuo Geng:** Supervision, Funding support. **Lin Fu:** Software, Investigation. **Longbing Zuo:** Software, Investigation. **Fangchao Lou:** Software. **Guidong Xu:** Methodology. **Guilian Li:** Writing—review & editing, Supervision.

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. Supporting information

Supplementary data associated with this article can be found in the online version at

Data availability

Data will be made available on request.

Just Accepted

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Electronic Supplementary Material

Interfacial water regulation in Co/FeP heterojunction enables high-rate nitrate-to-ammonia electroreduction and Zn-NO₃⁻ battery

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1. Experimental Section

1.1 Materials

All the chemicals purchased from commercial sources were used without further purification. Potassium hydroxide (KOH, 85%), Sodium salicylate ($C_7H_6O_3$, 99.5%), Sodium citrate ($C_6H_5O_7Na_3$, 98%), Sulfanilamide ($C_6H_8N_2O_2S$, 99.5%), Sodium hypochlorite (NaClO, available chlorine 7.5%), Ethanol (C_2H_6O , 99.5%) are procured from Shanghai Maclin Biochemical Technology Co.Ltd. Potassium nitrate-15N ($K_{15}NO_3$, 99 atom%), N-(1-naphthyl) ethylenediamine dihydrochloride ($C_{12}H_{14}N_2 \cdot 2HCl$), Potassium nitrate (KNO_3 , 99%), chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, 99%), Sodium hypophosphite monohydrate ($NaPO_2H_2 \cdot H_2O$, 99%) Acetonitrile Ferric (CH_3CN , 99.5%), chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, 99%) Sodium nitrite ($NaNO_2$, 99%), Sodium nitrosoferricyanide dihydrate ($C_5FeN_6Na_2O \cdot 2H_2O$, 99%), Ammonium chloride (NH_4Cl , 99.5%), Deuterium oxide (D_2O , 99.9%), Copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, 99%) are sourced from Shanghai Aladdin Biochemical Technology Co.Ltd. hydrochloric acid (HCl, 36-38%) are sourced from Chongqing Chuandong Chemical Co. Ltd. HCP331N Carbon Cloth (CC) Purchase Suzhou Sungrow Technology Co.Ltd.

1.2 Electrochemical measurements

Electrochemical measurements were conducted using a CS310X multi-channel potentiostat in a three-electrode configuration within an H-type electrolytic cell, with the two compartments separated by a Nafion 117 membrane. The catalysts fabricated on substrates with a geometric area of $0.5 \text{ cm} \times 0.5 \text{ cm}$ served as the working electrodes and were immersed in an aqueous electrolyte containing 1.0 M KOH and 0.1 M KNO_3 . A platinum foil electrode and a Hg/HgO electrode were employed as the counter and reference electrodes, respectively. Linear sweep voltammetry (LSV)

was performed at a scan rate of 5 mV s⁻¹ without iR compensation. Potentiostatic polarization (i-t) tests were carried out at various applied potentials and electrolyte concentrations for 1.0 h to quantify the FE and NH₃ yield. All reported potentials were converted to the reversible hydrogen electrode (RHE) scale using the equation:

$$E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.098 + 0.0591 \times \text{pH}.$$

Electrochemical impedance spectroscopy (EIS) was recorded with a 10 mV amplitude over a frequency range of 10 kHz–0.01 Hz. The double - layer capacitance (C_{dl}) was determined via cyclic voltammetry (CV) at scan rates of 20–100 mV s⁻¹ to estimate the electrochemical surface area (ECSA). All electrochemical tests were conducted with at least three independent replicate experiments.

1.3 Material characterization

High-resolution Scanning Electron Microscope (SEM) imaging was executed utilizing a Thermo Quattro S field emission system, Transmission Electron Microscope (TEM) analysis was conducted at 120 kV using a Philips CM 20 microscope, while High-Resolution TEM (HRTEM) imaging and EDS elemental mapping were performed on a FEI Tecnai Osiris microscope operating at 200kV. X-ray diffraction (XRD) patterns were acquired using a Bruker AXS D8-Advanced diffractometer with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). Raman spectroscopy was carried out with a WITec alpha300R confocal microscope under 532 nm excitation. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo SCIENTIFIC K-ALPHA system with non-monochromatic Al-K α radiation (1486.6 eV) at 150 W. In-situ FTIR monitoring was achieved using a Nicolet iS50 spectrometer equipped with an MCT detector. Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was performed on an Agilent 5110 spectrometer. The specific surface area and porosity analysis (BET) was conducted on a Micromeritics ASAP

2460 automated surface area and pore size analyzer. UV-Vis absorbance spectra were determined with a UV-2700i spectrophotometer. EPR spectroscopy was conducted using a Bruker A300 model, and ^1H NMR spectra were acquired on a 400 MHz Bruker spectrometer. (XPS Fitting Details: All XPS spectra were calibrated using the adventitious carbon C 1s peak at 284.8 eV as an internal reference, with a binding energy accuracy of ± 0.1 eV. Peak fitting was performed using a Gaussian-Lorentzian mixed function (G/L ratio fixed at 80:20) after Shirley-type background subtraction. The following constraints were applied:

Fe 2*p*: The area ratio of Fe 2*p*_{3/2} to Fe 2*p*_{1/2} was fixed at 2:1, with a spin-orbit splitting of 13.6 eV. The FWHM of the two spin-orbit components was constrained to be equal.

Co 2*p*: The FWHM was constrained to 1.2-1.6 eV, with a spin-orbit splitting of 15.0

eV and an area ratio of 2:1. P 2*p*: The P 2*p*_{3/2} and P 2*p*_{1/2} doublet was fitted with a spin-orbit splitting of 0.87 eV and an area ratio of 2:1. The uncertainty in peak positions is estimated to be ± 0.1 eV, and the relative error for peak areas is approximately $\pm 5\%$, depending on the signal-to-noise ratio and background subtraction.)

Deconvolution of the O-H stretching envelope was performed with PeakFit v4.12 software, utilizing Gaussian line shapes to resolve the spectral region spanning 3000-3600 cm^{-1} . In accordance with previously reported assignments, the band was resolved into three constituent peaks attributed to strongly hydrogen-bonded water (S-H₂O, centered at ~ 3200 cm^{-1}), weakly hydrogen-bonded water (W-H₂O, ~ 3400 cm^{-1}), and cation-coordinated free water (F-H₂O, ~ 3600 cm^{-1}). Fitting constraints restricted the full width at half-maximum (FWHM) of each sub-band to the range of 100-250 cm^{-1} , with a positional tolerance of ± 20 cm^{-1} permitted for each peak center. The fractional contribution of each water component was determined from the relative

integrated peak areas. All deconvolution procedures yielded goodness-of-fit values of $R^2 > 0.99$.

1.4 Treated CC preparation

The raw carbon cloth was soaked for 12 h using concentrated sulphuric acid and concentrated nitric acid at a volume ratio of 3:1, then washed with distilled water and anhydrous ethanol until neutral, and dried in a vacuum oven at 60°C.

1.5 Determination of ammonia

Pipette 1 mL of electrolyte and dilute it to a detection range of (50.0 mL). Accurately pipette 5 mL of diluted electrolyte into a 2.0 mL solution of 1.0 M NaOH + 5.0 wt% sodium citrate + 5.0 wt% salicylic acid. Then, 1 mL of 0.05 M NaClO and 0.2 mL of 1 wt% sodium nitroferricyanide were added into the above solution. After being stored in dark for 2 h, Ultraviolet visible (UV/vis) absorption spectra were collected, which exhibited an absorption peak at 655 nm for the stained solutions. The concentration-absorbance curve was obtained using standard ammonium chloride with different concentrations and used for calibration.

1.6 Determination of nitrate

Pipette 1 mL of electrolyte and dilute it to a detection range of (50.0 mL). Accurately pipette 5.00 mL of the diluted electrolyte and add 1 mL of 1 M HCl and 0.1 mL of 50 g/L of sulfamic acid to the solution. and the color was developed for 15 min. Subsequently, the absorbance was measured by the UV-vis spectrophotometry in the wavelength range of 200 and 300 nm. Nitrate-N final absorbance was obtained from the following equation: $A = A_{220\text{nm}} - 2A_{275\text{nm}}$. The corresponding absorbances for standard concentrations of KNO_3 solution were used to obtain the calibration curve.

1.7 Determination of nitrite

Pipette 1 mL of electrolyte and dilute it to a detection range of (50.0 mL). To

prepare the color reagents, 0.4 g Sulfanilamide and 0.02 g N-(1-naphthyl) ethylenediamine dihydrochloride were dissolved in a mixed solution containing 5 mL DI water and 1 mL phosphoric acid ($\rho = 1.70 \text{ g/mL}$). Next, 0.1 mL color reagent was added to the 5 mL diluted electrolyte. The solution was allowed to stand for 20 minutes before measuring the absorbance by UV-vis spectrophotometry in a wavelength range from 450 nm to 650 nm. The calibration curve was obtained by using the absorbance at a wavelength of 540 nm of a series of standard NaNO_2 solutions.

1.8 Calculations of NH_3 FE and NH_3 yield

The ammonia formation rate was calculated using the following equation:

$$R_{\text{NH}_3}(\text{mg h}^{-1}\text{cm}^{-2}) = \frac{C(\text{mg mL}^{-1}) * V(\text{mL})}{t(\text{h}) * A(\text{cm}^2)}$$

Where:

$c \text{ (mg mL}^{-1}\text{)}$: the detected NH_3 concentration,

$V \text{ (mL)}$: the volume of the electrolyte,

$t \text{ (h)}$: the reduction reaction time,

$A \text{ (cm}^2\text{)}$: the geometric area of the working electrode.

The Faradaic efficiency was determined with the following equation:

$$FE_{\text{NH}_3}(\%) = \frac{8 * F(C \text{ mol}^{-1}) * c(\text{mg mL}^{-1}) * V(\text{mL})}{17(\text{g mol}^{-1})Q(C) * 10^6}$$

Where:

$F \text{ (C mol}^{-1}\text{)}$: Faraday constant,

$M \text{ (g mol}^{-1}\text{)}$: the relative molecular mass of NH_3 ,

$Q \text{ (C)}$: the total charge during the reaction.

1.9 Calculation of NO_2^- yield and Faradaic efficiency

The ammonia formation rate was calculated using the following equation:

$$R_{NO_2^-} (mg\ h^{-1} cm^{-2}) = \frac{c(mg\ mL^{-1}) * V(mL)}{t(h) * A(cm^2)}$$

Where:

c ($mg\ mL^{-1}$): the detected NO_2^- concentration,

V (mL): the volume of the electrolyte,

t (h): the reduction reaction time,

A (cm^2): the geometric area of the working electrode.

The Faradaic efficiency was determined with the following equation:

$$FE_{NO_2^-} (\%) = \frac{2 * F(C\ mol^{-1}) * c(mg\ mL^{-1}) * V(mL)}{46(g\ mol^{-1}) * Q(C) * 10^6}$$

Where:

F ($C\ mol^{-1}$): Faraday constant,

M ($g\ mol^{-1}$): the relative molecular mass of NO_2^- ,

Q (C): the total charge during the reaction.

1.10 Calculation of NO_3^- removal efficiency

$$C_{NO_3^- - N} (\%) = \frac{C_0(NO_3^- - N) - C_t(NO_3^- - N)}{C_0(NO_3^- - N)} * 100\%$$

Where:

$C_0(NO_3^- - N)$: the initial concentration of NO_3^- .

$C_t(NO_3^- - N)$: the final concentration of NO_3^- .

1.11 Battery operation details

The Zn- NO_3^- battery was assembled in a two-compartment H-type cell separated by a Nafion 117 membrane. The cathode was Co/FeP/CC (geometric area: $0.25\ cm^2$), immersed in 50 mL of catholyte (1.0 M KOH + 0.1 M KNO_3). The anode was a

polished zinc foil (thickness: 0.2 mm, purity: 99.99%, 1.0 cm³), immersed in 50 mL of anolyte (1.0 M KOH). All tests were performed at room temperature (25 ± 2 °C). The cycling stability test was conducted via continuous galvanostatic charge–discharge at 10 mA cm⁻² on a Kesite battery testing system.

1.12 DFT calculation methods and parameters

All density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package. The projector augmented-wave (PAW) method was employed to describe the interaction between valence electrons and ionic cores, and the exchange-correlation energy was treated using the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA). The van der Waals interactions were considered using the DFT-D3-BJ correction. The plane-wave kinetic energy cutoff was set to 400 eV, and a 3 x 4 x 1 Monkhorst-Pack k-point mesh was used for Brillouin-zone sampling. The electronic energy and atomic force convergence criteria were set to 1 x 10⁻⁵ eV and 0.02 eV/Å, respectively. Spin polarization was included in all calculations.

2. Supporting figures

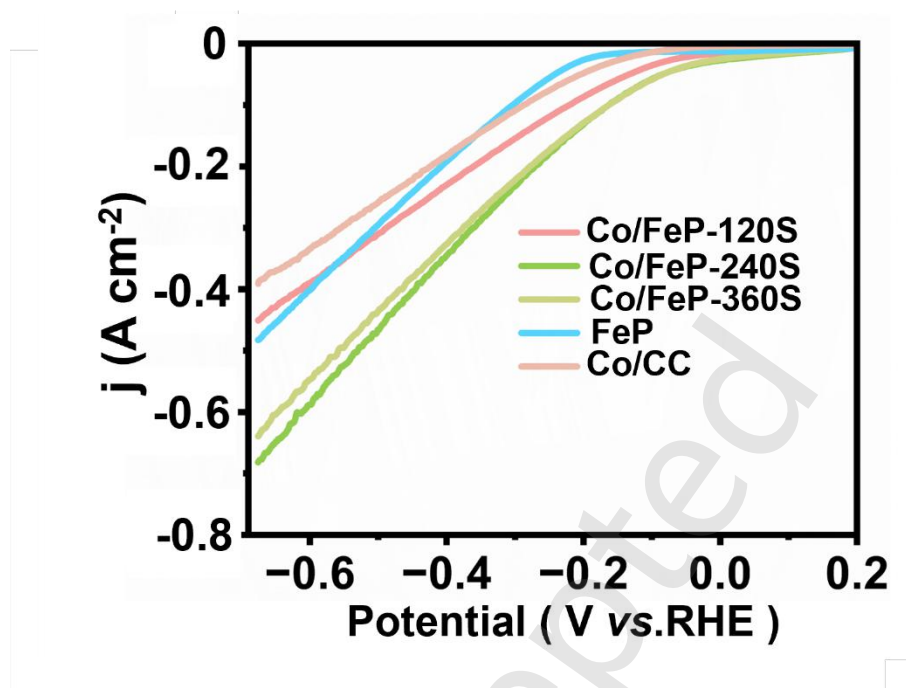


Figure S1. LSV of different catalysts in 1.0 M KOH + 0.1 M NO₃⁻.

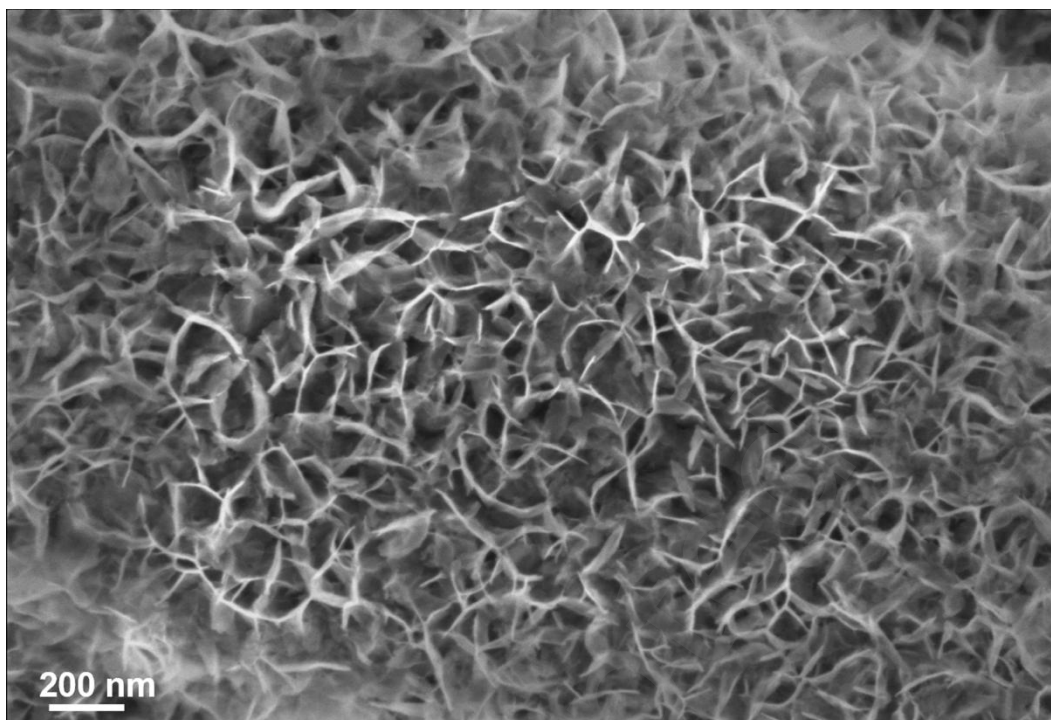


Figure S2. SEM image of Co/CC.

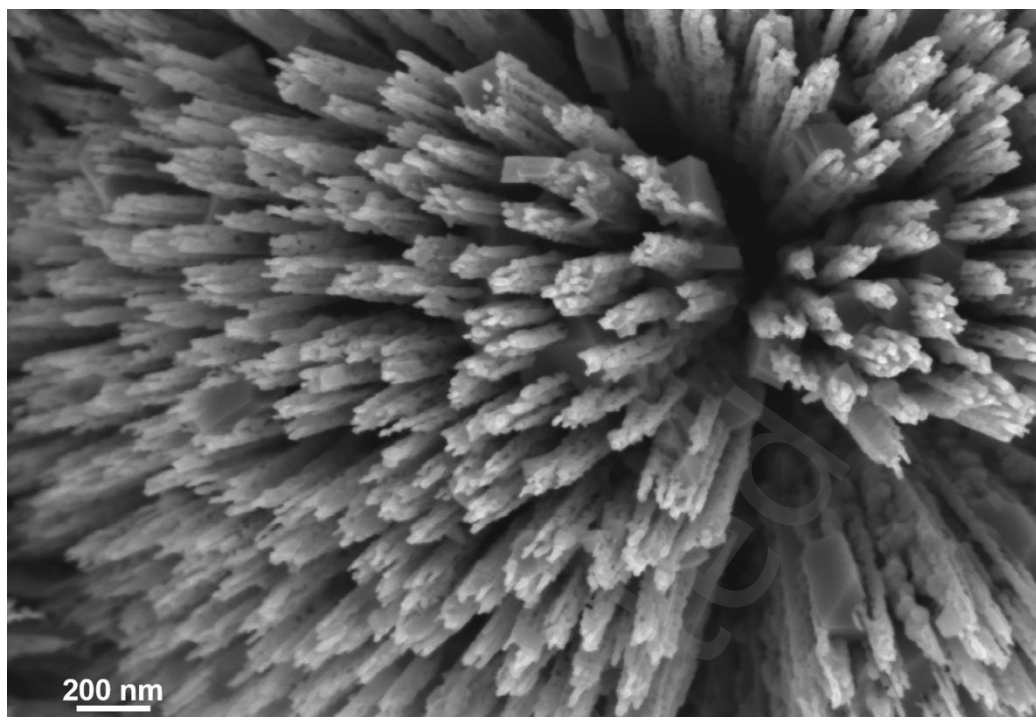


Figure S3. SEM image of FeP/CC.

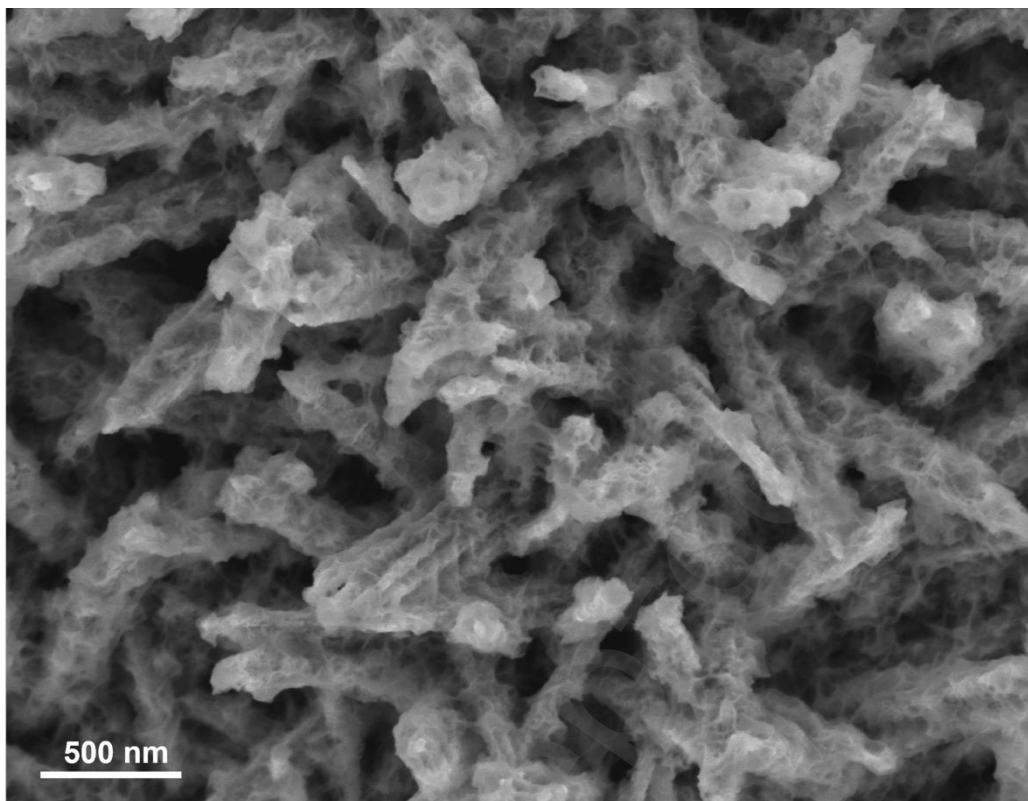


Figure S4. SEM image of Co/FeP/CC.

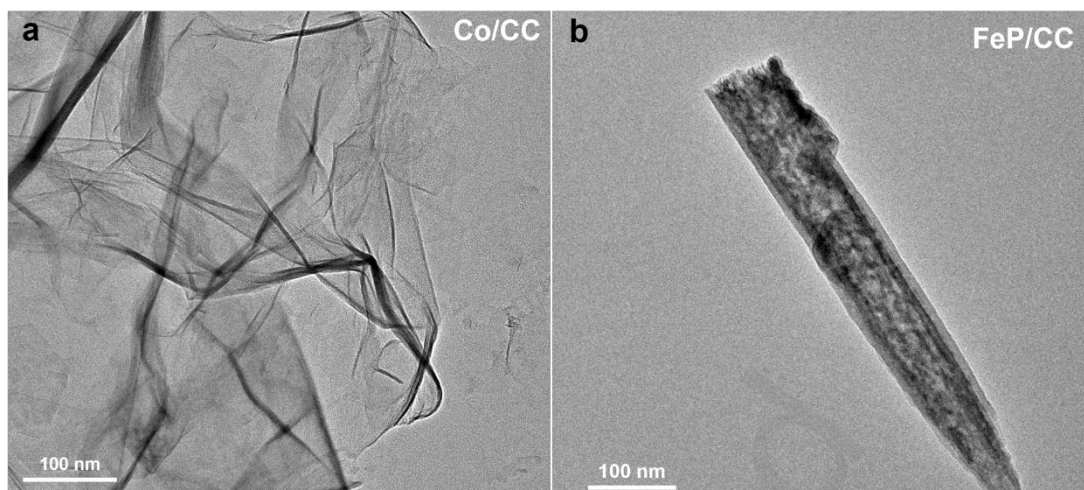


Figure S5. TEM image of (a) Co/CC and (b) FeP/CC.

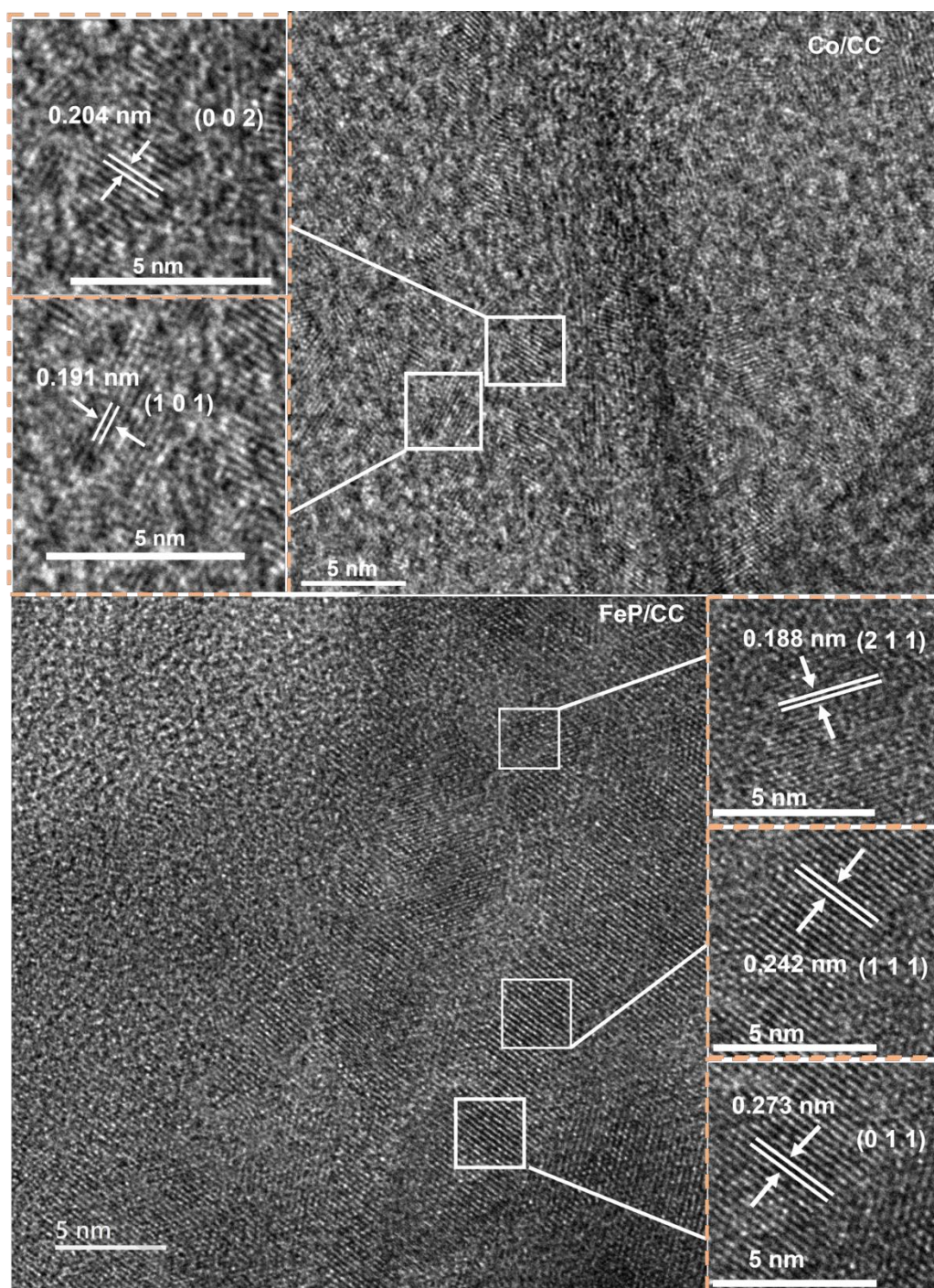


Figure S6. HRTEM image of (a) Co/CC and (b) FeP/CC.

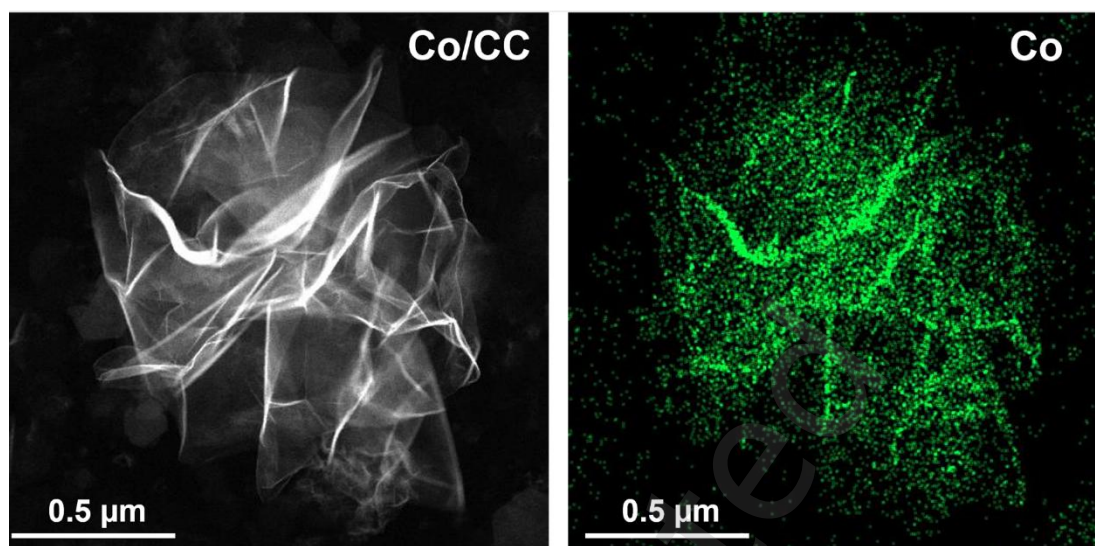


Figure S7. HAADF and corresponding EDS elemental mapping images of Co/CC.

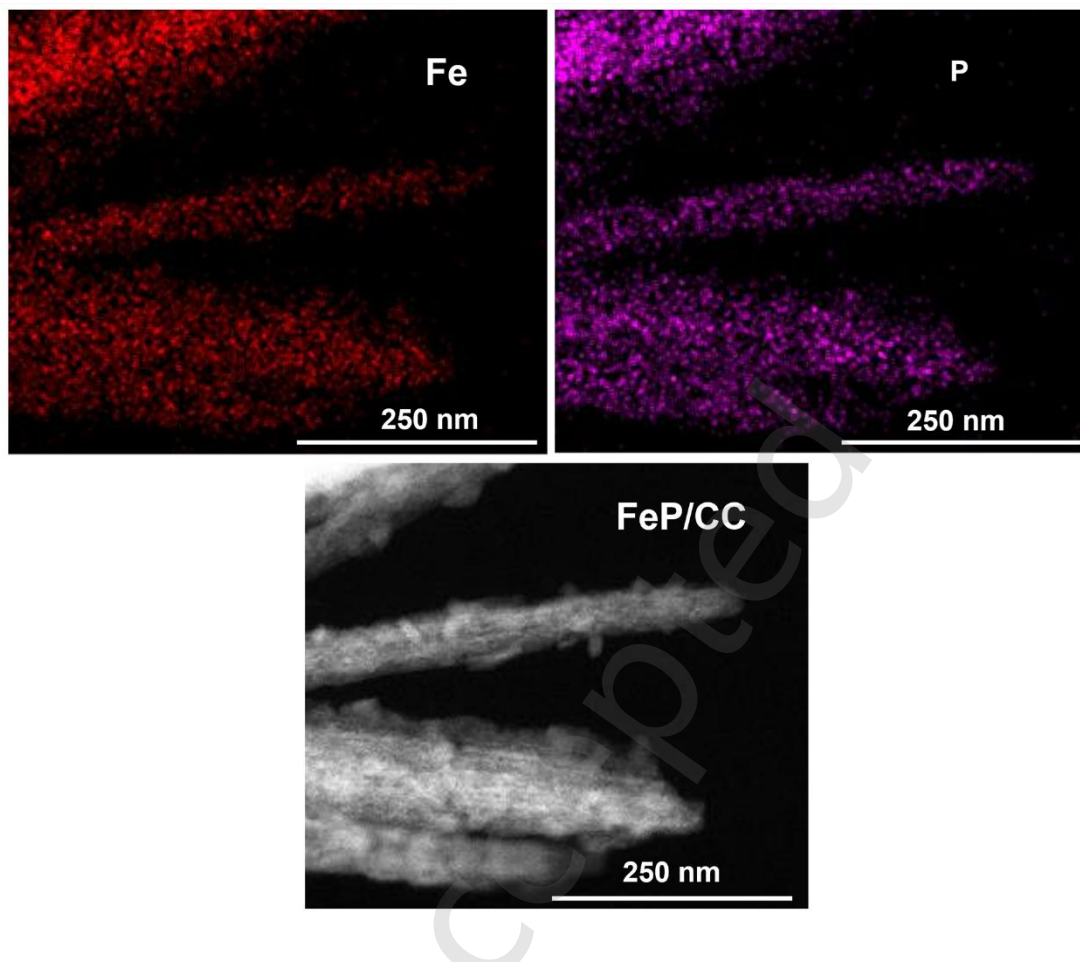


Figure S8. HAADF and corresponding EDS elemental mapping images of FeP/CC.

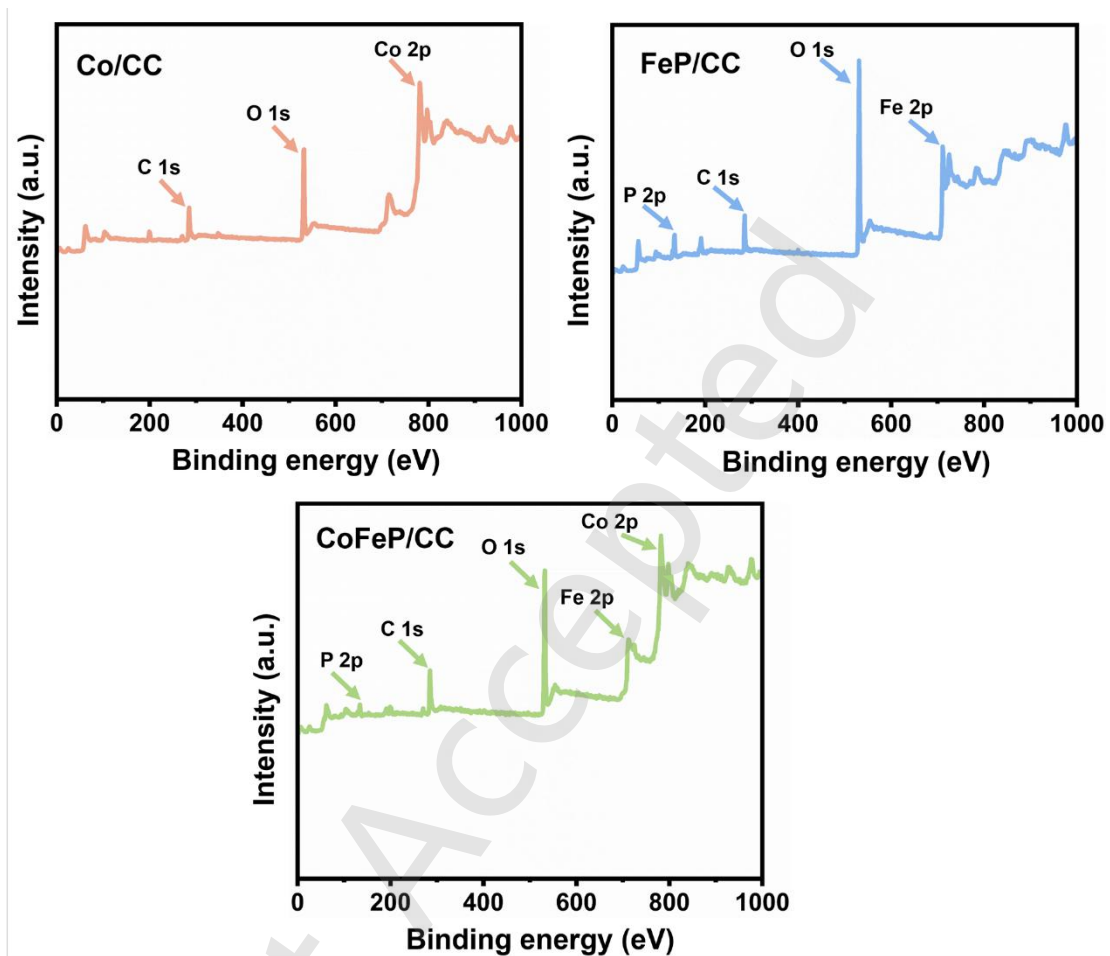


Figure S9. XPS analysis: full-survey scans of all catalysts.

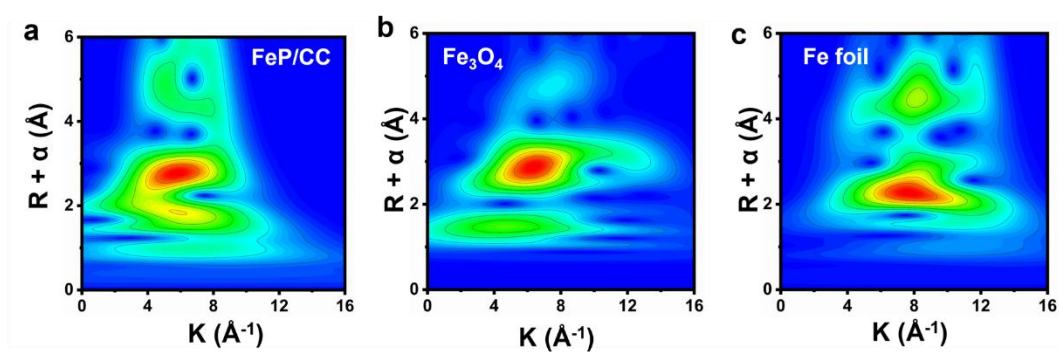


Figure S10. (a-C) WT of k^3 -weighted Fe K-edge of (a) FeP/CC, (b) Fe_3O_4 , and (c) Fe foil.

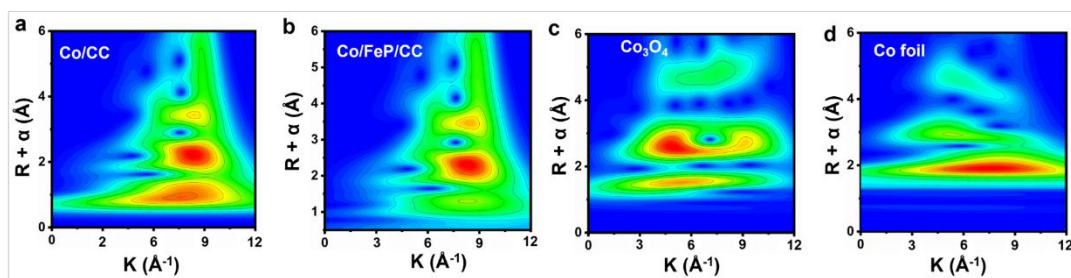


Figure S11. (a-d) WT of k^3 -weighted Co K-edge of (a) Co/CC, (b) Co/FeP/CC, (c) Co_3O_4 , and (d) Co foil.

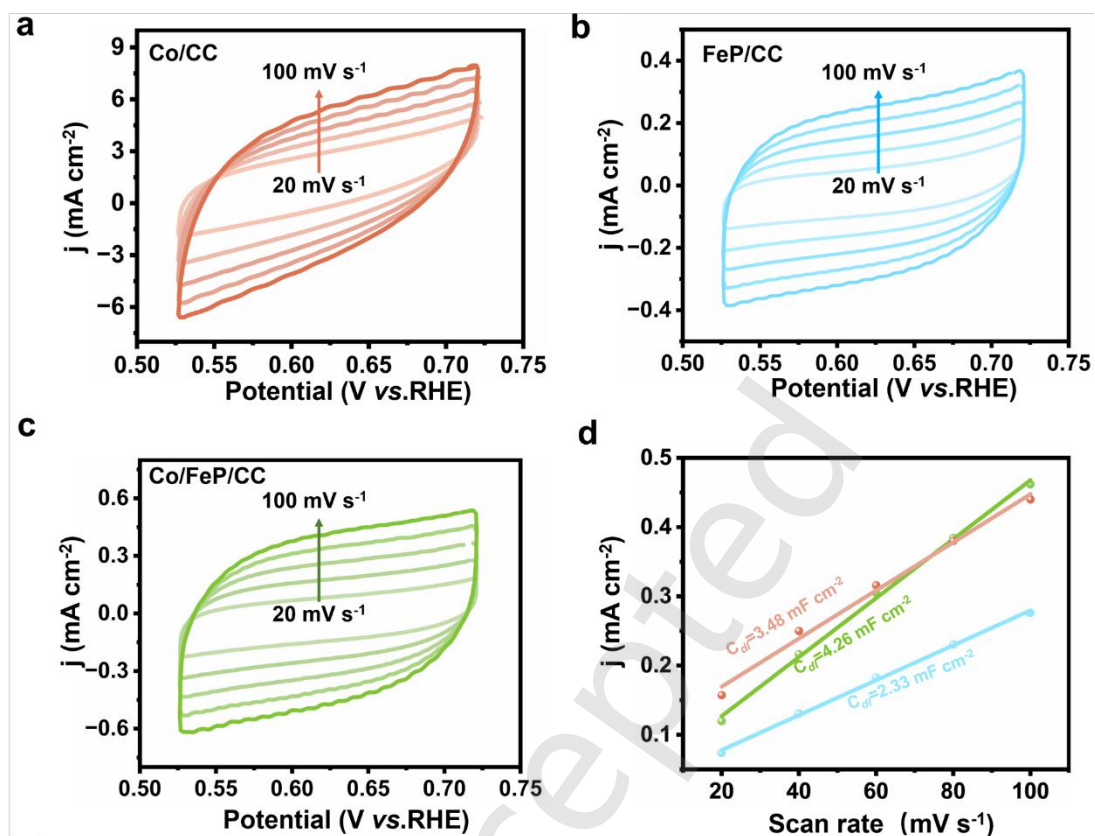


Figure S12. (a) Cyclic voltammograms of Co/CC, (b) FeP/CC and (c) Co/FeP/CC at different scan rates, and (d) the corresponding double-layer capacitances.

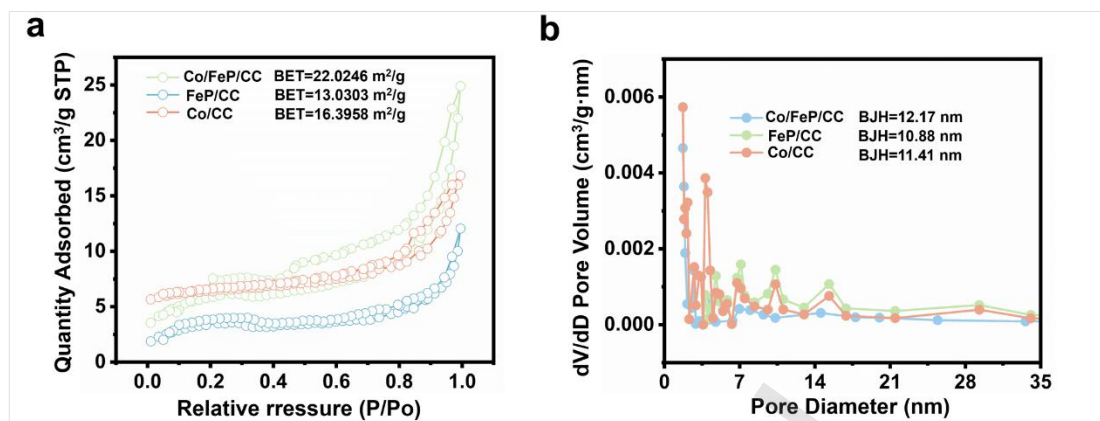


Figure S13 (a) Nitrogen adsorption–desorption isotherms of Co/CC, FeP/CC, and Co/FeP/CC at 77 K. (b) corresponding pore size distribution plots of the above samples.

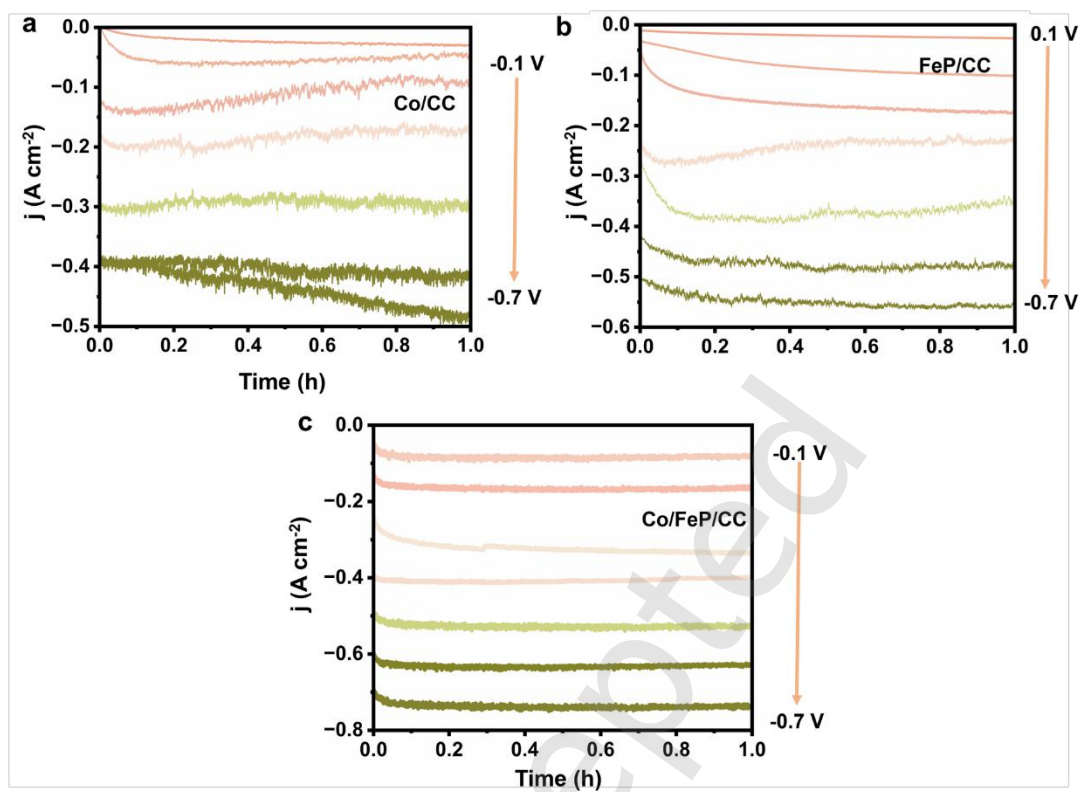


Figure S14. Current-time (i - t) curves of all catalysts in the potential range of 0.0 V to -0.7 V (vs. RHE).

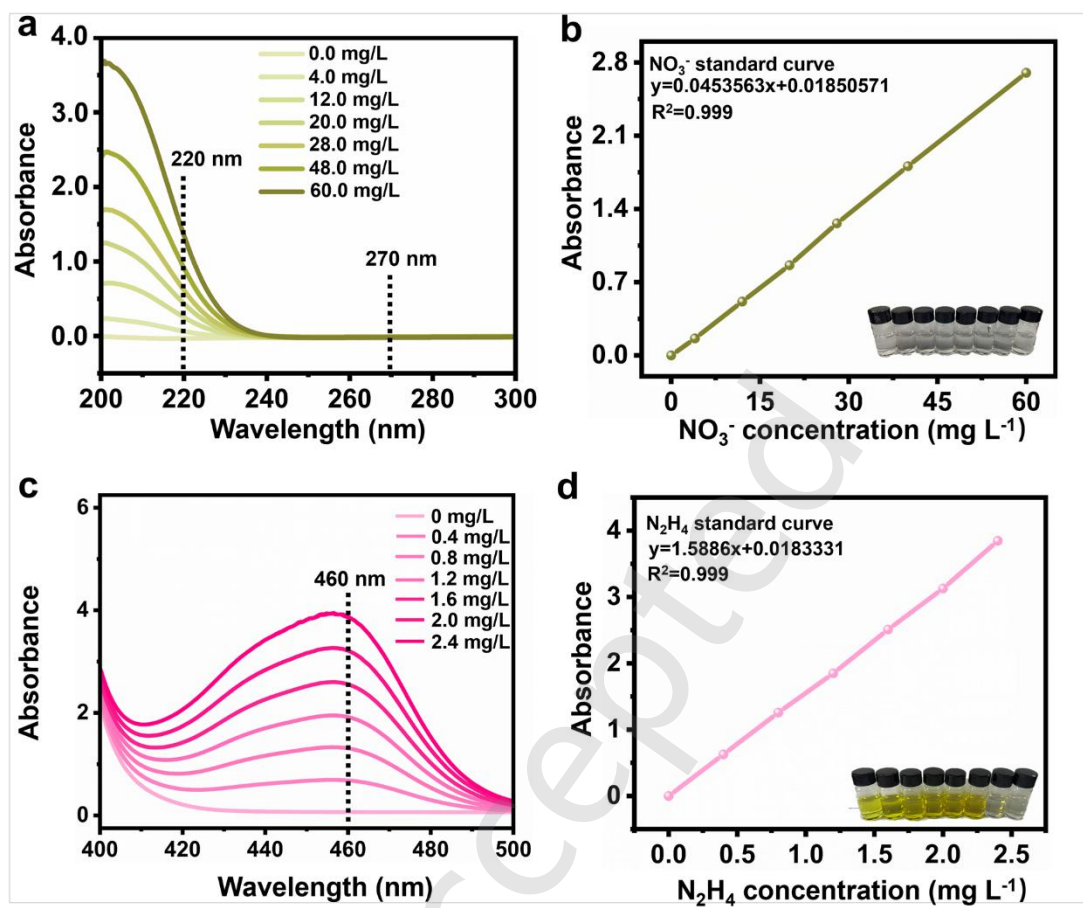


Figure S15. (a) Standard adsorption spectra of NO_3^- and (b) linear fitting. (c) Standard adsorption spectra of N_2H_4 and (d) linear fitting.

NO_3^- was determined by UV spectrophotometry at $\lambda = 220$ nm with background correction at 275 nm. The calibration range was 0-60.0 mg/L, with a regression equation of $y = 0.0453563x + 0.01850571$ and $R^2 = 0.99974$, LOD=0.066 mg/L.

N_2H_4 was determined by the *p*-dimethylaminobenzaldehyde colorimetric method ($\lambda = 460$ nm). The calibration range was 0-2.4 mg/L, with a regression equation of $y = 1.5886x + 0.0183331$ and $R^2 = 0.99948$, LOD=0.066 mg/L.

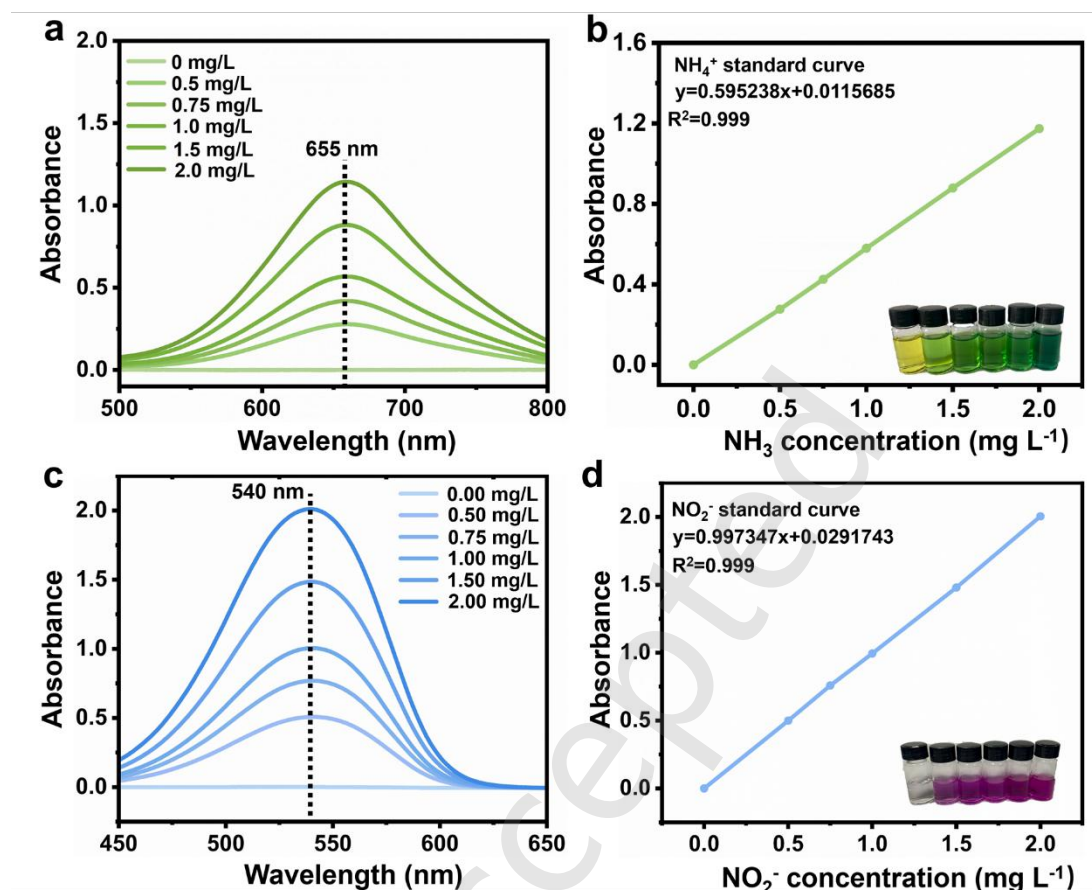


Figure S16. (a) Standard adsorption spectra of ammonia and (b) their linear fitting. (c) Standard adsorption spectra of NO_2^- and (d) linear fitting.

NH_4^+ was determined by the reagent method ($\lambda = 655 \text{ nm}$). The calibration range was 0-2.0 mg/L, with a regression equation of $y = 0.595238x + 0.0115685$ and $R^2 = 0.99925$, LOD=0.02 mg/L.

NO_2^- was determined by the sulfanilamide-naphthylethylenediamine colorimetric method ($\lambda = 540 \text{ nm}$). The calibration range was 0-2.00 mg/L, with a regression equation of $y = 0.997347x + 0.0291743$ and $R^2 = 0.99982$, LOD=0.003 mg/L.

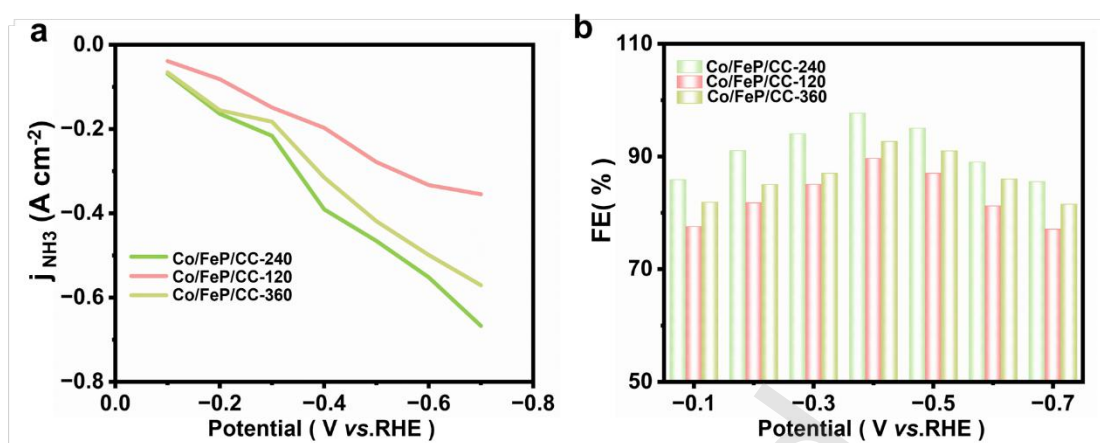


Figure S17. (a) Comparison of the NH₃ partial current density j_{NH_3} (A cm⁻²) and (b) FE for Co/FeP/CC catalysts prepared at different electrodeposition times (120, 240, and 360 s).

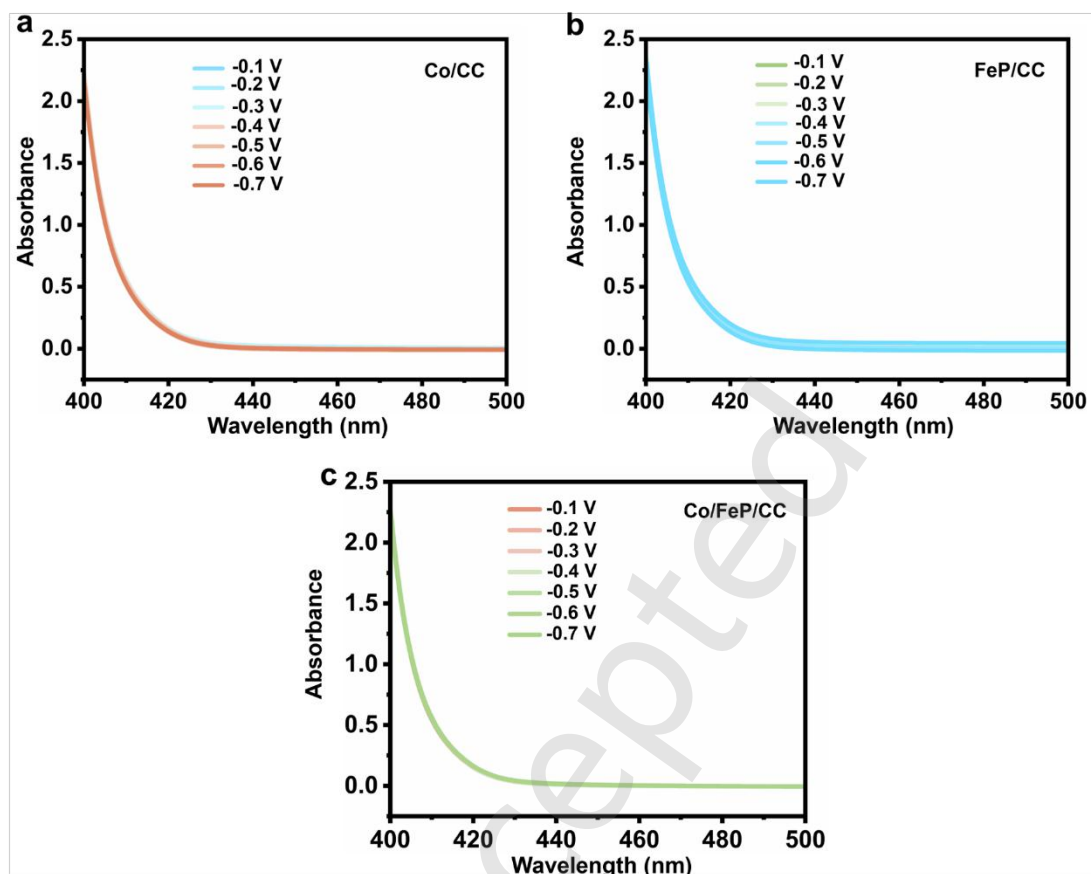


Figure S18. Detection of N_2H_4 in the e-NO_3^- RR products of all catalysts at various potentials using full-spectrum UV-vis spectroscopy.

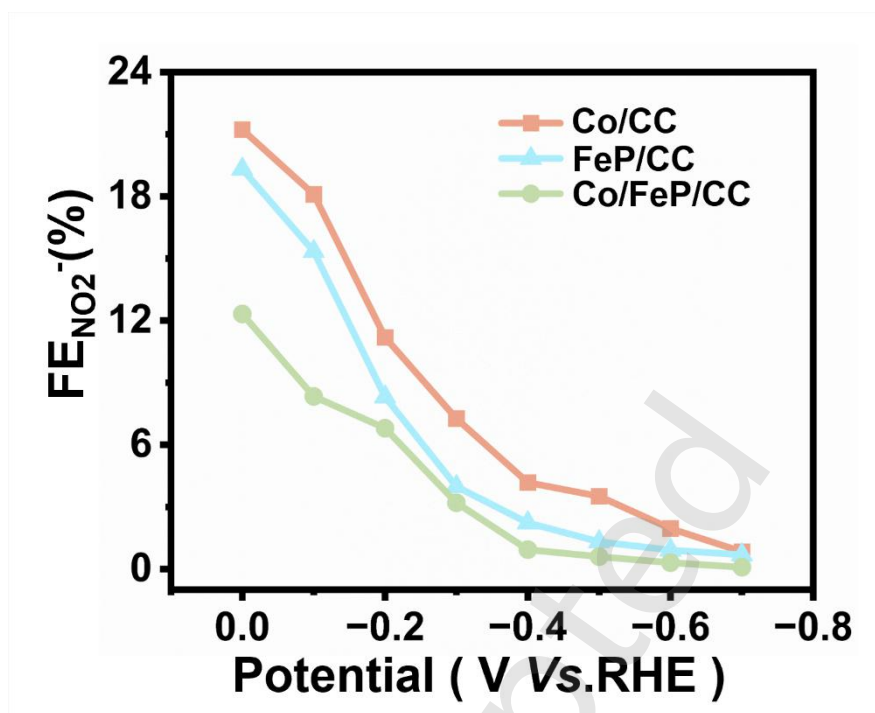


Figure S19. $FE_{NO_2^-}$ of Co/CC, FeP/CC and Co/FeP/CC at different potentials in 1.0 M KOH with 0.1 M NO_3^- .

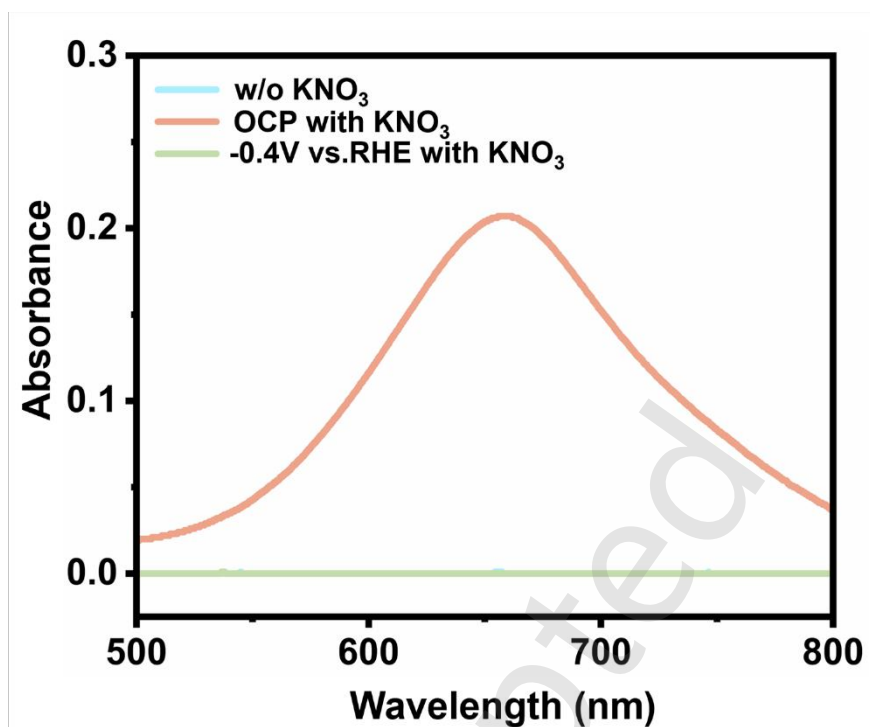


Figure S20. UV-Vis full-spectrum scans of Co/FeP/CC after polarization at -0.4 V (vs. RHE) for 1 h in electrolytes with and without NO_3^- , and after immersion without applied voltage for 1 h.

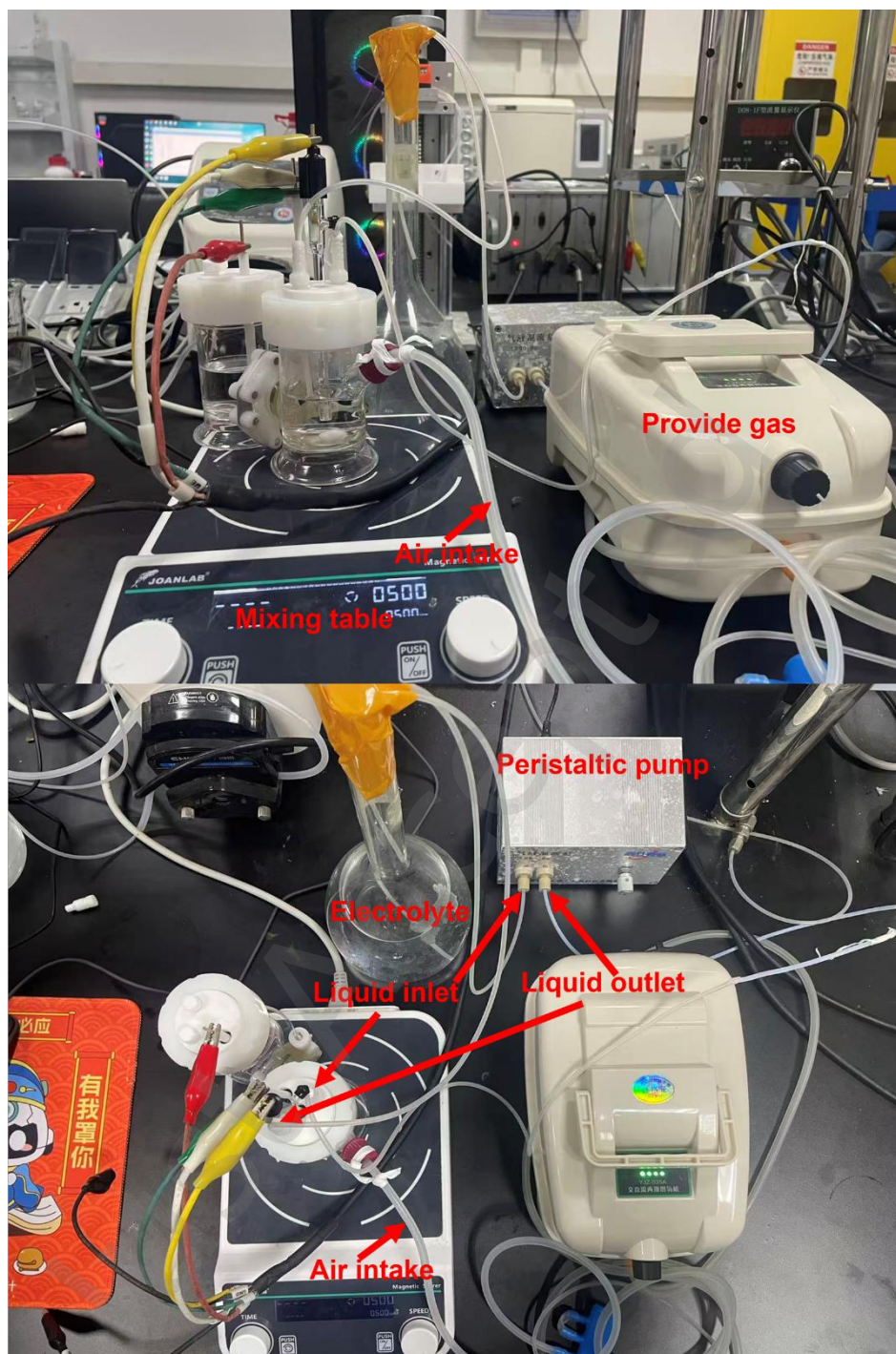


Figure S21. Photograph of the 100 h stability test of Co/FeP/CC at -0.4 V vs. RHE.

The test was conducted in a flowing electrolyte system. The electrolyte was pumped from a volumetric flask into the H-type electrolytic cell at a constant flow rate of 30 mL min⁻¹ using a peristaltic pump, with the circulated electrolyte returning to the reservoir. Meanwhile, air was introduced into the H-type electrolytic cell, and

the air pressure generated pushed the electrolyte in the cell back into the volumetric flask. During the experiment, fresh nitrate solution was periodically supplemented into the reservoir (at 20 h intervals) to maintain the NO_3^- concentration in the electrolytic cell near the initial level, ensuring a sufficient supply of NO_3^- throughout the entire 100 h test period.

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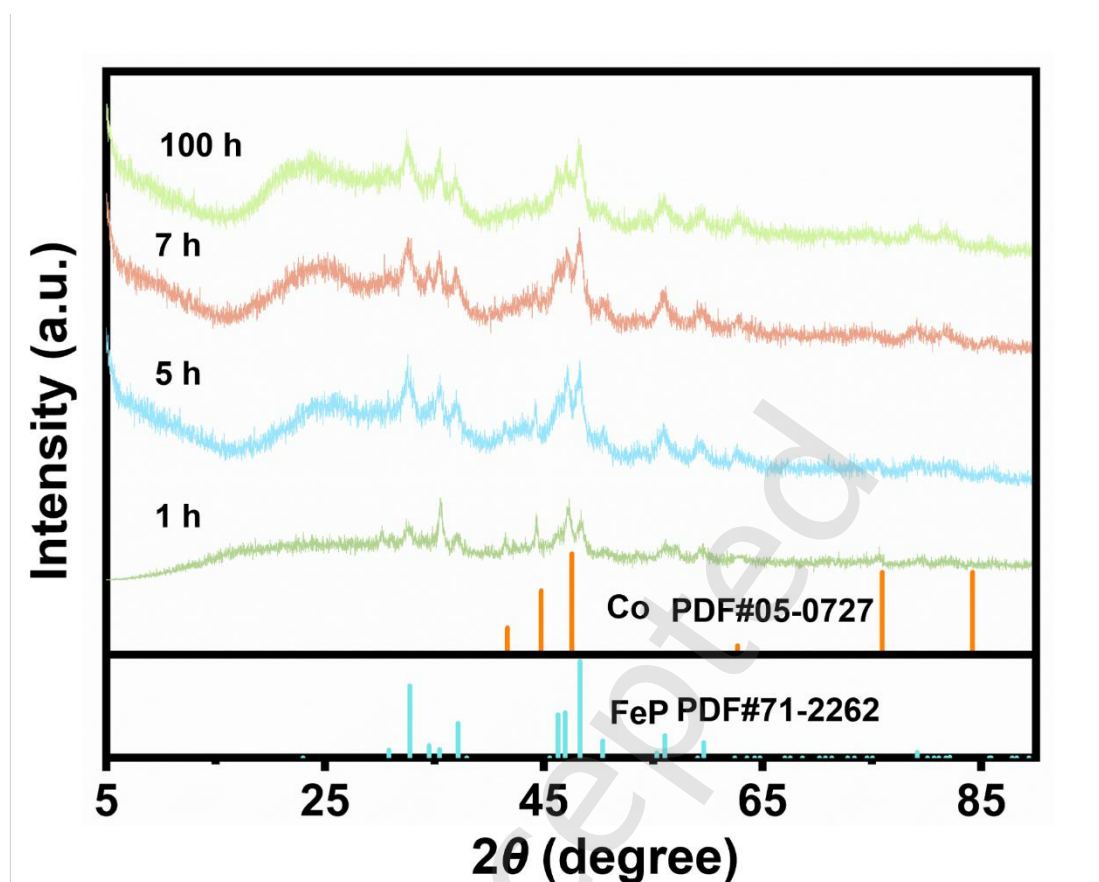


Figure S22. In situ XRD patterns of Co/FeP/CC

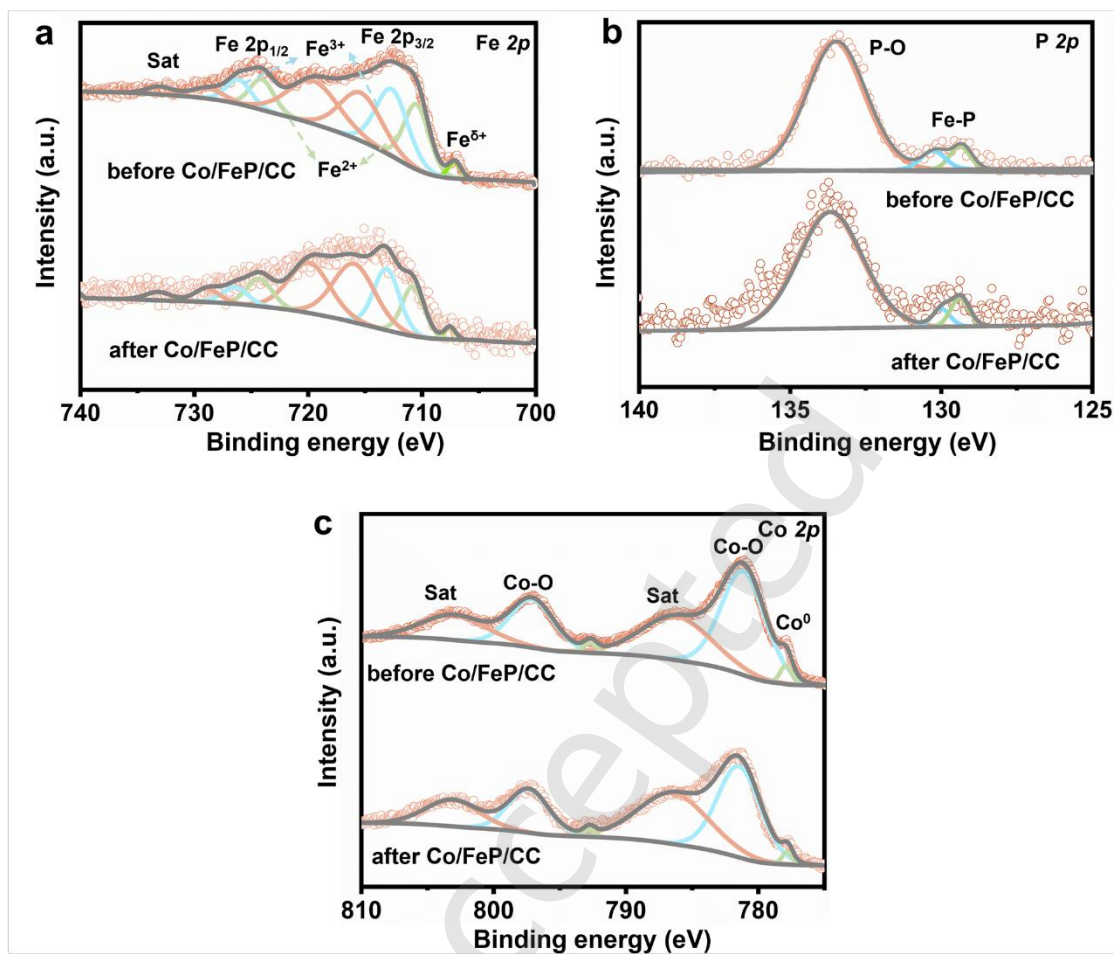


Figure S23. XPS spectra showing (a) Fe 2p, (b) P 2p, (c) Co 2p core levels before/after $e\text{-NO}_3^-$ RR.

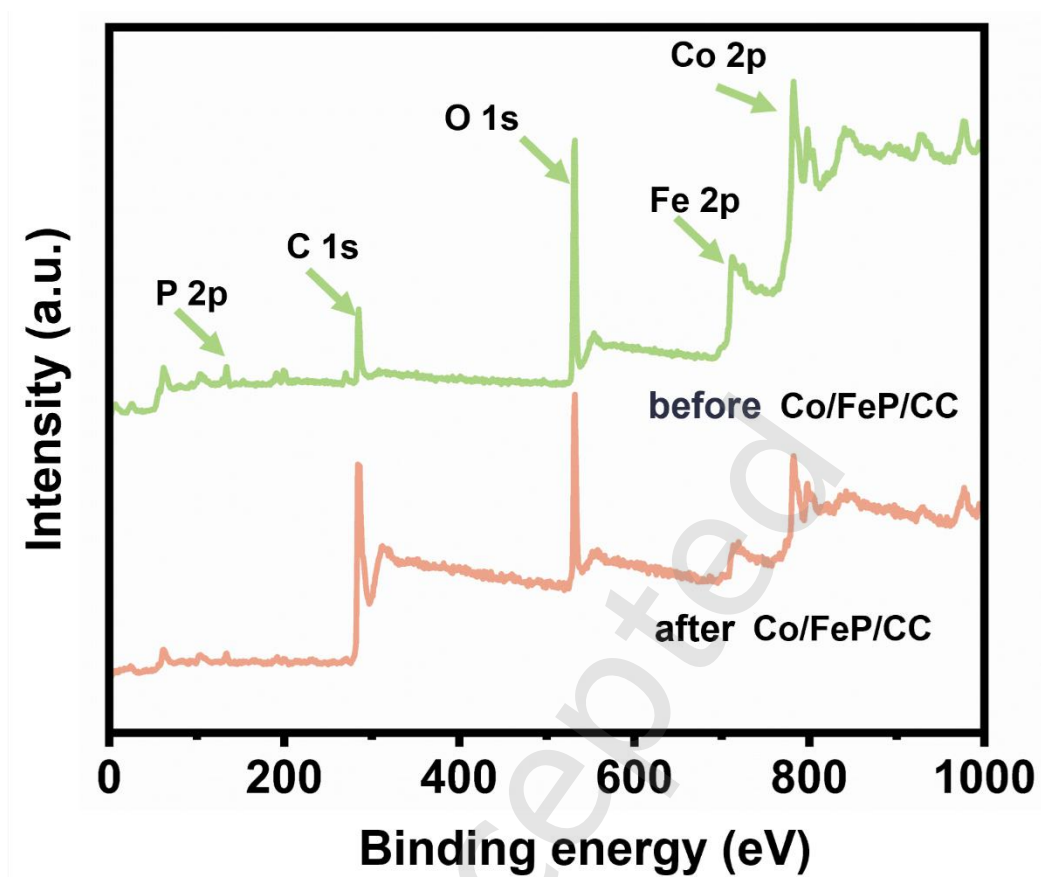


Figure S24. XPS survey spectra of Co/FeP/CC before and after reaction.

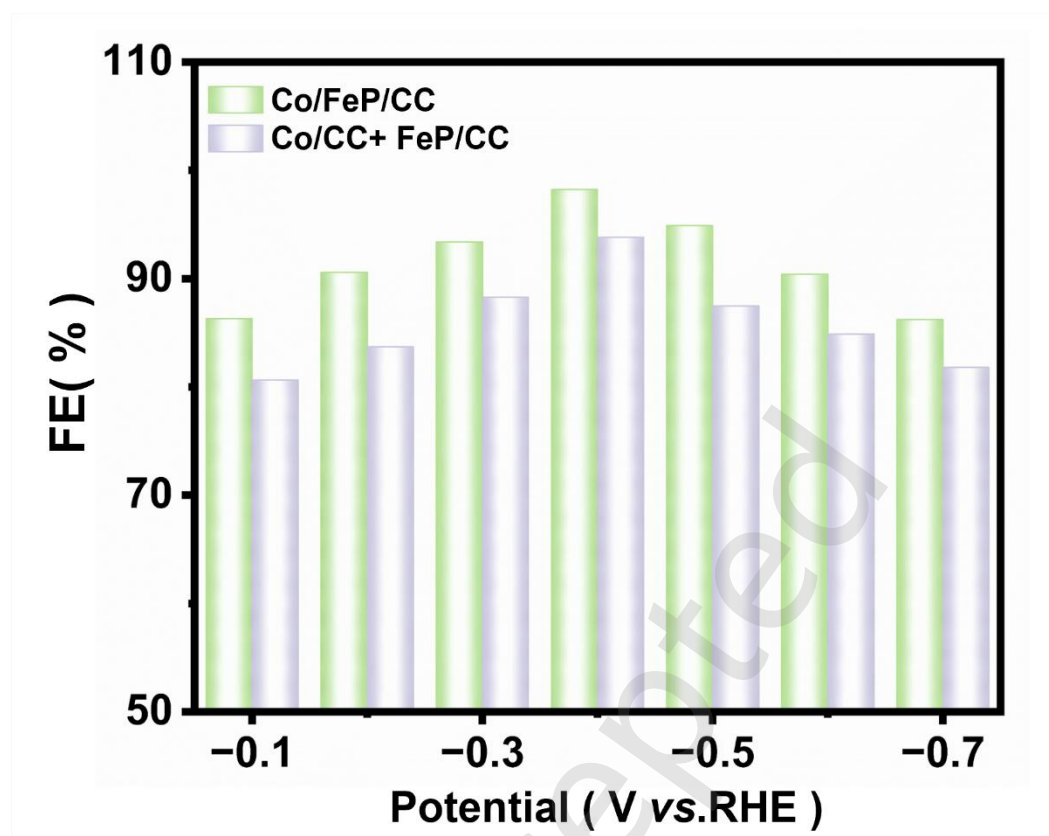


Figure S25. Comparison of NH_3 FE between a physical mixture of Co/CC and FeP/CC (1:1 mass ratio) and the Co/FeP/CC heterostructure under identical conditions (1.0 M KOH + 0.1 M KNO_3 , -0.4 V vs. RHE).

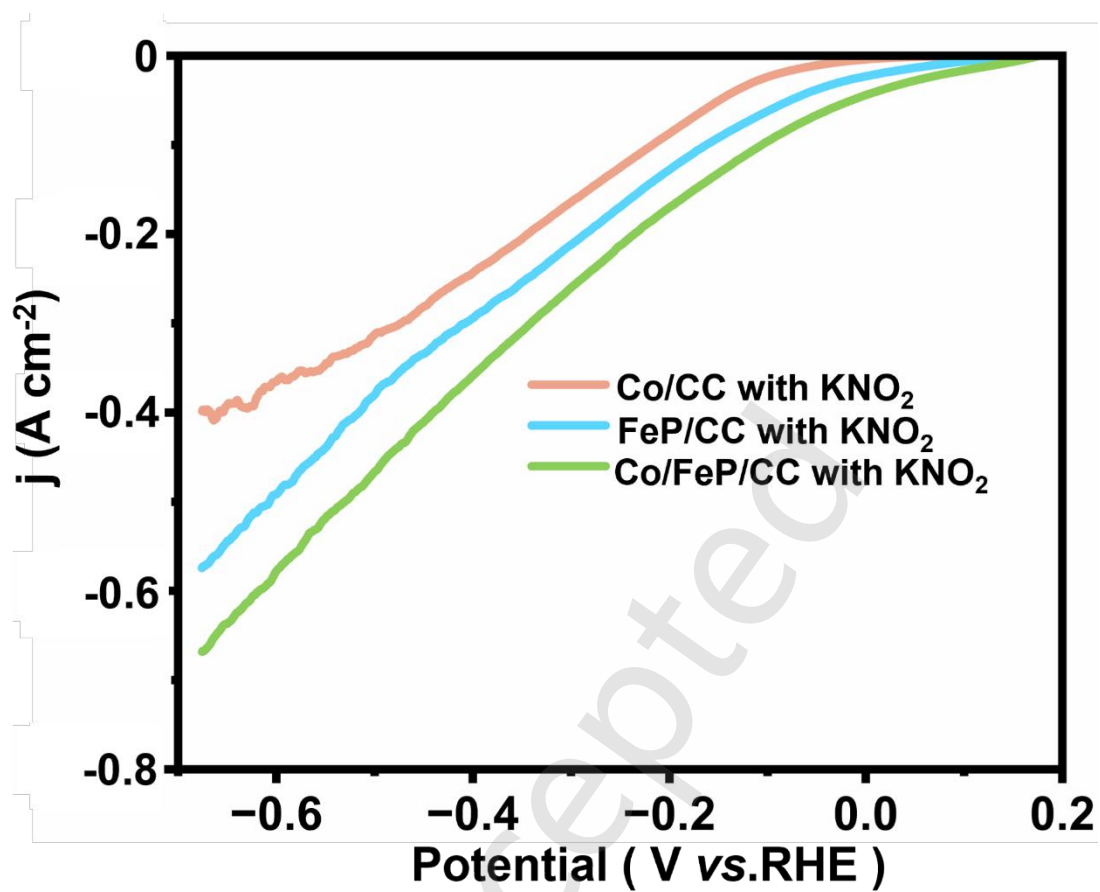


Figure S26. e-NO₂⁻ RR performance of different catalysts.

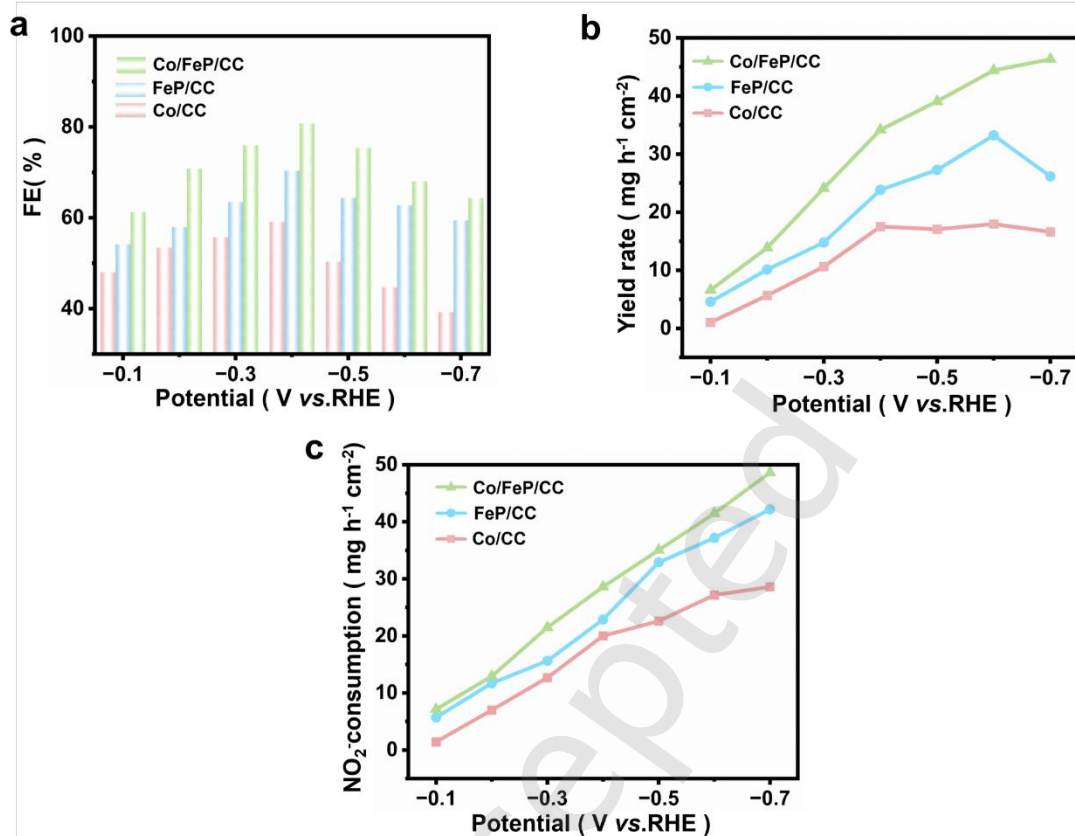


Figure S27. (a) NH₃ FE, (b) NH₃ yield rate, and (c) NO₂⁻ consumption of Co/CC, FeP/CC, and Co/FeP/CC at various potentials in 1.0 M KOH + 0.1 M NO₂⁻.

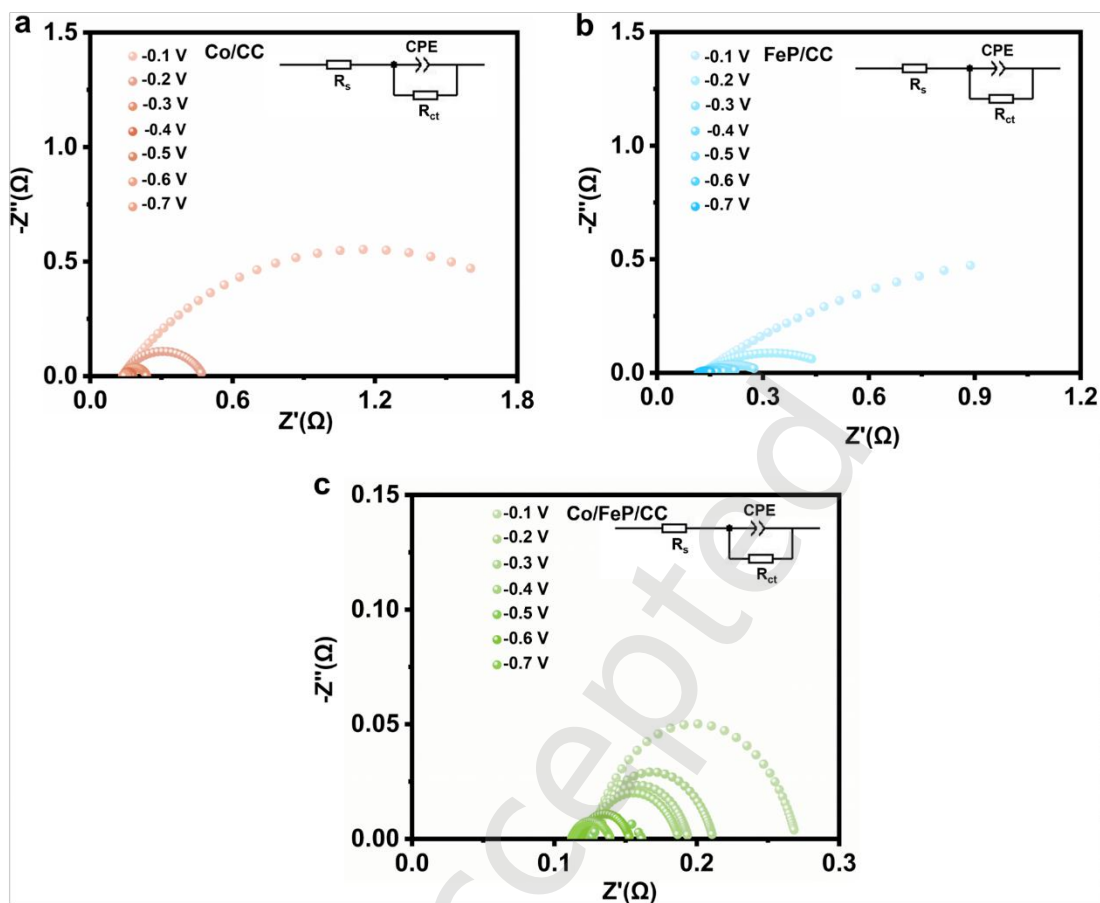


Figure S28. Nyquist plots of (a) Co/CC (b) FeP/CC, and (c) Co/FeP/CC in 1.0 M KOH + 0.1 M NO_3^- electrolyte at different potentials (vs. RHE).

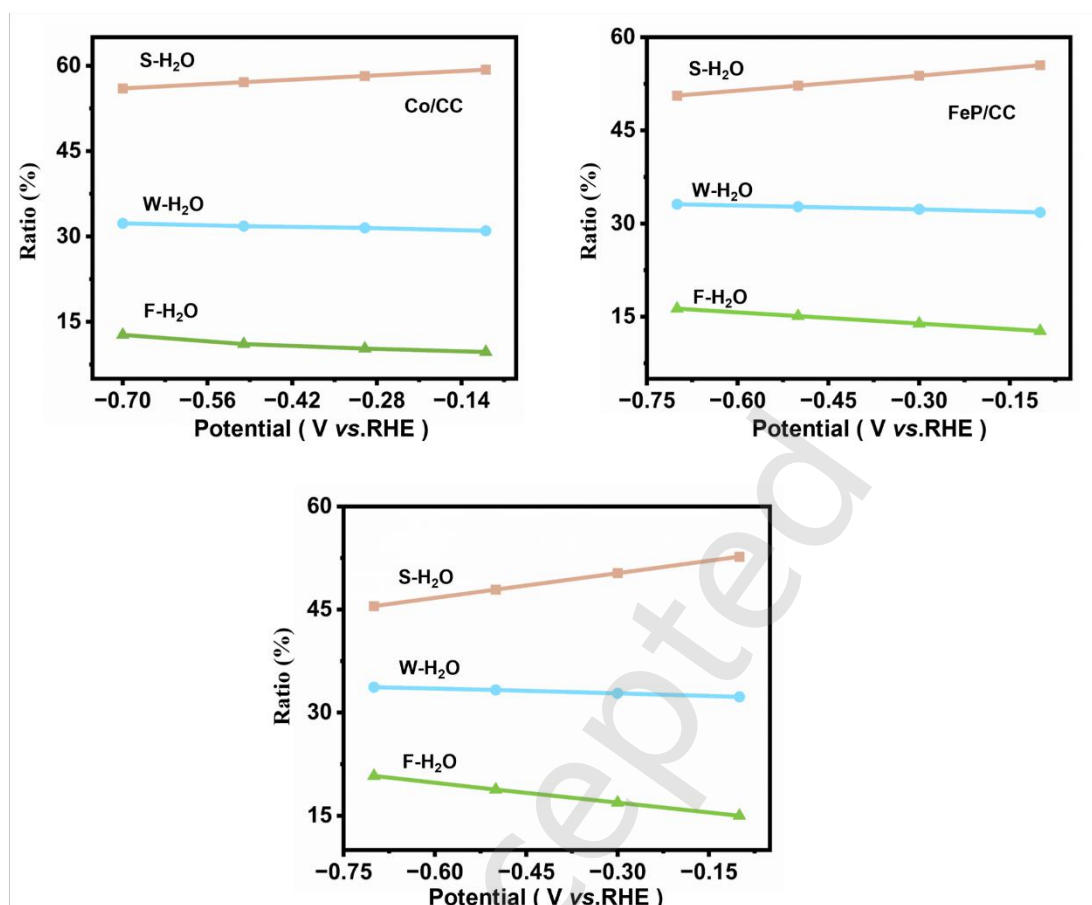


Figure S29. Different water content distribution.

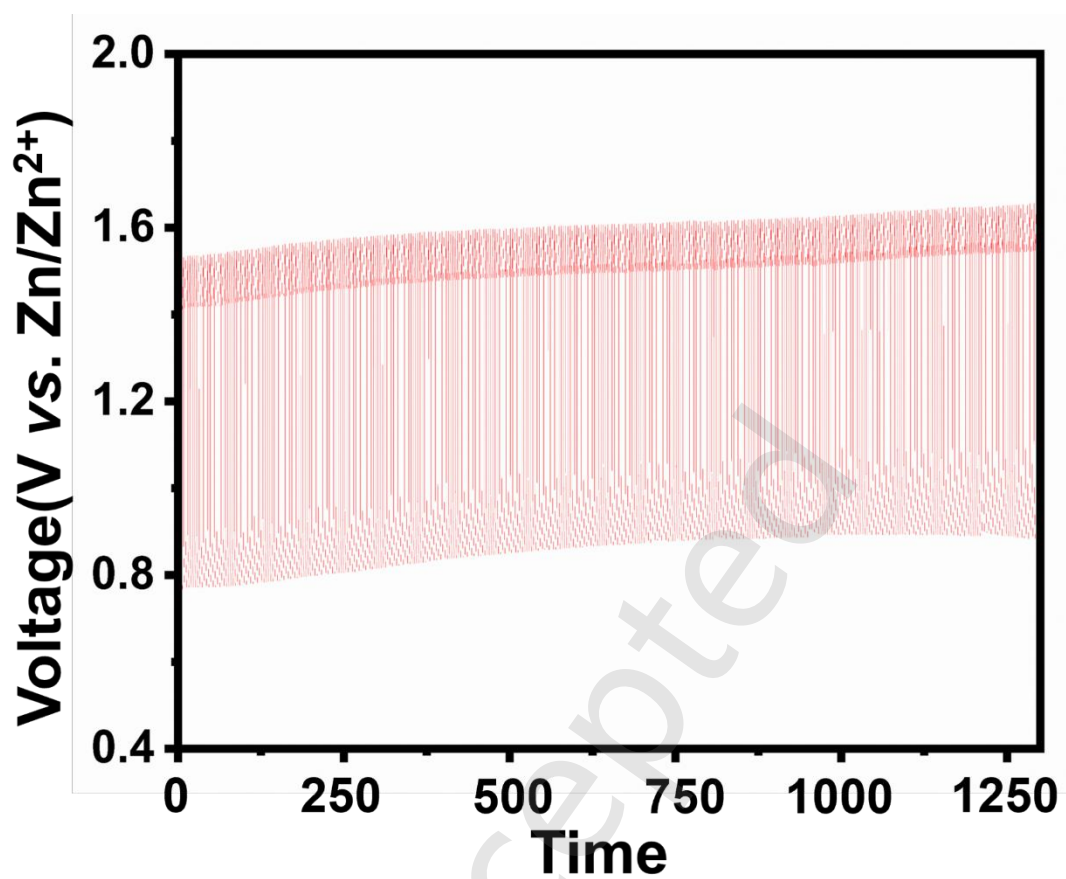


Figure S30. Charge-discharge curves of the Co/FeP/CC-based Zn-NO₃⁻/Zn-NO₂⁻ battery at a fixed current density of 60 mA cm⁻².

Table S1: The contents of Fe and P in FeP/CC, as well as Co, Fe, and P in Co/FeP/CC, were determined by ICP-OES.

Catalyst	Fe(Wt.%)	P (Wt.%)	
FeP/CC	9.6913	3.5152	
FeP (Fe/P = 1.53:1, atomic ratio)			
Catalyst	Co (Wt.%)	Fe (Wt.%)	P (Wt.%)
Co/FeP/CC	2.4710	9.8777	3.5349
Co/FeP (Fe/P =1.56:1, atomic ratio)			

Table S2:The mass loadings of different catalysts

Catalyst	FeP/CC	Co/FeP/CC
Total mass	16.2 mg	28.1 mg
Carbon cloth quality	14.061 mg	23.626 mg
FeP quality	1.594 mg	2.783 mg
FeP loading	6.38 mg.cm ⁻¹	6.26 mg.cm ⁻¹
Co quality	/	0.695 mg
Co loading	/	1.58 mg.cm ⁻¹

Table S3:Comparative analysis of total pore volume for Co/CC, FeP/CC, and Co/FeP/CC.

Catalysts	Total pore volume (cm ³ g ⁻¹)
Co/CC	0.016
FeP/CC	0.021
Co/FeP/CC	0.039

Table S4. Comparison of the catalytic performances of Co/FeP/CC with other reported eNO₃⁻RR electrocatalysts.

Catalyst	Electrolyte	NH ₃ yield rate (mg h ⁻¹ cm ⁻²)	Testing duration (h)	FE(%)	Reference
MoS ₂ -MoSe ₂ -2	0.1 M NaOH + 0.1 M NO ₃ ⁻	3.2@-0.5V	N/A	92.90	[1]
Cu ₂ O/Cu	0.5 M Na ₂ SO ₄ + 0.1 M NO ₃ ⁻	2.79@-0.45 V	1h	93.20	[2]
Ni-Co ₃ O ₄ NSs	0.1 M K ₂ SO ₄ + 0.1 M NO ₃ ⁻	18.39 @-0.25 V	1h	92.10	[3]
Mn-CeO _{2-x}	1 M KOH + 1 M NO ₃ ⁻	17.2 @-0.6 V	1h	91.80	[4]
Co ₂ B@MXene	0.1 M K ₂ SO ₄ + 0.1 M KNO ₃	7.34 @-0.7 V	1h	92.13	[5]
MoFe-NC	0.1 M NaOH + 0.1 M NO ₃ ⁻	4.43 @-0.6 V	1h	91.70	[6]
CuCo-SNC	1 M KOH + 0.1 M NO ₃ ⁻	14.96 @-0.3 V	1h	97.80	[7]
CuO/Bi ₂ CuO ₄ -450	1 M NaOH + 0.01 M NO ₃ ⁻	9.17 @-0.5 V	2h	96.49	[8]
Cu ₂ O@Ni(OH) _{2-x}	0.5 M Na ₂ SO ₄ + 0.1 M NO ₃ ⁻	9.49 @-0.35 V	1h	97.40	[9]
Co/FeP/CC	1 M KOH + 0.1 M NO ₃ ⁻	31.6 @-0.4 V	1h	98.23	This work

Table S5. Nitrogen balance of NO_3^- -N, NH_3 -N, and NO_2^- -N (mmol L^{-1}) (As the volume is the same, the concentration ratio is equal to the molar ratio).

Time (h)	NO_3^- -N	NO_2^- -N	NH_3 -N	Sum of the three N-species
0.0	100.00	0.00	0.00	100.00
1.0	84.40	3.00	13.60	101.00
2.0	71.90	3.60	23.50	99.00
3.0	58.40	2.10	38.4	101.10
4.0	49.20	1.34	50.36	100.90
5.0	32.20	1.02	67.77	100.99
6.0	26.00	0.65	75.35	102.00
7.0	14.40	0.32	85.32	100.04
8.0	5.20	0.14	95.08	100.42
9.0	1.30	0.00	98.56	99.86

Table S6:The metal leaching concentrations of Co/FeP/CC after the 100 h stability test were measured by ICP-OES.

Catalyst	Co(mg/L)	Fe(mg/L)
Co/FeP/CC	0.046	0.213

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Table S7: The solution R_s and the potentials required to achieve -50 mA cm^{-2} for Co/CC, FeP/CC, and Co/FeP/CC in 1.0 M KOH + 0.1 M KNO₃ electrolyte.

Catalyst	Co/CC	FeP/CC	Co/FeP/CC
Solution Resistance (Ω)	0.1379	0.1174	0.1195
Current Density j (mA cm^{-2})	-50	-50	-50
Required Potential E (V vs. RHE)	-0.065	-0.2344	-0.2254

Table S8: Comparison of IR Drop and Target Potential for Co/CC, FeP/CC, and Co/FeP/CC

Catalyst	IR Drop (V)	Target Potential (V)	IR Contribution Percentage
Co/CC	0.0069	-0.0650	10.6%
FeP/CC	0.0059	-0.2344	2.5%
Co/FeP/CC	0.0060	-0.2254	2.7%

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