

***In situ* synchrotron radiation unveils tandem electrocatalytic mechanism in nitrate-to-ammonia conversion enhanced by electron delocalization between cobalt oxide and copper**

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In Situ Synchrotron Radiation Unveils Tandem Electrocatalytic Mechanism in Nitrate-to-Ammonia Conversion Enhanced by Electron Delocalization between Cobalt Oxide and Copper

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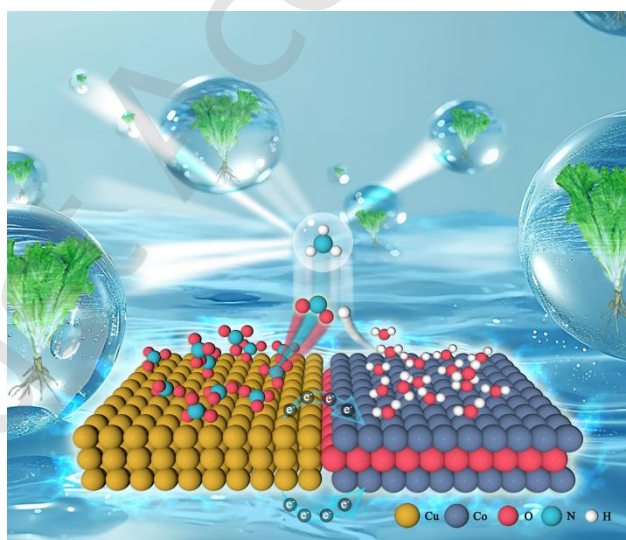
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The designed CoO/Cu-CF heterostructure catalyst features functionally integrated dual active sites that enhance nitrate adsorption and H^+ generation capability, thereby significantly improving its NO_3RR performance. Furthermore, this catalyst enables the conversion of nitrate into fertilizer for lettuce cultivation, contributing to sustainable nitrogen management.

In situ synchrotron radiation unveils tandem electrocatalytic mechanism in nitrate-to-ammonia conversion enhanced by electron delocalization between cobalt oxide and copper

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ABSTRACT: Cu-based electrocatalysts are cost-effective and highly selective for electrochemical nitrate-to-ammonia reduction (NO₃RR) but suffer from limited active hydrogen (H*) supplying, competing hydrogen evolution, and ill-defined active sites. Here, we demonstrate that CoO facilitates water dissociation to generate and capture H*, which migrates to neighboring Cu sites and both enhances NO₃RR performance and suppresses hydrogen evolution on the CoO/Cu heterostructure by electron delocalization. *In situ* synchrotron radiation analyses reveal that metallic Cu strongly adsorb and electronically activate NO₃⁻, CoO dissociate water to supply H*, and dynamic modulation of metal valence states and coordination environments synergistically enhances activity and stability by sustaining electron delocalization induced by electron transfer from Cu to CoO. Complementary *in situ* and *ex situ* spectroscopies delineate a stepwise reduction pathway (NO₃⁻ → NO₃[•] → NO[•] → NOH[•] → NHOH[•] → NH[•] → NH₂[•] → NH₃[•]), while the built-in electric field generated by the electron delocalization can accelerate the overall kinetics. At -0.4 V versus RHE, the catalyst attains a 95% NH₃ Faradaic efficiency and a yield rate of 14,321 μg h⁻¹ cm⁻². In a flow cell, it sustains 200 mA cm⁻² for over 220 h. Fertilizer trials using recovered NH₄Cl markedly improve lettuce yield and survival, confirming the practical viability of this electrocatalytic strategy.

KEYWORDS: electron delocalization, active hydrogen, dynamic mechanism, nitrate reduction reaction

1 Introduction

Ammonia is one of the most important chemical feedstocks, underpinning fertilizer manufacture and the synthesis of numerous nitrogen-containing compounds [1–3]. Today, more than 90% of global ammonia is produced via the Haber–Bosch process, which operates at 20–30 MPa and 300–500 °C [4,5]. This energy-intensive route consumes 2–5% of the world's energy supply (≥ 8.6 EJ year⁻¹) and emits 400–450 Mt CO₂ annually, motivating the search for more sustainable alternatives [6,7]. In response to growing energy and environmental concerns, the electrochemical nitrate reduction reaction (NO₃RR) has emerged as a sustainable route to ammonia, driven by the combined imperatives of environmental management, energy transition, and resource recycling. From an environmental perspective, NO₃RR enables efficient removal of nitrate pollutants from industrial and agricultural wastewater under ambient conditions. On the energy front, utilizing renewable electricity for ammonia synthesis offers a low-carbon alternative to the energy-intensive Haber–Bosch process, contributing to global carbon neutrality goals. From a resource standpoint, converting waste nitrate into valuable ammonia fertilizer facilitates the establishment of a distributed green ammonia system, thereby enhancing both energy security and food supply resilience [8–10]. Mechanistically, NO₃RR proceeds via an eight-electron pathway (NO₃⁻ → NO₂⁻ → NH₃), in which the initial two-electron reduction to nitrite and the subsequent

six-electron hydrogenation steps critically depend on efficient proton/electron management and the suppression of the competing hydrogen evolution reaction (HER) [11,12].

Precious metals (e.g., Pt, Pd) offer strong adsorption and activation of NO₃⁻ and intermediates but suffer from high cost and scarce availability [13,14]. By contrast, transition metals are inexpensive and possess tunable electronic structures, making them potential candidates for practical NO₃RR applications. For example, Cu aligns its d orbitals with the LUMO π orbitals of NO₃⁻ to favor NO₃⁻ → NO₂[•] conversion and partially prevent HER [15]. However, Cu exhibits sluggish water dissociation, leading to inadequate active hydrogen (H*) supply and capture, as well as high energy barriers for nitrite hydrogenation/deoxygenation [16,17]. Conversely, in the CoO phase, octahedrally coordinated Co²⁺ undergo crystal-field splitting of their fivefold-degenerate d orbitals into a low-energy t_{2g} triplet (d_{xy}, d_{yz}, d_{xz}) and a high-energy e_g doublet (d_{x²-y²}, d_{z²}) [18]. Although this electronic configuration facilitates water dissociation, it is accompanied by weak NO₃⁻ adsorption and persistent competition from the HER [19]. We thus envision that a rationally designed Cu and CoO heterojunction could synergize the favorable NO₃⁻ activation of Cu with the robust water dissociation and H* provision of CoO, while electronic coupling at the interface would tune the catalyst d-band center and optimize intermediate adsorption/desorption. Yet, realizing such a dual-site architecture with intimate

contact and controlled electronic interaction remains a significant challenge.

Herein, we report the synthesis of a CoO/Cu heterostructures grown on copper foam (CoO/Cu-CF) using a combination of electrodeposition and pyrolysis strategies. In NO₃RR process, CoO dramatically lowers the barrier for water dissociation by electron delocalization, while capturing and supplying H⁺ to adjacent Cu sites. *In situ* infrared spectroscopy and differential electrochemical mass spectrometry (DEMS) trace the eight - electron coupled nine-proton pathway (NO₃^{*} → NO₂^{*} → NO^{*} → NOH^{*} → NHOH^{*} → NH^{*} → NH₂^{*} → NH₃^{*}). *In situ* X-ray absorption spectroscopy analyses elucidate that metallic Cu exhibits a robust adsorption and electronic activation of NO₃⁻, while CoO facilitates water dissociation to provide H⁺. The dynamic modulation of metal valence states and coordination environments works synergistically to significantly enhance both catalytic activity and stability. Furthermore, the formation of built-in electric field within the CoO/Cu heterostructure significantly enhances the charge transfer efficiency and ensures a sufficient electron supply for the NO₃RR. As a result, CoO/Cu-CF achieves a peak NH₃ Faradaic efficiency of 95% at -0.4 V vs RHE with a production rate of 14,321 μg h⁻¹ cm⁻² in an H-cell. When deployed in a flow electrolyzer at 200 mA cm⁻², it maintains 85.6% FE over 220 h, delivering 34,800 μg h⁻¹ cm⁻² of NH₃. The recovered product directly applied as fertilizer, boosts lettuce yield and survival by 3.1 - fold and 1.5 - fold, respectively, while shortening the cultivation cycle. This work demonstrates a purposeful heterojunction design that integrates pollutant remediation with energy - efficient chemical production.

2 Experimental

2.1 Synthesis of CoO/Cu-CF catalysts

Commercial Cu foam was ultrasonically cleaned in anhydrous ethanol for 10 min and then in 1.0 M HCl for 10 min. After rinsing thoroughly with deionized water and ethanol, the foam was immersed in an aqueous solution of 0.25 M (NH₄)₂S₂O₈ and 1.0 M NaOH for 15 min at room temperature. Then, it was rinsed again with deionized water and ethanol and dried under vacuum at 40 °C to yield Cu(OH)₂-CF. During this step, the foam surface turned cyan and the solution turned blue, indicating the *in situ* formation of Cu(OH)₂. Subsequently, CoO/Cu-CF precursor (namely pre-CoO/Cu-CF) was prepared by electrodeposition using Cu(OH)₂-CF as the working electrode, a carbon rod as the counter electrode, and an Ag/AgCl electrode as the reference. The electrolyte comprised 15 mM Na₂SO₄ and 25 mM CoCl₂·6H₂O. Electrodeposition was carried out by cyclic voltammetry between -0.2 and -0.6 V (vs. Ag/AgCl) at a scan rate of 3 mV s⁻¹ for five cycles. Finally, the pre-CoO/Cu-CF was annealed under the H₂/Ar (v/v = 10:90) atmosphere at 250 °C for 2 h (2 °C min⁻¹ heating rate).

2.2 Synthesis of Cu-CF catalysts

The Cu(OH)₂-CF was reduced at 250 °C for 2 h with the heating rate of 2 °C min⁻¹ under the H₂/Ar (v/v = 10:90) atmosphere, thus the Cu-CF was obtained.

2.3 Synthesis of CoO/CC catalysts

Carbon cloth (CC) was rendered hydrophilic by immersion in a 1:3 (v/v) mixture of concentrated HNO₃ and H₂SO₄ at room

temperature for 12 h. The treated CC was then sequentially sonicated for 10 min each in acetone, ethanol, and deionized water to remove residual contaminants. Finally, CoO/CC were prepared by the same electrodeposition and thermal annealing procedures above.

2.4 Electrochemical Performance Test

Electrochemical performance was evaluated in an H-cell configuration using Nafion 211 as the ion-exchange membrane. A three-electrode assembly was employed the synthesized samples (1.0 × 1.0 cm) served as the working electrode (cathode), a carbon rod as the counter electrode (anode), and a reversible hydrogen electrode (RHE) in 1.0 M KOH as the reference. The cathodic electrolyte consisted of 1.0 M KOH containing 0.1 M KNO₃, while the anodic electrolyte was 1.0 M KOH. All the electrochemical tests were conducted using an Autolab workstation. Prior to nitrate electroreduction, linear sweep voltammetry (LSV) was performed at 100 mV s⁻¹ between 0.5 V and -0.6 V until the polarization curves reached steady state. The inner resistance was determined by potentiostatic electrochemical impedance spectroscopy (EIS) over the frequency range 0.1 Hz to 100 kHz. The double-layer capacitance (*C_{dl}*) of the catalyst was calculated as following equation:

$$C_{dl} = \frac{i_c}{v} \quad (1)$$

where *i_c* is the charging current density (mA cm⁻²), defined as half the difference between anodic and cathodic currents, and *v* is the scan rate (mV s⁻¹). Cyclic voltammetry for *C_{dl}* determination was conducted in a non-Faradaic potential window in 1.0 M KOH at scan rates of 20, 30, 40, 50, and 60 mV s⁻¹.

2.5 Electrochemical NO₃RR Performance in a Flow Cell

Nitrate electroreduction was performed at room temperature in a flow electrolyzer separated by an anion exchange membrane. A Gamry potentiostat/galvanostat controlled the electrochemical measurements. Both the catholyte and anolyte were circulated at 8 mL min⁻¹. The cathode was a 1 × 1 cm CoO/Cu-CF for NO₃RR, and the anode was commercial Ni foam for water oxidation. The two-electrode flow cell electrolyzer employed a cathodic electrolyte of 1.0 M KOH + 0.1 M KNO₃ for NH₃ synthesis and an anodic electrolyte of 1.0 M KOH for water oxidation process.

3 Results and discussion

3.1 Synthesis and structural characterizations of catalysts

The synthetic scheme of the CoO/Cu-CF is illustrated in Fig. 1(a). Initially, the pretreated Cu foam underwent chemical oxidation to form Cu(OH)₂ nanorod arrays (namely Cu(OH)₂-CF) approximately 200 nm in diameter (Fig. S1 in the Electronic Supplementary Material (ESM)). Cobalt species were then electrodeposited onto the roughened Cu nanorods to generate nanodendritic structures (Fig. S2 in the ESM). Ultimately, a controlled pyrolytic treatment was adapted to fabricate CoO/Cu-CF heterostructure, endowing it with a robust oxide-metal interface, abundant exposed active sites, and enhanced electrical conductivity. Scanning electron microscopy (SEM) images reveal that the nanoparticles self-assemble into one-dimensional structures, forming interconnected and dense networks on the

copper foam surface (Fig. S3 in the ESM). Such hierarchical architecture not only accelerates charge transfer and mass transport but also significantly improves the electrocatalytic activity and stability of catalyst [20]. As shown in Fig. 1(b), the TEM image displays brighter outer regions, likely corresponding to CoO nanoclusters or nanoparticles (highlighted by the red dashed circles), surrounding the darker Cu-rich cores. The high-resolution TEM (HRTEM) image clearly resolves lattice fringes corresponding to the Cu (111) and CoO (111) planes (Fig. 1(c)), providing direct evidence for the formation of the CoO/Cu heterostructure. Elemental mapping confirms a uniform distribution of Cu, Co, and O throughout the CoO/Cu-CF

catalyst (Figs. 1(d) and 1(e)). Moreover, Co and O exhibit broader spatial dispersion than Cu, confirming successful CoO integration with Cu and the formation of CoO/Cu heterostructures. For comparison, $\text{Cu}(\text{OH})_2\text{-CF}$ was directly thermally reduced to prepare Cu-CF with a metallic Cu phase, preserving its rod-like morphology and increasing surface roughness (Fig. S4 in the ESM). Using the same electrodeposition combined with thermal treatment procedure, CoO was deposited onto carbon cloth to prepare CoO/CC, resulting in nanosheet networks uniformly covering the carbon fibers (Fig. S5 in the ESM).

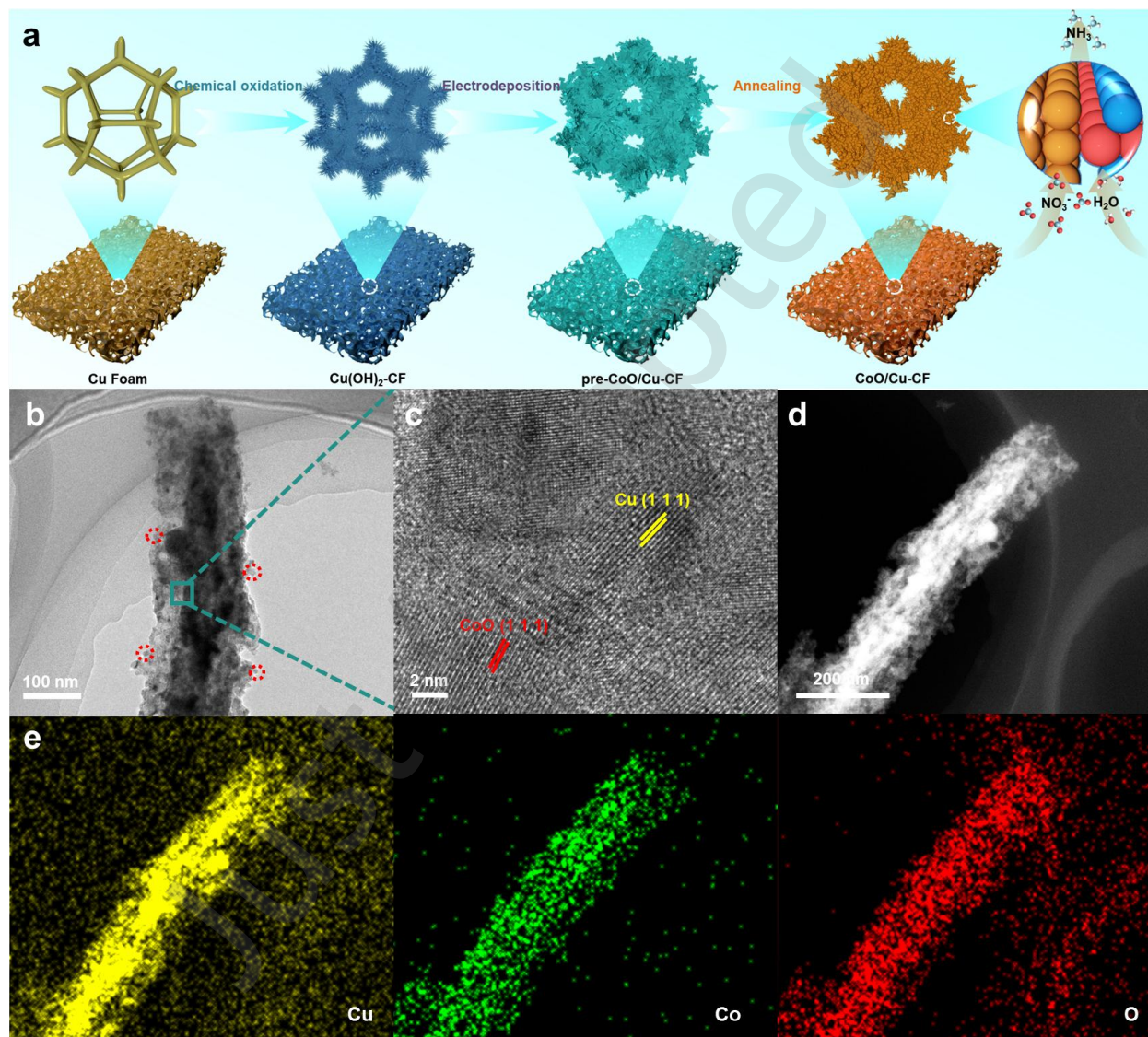


Figure 1 Synthetic scheme and morphological characterizations. (a) Synthetic illustration of CoO/Cu-CF. (b) TEM, (c) HRTEM and (d,e) EDS element mapping images of CoO/Cu-CF.

As shown in Fig. 2(a), the powder X-ray diffraction (XRD) pattern of CoO/Cu-CF displays peaks corresponding to CoO (PDF #09-0402) and Cu (PDF #03-1005), confirming the successful formation of CoO/Cu heterostructures. X-ray photoelectron spectroscopy (XPS) was employed to characterize the catalyst's surface composition and bonding structure. The survey spectrum and elemental ratios revealed the presence and relative abundances of Cu, Co, and O on the catalyst surface (Fig. S6 in the ESM). In the high-resolution Cu 2p XPS

spectrum, peaks at 932.6 eV ($2p_{3/2}$) and 952.4 eV ($2p_{1/2}$) are attributed to Cu^0/Cu^+ , whereas peaks at 934.6 eV and 954.5 eV correspond to Cu^{2+} species (Fig. 2(b)) [21]. The detected oxide state probably originates from either partial surface oxidation during air exposure or the electron interaction of between Cu and CoO. The Co 2p spectrum in Fig. 2(c) exhibits Co $2p_{3/2}$ and $2p_{1/2}$ signals accompanied by satellite features, confirming Co^{2+} as the dominant oxidation state [22]. Notably, the Cu 2p peaks in CoO/Cu-CF shift to higher binding energies compared with

Cu-CF, while the Co 2p peaks shift to lower energies relative to CoO/CC. These shifts provide clear evidence of electron delocalization at the Cu/CoO heterostructure interface and indicate electron transfer from Cu to CoO. This electron transfer may induce a built-in electric field, enhancing charge transfer efficiency and accelerating the eight-electron transfer process in the NO_3RR .

X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy provide detailed information on the oxidation state and local coordination environment of metal sites. As shown in Fig. 2(d), the Cu K-edge absorption onset for CoO/Cu-CF falls between those of Cu foil and Cu_2O , indicating an average copper oxidation state between 0 and +1. In contrast, the Cu K-edge of the pure Cu catalyst coincides with that of Cu foil, confirming a fully metallic Cu^0 state. This edge shift signifies partial electron depletion at the Cu centers in CoO/Cu-CF. Fourier-transformed EXAFS (FT-EXAFS, Fig. 2(e)) of CoO/Cu-CF exhibits two main peaks at 1.43 Å and 2.10 Å, corresponding to the first coordination shell of Cu–O bonds and the inner coordination shell of Cu–Cu bonds, respectively. EXAFS fitting exhibits a Cu–Cu coordination number of 4.9, markedly lower than the bulk value of 12 (Fig. S7 and Table S1 in the ESM). Such

undercoordinated surface atoms characterization can enhance electrocatalytic activity [23]. The observed Cu–O coordination is consistent with the XPS analyses. Wavelet-transform EXAFS (WT-EXAFS) contour maps generated with a Morlet wavelet further substantiate these assignments, revealing distinct oscillatory features at approximately 6.65 Å^{-1} (Cu–O) and 7.8 Å^{-1} (Cu–Cu) (Fig. 2(f)). Normalized Co K-edge XANES spectra in Fig. 2(g) show that the Co oxidation state in CoO/Cu-CF is lower than in CoO/CC and CoO foil, indicating electron transfer from Cu to Co, which is supported by the Co 2p XPS results. The FT-EXAFS spectrum of CoO/Cu-CF features two main peaks at 1.53 and 2.57 Å (Fig. 2(h)), respectively, attributed to Co–O bonds in the first coordination shell and Co–O–Co bonds in the second shell. Conventional *R*-space FT-EXAFS cannot separate any Co–Co contributions because they overlap with the strong Co–O–Co signal (Fig. S8 and Table S2 in the ESM) [24]. However, Morlet wavelet-transform EXAFS resolves an oscillation at 7.5 Å^{-1} (Co–O) alongside distinct features at 4.5 and 8.25 Å^{-1} assignable to Co–Co interactions (Fig. 2(i)). Such observation confirms that CoO exists as discrete nanoclusters or nanoparticles, rather than as isolated dopant atoms on the Cu support.

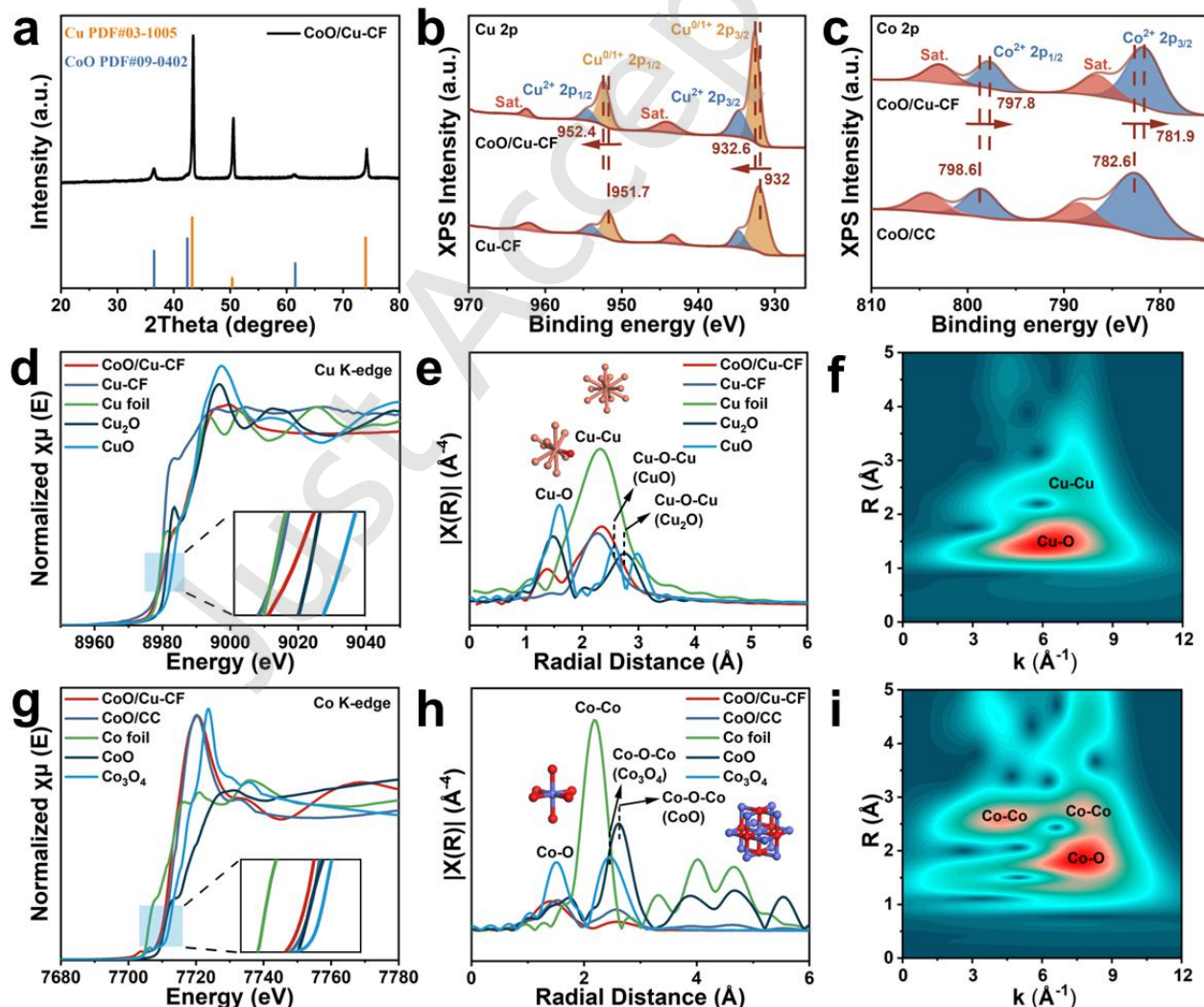


Figure 2 Structural characterizations. (a) XRD patterns of CoO/Cu-CF. XPS spectra of (b) Cu 2p of CoO/Cu-CF and Cu - CF, and (c) Co 2p of CoO/Cu-CF and CoO/CC. (d) Normalized XANES spectra, (e) FT-EXAFS spectra, and (f) WT-EXAFS contour maps of Cu K-edge for CoO/Cu-CF, Cu-CF and reference samples. (g) Normalized XANES spectra, (h) FT-EXAFS spectra, and (i) WT-EXAFS contour maps of Co K-edge for CoO/Cu-CF, CoO/CC and reference samples.

3.2 Evaluation of Electrochemical NO₃RR Performance

The performance of electrochemical NO₃RR was evaluated in an H-type cell, utilizing a cathodic electrolyte of 1.0 M KOH and 0.1 M KNO₃, alongside an anodic electrolyte of 1.0 M KOH. As illustrates in Fig. 3(a), linear sweep voltammetry (LSV) curves clearly demonstrate that the CoO/Cu-CF catalyst exhibits a higher geometric current density in the cathodic electrolyte containing KNO₃ (solid line) compared to that in the electrolyte without KNO₃ (dashed line). The results indicate that CoO/Cu-CF demonstrates significantly greater activity for the electrochemical NO₃RR compared to the HER. In contrast, the current densities observed for the Cu-CF and CoO/CC catalysts are relatively lower, suggesting that when Cu and Co function as isolated active sites, their effectiveness in NO₃RR is constrained. The CoO/Cu-CF exhibits a Tafel slope of 58.67 mV dec⁻¹, which is substantially lower than the slopes observed for Cu-CF of 145.22 mV dec⁻¹ and CoO/CC of 146.79 mV dec⁻¹ (Fig. 3(b)). Electrochemical impedance spectroscopy (EIS) analysis demonstrates that CoO/Cu-CF has the smallest Nyquist semicircle diameter among all samples, indicating enhanced charge-transfer efficiency and accelerated charge-transfer kinetics, thereby confirming its superior catalytic performance (Fig. S9 in the ESM) [25]. It indicates that the combination of CoO and Cu enhances electron transfer at the catalyst–electrolyte interface, thereby accelerating the overall

reaction kinetics. The products of electrochemical NO₃RR were analyzed at different potentials using chronoamperometry.

The reduction products, including NO₃⁻, NO₂⁻, and NH₃, were further quantified using ultraviolet-visible (UV-Vis) spectroscopy spectrophotometric colorimetry (Figs. S10–12 in the ESM). The Faradaic efficiency for ammonia production (FE_{NH₃}) of the CoO/Cu-CF catalyst remains above 80% at all assessed potentials (Fig. 3(c)). Notably, the FE_{NH₃} of CoO/Cu-CF reaches 95% at -0.4 V vs. RHE, which is considerably higher than that of Cu-CF (74.2%) and CoO/CC (44.2%). Furthermore, the ammonia production rate of the CoO/Cu-CF exceeds that of both Cu-CF and CoO/CC at all applied potentials (Fig. 3(d)). It is particularly noteworthy that the CoO/Cu-CF achieves a peak production rate of 16,762 μg h⁻¹ cm⁻² at -0.5 V vs. RHE, which is about 1.3 times and 4.1 times higher than that of the Cu-CF and CoO/CC, respectively. ¹⁵N isotope labeling experiments, together with control NO₃RR tests under various conditions, confirm that the produced ammonia originates exclusively from the nitrate in the electrolyte, excluding any contribution from nitrogen-containing impurities or environmental N₂/NH₃ contamination (Fig. S13 in the ESM). Additionally, the relatively high double-layer capacitance (C_{dl}) of CoO/Cu-CF indicates that the Cu/CoO heterostructure offers a significantly greater number of active sites, thereby markedly enhancing electrochemical NO₃RR activity (Figs. S14–15 in the ESM).

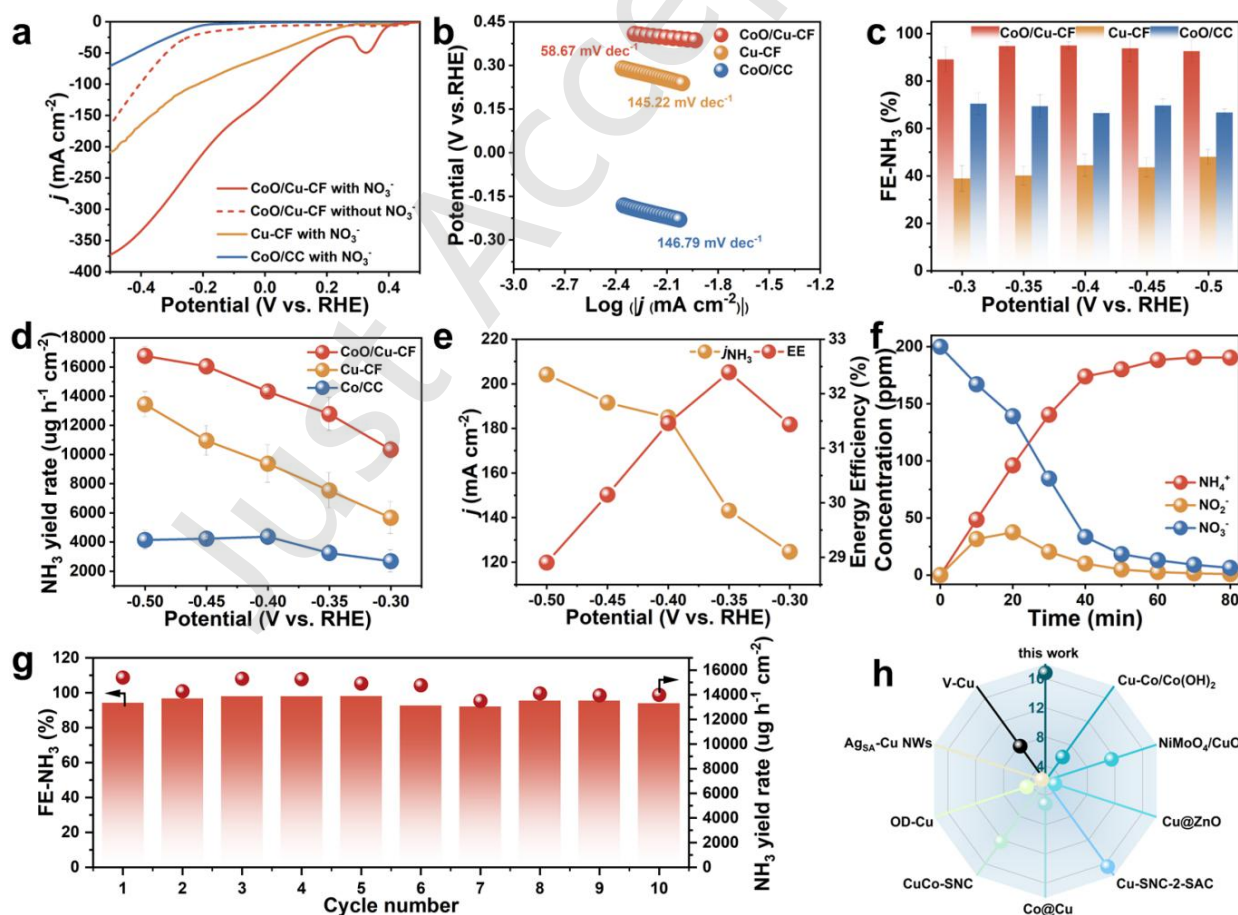


Figure 3 Electrochemical NO₃RR performance in H-type cell. (a) LSV curves of all compared samples in 1.0 M KOH with or without NO₃⁻. (b) Tafel slopes, (c) FE_{NH₃} and (d) NH₃ yield rate of all compared samples in 1.0 M KOH with NO₃⁻ under different potentials. (e) EE and *j*_{NH₃} of CoO/Cu-CF at different potentials. (f) Complete nitrate removal using CoO/Cu-CF with an initial 200 ppm KNO₃ electrolyte at -0.4 V vs. RHE. (g) FE_{NH₃} and NH₃ yield rate of CoO/Cu-CF at -0.4 V vs. RHE during 10 cycles. (h) Comparing the NH₃ yield of CoO/Cu-CF with the reported electrocatalysts.

Fig. 3(e) presents the ammonia partial current density (j_{NH_3}) and energy efficiency (EE) of CoO/Cu-CF under various applied potentials. At -0.5 V vs. RHE, CoO/Cu-CF achieves a j_{NH_3} of 204.2 mA cm^{-2} , which is approximately twice and 4.4 times higher than that of Cu-CF and CoO/CC (Fig. S16 in the ESM), respectively, indicating significantly enhanced intrinsic catalytic activity. At -0.35 V vs. RHE, the EE of CoO/Cu-CF reaches 32.4%, representing a 2.5-fold and 1.5-fold improvement over Cu-CF and CoO/CC, respectively, highlighting its economic feasibility for large-scale applications. To evaluate the practical applicability of CoO/Cu-CF, nitrate removal experiments were conducted in simulated wastewater containing 200 ppm NO_3^- -N ($\sim 0.0143 \text{ M KNO}_3$) at -0.4 V vs. RHE. As shown in Fig. 3(f), after 80 min nearly all NO_3^- can be converted to NH_3 , leaving residual NO_3^- (0.85 ppm) and NO_2^- (6.31 ppm) concentrations well below World Health Organization (WHO) drinking-water limits [26]. When the

nitrate concentration and initial pH vary within a certain range, the FE consistently remains above 80%, and the ammonia yield, EE, and j_{NH_3} all exhibit excellent performance (Figs. S17–S18 in the ESM), indicating that the catalyst possesses good tolerance to changes in substrate concentration and pH. To further investigate the durability, CoO/Cu-CF underwent 10 consecutive electrolysis cycles at -0.4 V vs. RHE (Fig. 3(g)). It can be seen that the FE_{NH_3} remains $\geq 90\%$ with a high yield rate of $14,106 \mu\text{g h}^{-1} \text{ cm}^{-2}$, indicating that excellent electrocatalytic stability of CoO/Cu-CF. A series of post-stability characterizations confirm that the CoO/Cu-CF exhibits excellent structural stability, with the CoO/Cu heterostructure well preserved and no significant Cu oxidation or Co leaching observed (Figs. S19–21 in the ESM). When benchmarked against recent nitrate-to-ammonia electrocatalysts, it outperforms the reported advanced electrocatalysts in NH_3 yield rate (Fig. 3(h) and Table S4 in the ESM).

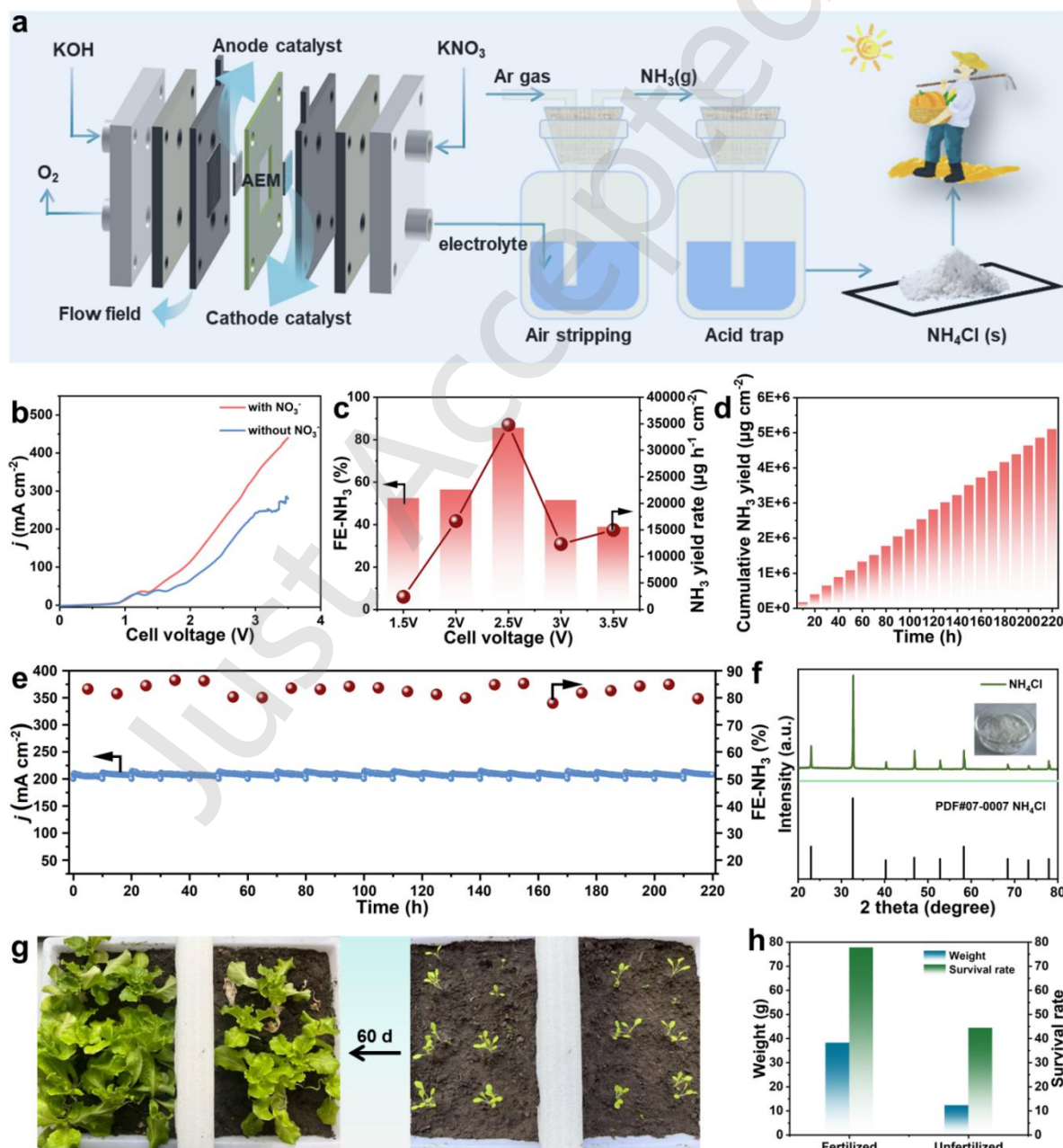


Figure 4 Electrochemical NO_3RR performance CoO/Cu-CF tested in flow cell. (a) Schematic illustration of flow cell and NH_3 recovery. (b) LSV curves (without IR compensation) with or without NO_3^- at the cathode. (d) FE and yield rate of NH_3 at different cell voltages. (e). Long-term stability

over CoO/Cu-CF in a flow cell at 2.5 V vs. Cell. (f) XRD pattern of the extractive NH_4Cl powder from the electrolyte after stability test. (g) Photographs comparing lettuce growth with ammonium chloride fertilization (left) and without fertilization (right).

A two-electrode flow cell is further used to estimate the performance of CoO/Cu-CF, in which the cathodic NO_3RR couples with anodic oxygen evolution reaction (Fig. 4(a)). The detailed photographs of the test setup are provided (Fig. S22 in the ESM). Subsequently, $\text{NH}_4\text{Cl(s)}$ will be extracted from the treated electrolyte and used as a fertilizer for crop cultivation, aiming to improve energy utilization efficiency. The LSV curve shown in Fig. 4(b) indicates a significant increase in current density after the addition of 0.1 M KNO_3 , confirming that the NO_3RR occurs at the cathode. The FE_{NH_3} exhibits a volcano-like trend with voltage, reaching its peak of 84% at 2.5 V vs. Cell with an NH_3 yield rate as high as $34,800 \mu\text{g h}^{-1} \text{cm}^{-2}$ (Fig. 4(c)). Even after 220 h, the NH_3 yield rate and FE remain stable with a total of 5,000,000 μg of $\text{NH}_3(\text{aq})$ produced (Figs. 4(d) and 4(e)), demonstrating the exceptional stability of CoO/Cu-CF in practical production. Air stripping technology has been effectively utilized in the treatment of industrial wastewater to extract $\text{NH}_3(\text{g})$, resulting in a valuable final product [27]. Fig. 4(a) illustrates that under operational conditions of 70 °C and airflow, $\text{NH}_3(\text{g})$ can be efficiently removed from the treated electrolyte. During the $\text{NH}_3(\text{g})$ recovery process, hydrochloric acid is employed to capture the gas, forming aqueous ammonium chloride ($\text{NH}_4\text{Cl(aq)}$). A rotary evaporator is then used to facilitate the separation of solid ammonium chloride ($\text{NH}_4\text{Cl(s)}$). The XRD pattern depicted in Fig. 4(f) verifies that $\text{NH}_4\text{Cl(s)}$ was successfully obtained from the treated nitrate solution. Subsequently, we utilized the harvested $\text{NH}_4\text{Cl(s)}$ as a fertilizer for lettuce cultivation. Fig. 4(g) presents digital photographs comparing lettuce yields when grown with and without the $\text{NH}_4\text{Cl(s)}$ fertilizer. The statistical analysis shown in Fig. 4(h) reveals that the prepared $\text{NH}_4\text{Cl(s)}$ significantly enhanced lettuce growth, with yield and survival rates 3.1 times and 1.5 times greater, respectively, than those of the unfertilized control (Fig. S23 in the ESM). The practical applications demonstrate that $\text{NH}_4\text{Cl(s)}$ produced via electrochemical NO_3RR confers significant advantages for crop cultivation. It should be noted that although ammonium chloride was employed in this study for product validation due to its stability and ease of handling, the long-term agricultural application of chloride-based fertilizers may contribute to soil salinization. Additionally, the present study was conducted using model nitrate solutions to establish a well-controlled system for mechanistic investigation. While the catalyst demonstrates promising performance across a wide range of nitrate concentrations and pH conditions, and achieves nearly complete nitrate removal in simulated low-concentration wastewater, validation using real industrial or agricultural wastewater, along with the conversion of electrochemically produced ammonia into more sustainable solid fertilizers such as ammonium bicarbonate, remains an essential next step toward practical application.

3.3 Operando Mechanism Study

Sufficient hydrogen radicals ($\text{H}^\bullet$) are critical for efficient NO_3RR , since the hydrogenation steps depend directly on proton availability [28]. When tert-butanol (t-BuOH), a specific $\text{H}^\bullet$ scavenger, was introduced to probe the role of hydrogen

radicals, the current density, FE_{NH_3} and NH_3 yield all decreased (Fig. 5(a) and Fig. S24 in the ESM). It confirms that $\text{H}^\bullet$ are indispensable for NO_3RR . The $\text{H}^\bullet$ formation was further quantified by liquid-phase electron paramagnetic resonance (EPR) spectroscopy using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the spin trap. In 1.0 M KOH, nine characteristic peaks with an intensity ratio of 1:1:2:1:2:1:2:1:1 match the DMPO-H adduct (Fig. 5(b)), thus verifying $\text{H}^\bullet$ generation [29]. Moreover, the DMPO-H signal intensities increase in the order $\text{Cu-CF} < \text{CoO/CC} < \text{CoO/Cu-CF}$, indicating that CoO enhances the HER activity to generate H and thereby promotes the hydrogenation of NO_2^* intermediates. Notably, in a 1.0 M KOH electrolyte containing 0.1 M KNO_3 , the DMPO-H signal is almost undetectable for both Cu-CF and CoO/Cu-CF, suggesting rapid $\text{H}^\bullet$ consumption during the electrochemical NO_3RR . The EPR peak intensity of CoO/CC decreases only slightly compared to the KNO_3 -free solution, indicating that CoO is less effective than Cu at converting NO_3^* to NO_2^* and therefore retains a larger pool of $\text{H}^\bullet$ radicals on its surface. By contrast, in the CoO/Cu-CF, the generated and captured $\text{H}^\bullet$ on CoO is rapidly transferred to NO_2^* intermediates on Cu, facilitating its subsequent hydrogenation to NH_3 .

CV curves in 1.0 M KOH were then used to probe the surface adsorbed active hydrogen (H^*) species (Fig. 5(c)) [30]. During the anodic sweep, the H^* oxidation peak intensity follows the order $\text{CoO/Cu-CF} > \text{CoO/CC} > \text{Cu-CF}$. *In situ* Bode plot analysis further confirms that CoO promotes H_2O dissociation and supplies abundant H^* species to drive the hydrogenation of NO_3RR intermediates, while the electron delocalization effect facilitates the rapid consumption of H^* by nitrate, effectively suppressing HER (Figs. S25-26 in the ESM). The kinetic properties on different catalysts were further investigated to elucidate the reaction mechanism, focusing on the rate constants k_1 for the conversion of NO_3^- to NO_2^- , and k_2 for the conversion of NO_2^- to NH_3 [31]. The k_1 value for CoO/Cu-CF was found to be 0.00701 min^{-1} , which is approximately 1.9 times and 4.9 times higher than that of Cu-CF (0.00367 min^{-1}) and CoO/CC (0.00142 min^{-1}), respectively (Fig. S27 in the ESM). The result suggests that electron transfer at the Cu/CoO heterostructure interface enhances the reaction kinetics for the conversion of NO_3^- to NO_2^- . Furthermore, the k_2 value for CoO/Cu-CF is 3.8 times and 1.5 times greater than that of Cu-CF and CoO/CC, respectively. Notably, the k_2 value for CoO/CC exceeds that of Cu-CF, which can be attributed to the enhanced H^* supply capability of CoO that facilitates the conversion of NO_2^- to NH_3 .

In situ attenuated total reflection Fourier transform infrared (ATR-FTIR) measurements were conducted to investigate the mechanism of NO_3RR on CoO/Cu-CF from open circuit potential (OCP) to -0.5 V vs. RHE (Fig. S28 in the ESM). Lowering the potential to -0.1 V generated a pronounced band at 1659 cm^{-1} (H_2O^*) and a concurrent OH^* at 3485 cm^{-1} , confirming that adsorbed water functions as the proton donor in the NO_3RR [32]. As the applied potential was progressively lowered, the intensity of the band associated with surface-adsorbed NO_3^* at 1315 cm^{-1} gradually weakened [33]. This phenomenon arises because higher overpotentials accelerate the reaction kinetics, boosting nitrate consumption, while the rate of

nitrate adsorption lags behind. Furthermore, a new peak at 1410 cm^{-1} attributed to adsorbed NH_3^* gradually emerges and intensifies [34], indicating the conversion of NO_3^- to NH_3 . The appearance of NH_2^* at 2850 and 2915 cm^{-1} , together with the NH_3^* at 1443 cm^{-1} , confirms that NH_3 forms via the stepwise deoxygenation and hydrogenation of NO_3^- by H^* [35]. Notably,

no significant spectral changes are observed upon further lowering the potential, indicating that the CoO/Cu heterojunction provides enough adsorption sites for both nitrate and water, as well as active sites for water splitting hydrogen evolution and the reduction of nitrate to ammonia.

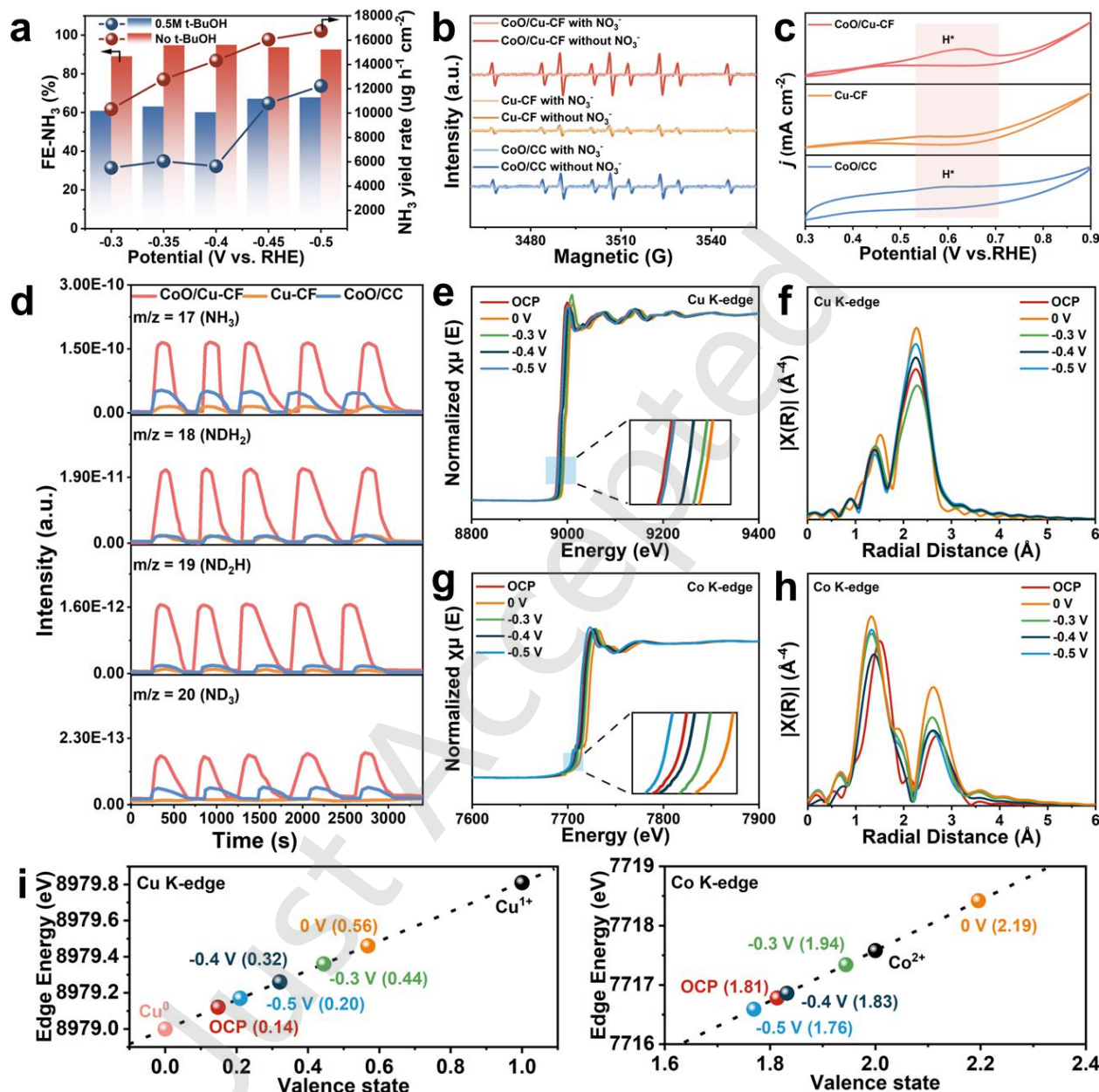


Figure 5 *In situ* characterizations and mechanism study of electrochemical NO_3RR . (a) FE_{NH_3} and NH_3 yield rate of CoO/Cu-CF in 1.0 M KOH + 0.1 M KNO_3 with or without t-BuOH. (b) EPR spectra of all compared samples in 1.0 M KOH with or without NO_3^- . (c) The CV curves of H^* peaks in 1.0 M KOH for all compared samples. (d) Online DEMS of CoO/Cu-CF, Cu-CF and CoO/CC for isotope labeling hydrogen during electrochemical NO_3RR . (e) Normalized *in situ* XANES and (f) FT-EXAFS spectra of Cu K-edge, (g) Normalized *in situ* XANES and (h) FT-EXAFS spectra of Co K-edge for CoO/Cu-CF in 1.0 M KOH + 0.1 M KNO_3 . (i) Corresponding average oxidation state of Cu and Co in the CoO/Cu-CF from *in situ* XANES.

Online differential electrochemical mass spectrometry (DEMS) was employed to detect intermediates and products, thereby revealing the reaction pathway of the NO_3RR . During a 600 s potentiostatic measurement at -0.4 V vs. RHE, CoO/Cu-CF exhibited mass-to-charge (m/z) signals at 16, 17, 30, 31, 32, and 46, corresponding to NH_2 , NH_3 , NO, NOH, NHOH, and NO_2 , respectively (Fig. S29 in the ESM). *In situ* ATR-FTIR spectroscopy and DEMS analyses demonstrate that the NO_3RR

on CoO/Cu-CF proceeds via an initial two-electron reduction of NO_3^- to NO_2^- , followed by a six-electron reduction of NO_2^- to NH_3 . Accordingly, the reaction pathway is proposed as: $\text{NO}_3^* \rightarrow \text{NO}_2^* \rightarrow \text{NO}^* \rightarrow \text{NOH}^* \rightarrow \text{NHOH}^* \rightarrow \text{NH}^* \rightarrow \text{NH}_2^* \rightarrow \text{NH}_3$. To determine the origin of active hydrogen, the catalysts were subjected to electrochemical pretreatment via potentiostatic electrolysis in 1.0 M KOH with D_2O as the solvent for 100 s, enabling the generation and capture of D^* through water

dissociation. Subsequent online DEMS analysis was conducted with an electrolyte composed of 0.1 M KNO_3 and 1.0 M KOH in H_2O . As shown in Fig. 5(d), distinct signals at $m/z = 18$, 19, and 20, corresponding to NDH_2 , ND_2H , and ND_3 , respectively, were observed for the CoO/Cu-CF. The detection of ND_3 for CoO/CF and its absence in Cu/CF confirms that active hydrogen primarily originates from CoO, indicating its transfer to adjacent Cu for nitrate reduction to ammonia. The enhanced NH_3 signal on Cu-CF further indicates that Cu serves as the main active site for nitrate adsorption. Additionally, CoO/Cu-CF consistently shows the highest signals for all ammonia-related products, highlighting the synergistic interaction between CoO and Cu. To elucidate the active phase, *in situ* Raman spectroscopy was performed at potentials ranging from OCP to -0.4 V vs. RHE (Fig. S30 in the ESM). The persistence of the CoO peak at increasingly negative potentials indicates its structural stability during the reduction of NO_3^- [36]. No signals corresponding to copper oxide were detected, suggesting that the catalytically active sites comprise metallic Cu and CoO. Additionally, the peak at 1048 cm^{-1} attributes to the symmetric stretching of NO_3^- , along with the absence of any signals about NO_2^- , implies that NO_2^* intermediates are rapidly converted at the surface of CoO/Cu-CF [31].

ATR-FTIR and Raman spectroscopy can only probe the interaction strength between exogenous species (e.g., reactants, intermediates, and products) adsorbed on the catalyst surface active sites, but they cannot reveal changes in the electronic state or local structure of the metal sites. To more precisely elucidate the relationship between structure and performance of the catalyst, we employed *in situ* XAFS spectroscopy to investigate the structural evolution of CoO/Cu-CF during the NO_3RR . Fig. 5(e) and 5(g) show the Cu K-edge and Co K-edge XANES spectra, respectively, recorded as the potential was stepped down from OCP to -0.5 V. When the potential decreased from OCP to 0 V, both the Cu and Co absorption edges shift to higher energy. The shift is attributed to sluggish reaction kinetics at low overpotentials, namely the limited conversion of surface adsorbed water into H^* on Co impedes timely reduction of NO_3^- adsorbed on Cu. First-derivative analysis of the absorption edge enabled quantification of metal oxidation states at each potential [25,37]. As shown in Fig. 5(i), the average Cu oxidation state rises from $+0.14$ at OCP to $+0.56$ at 0 V in the presence of NO_3^- . In contrast, the average oxidation state of Cu shows only a negligible increase of 0.06 under the same potential window in 1.0 M KOH without NO_3^- (Fig. S31e and Table S5 in the ESM). This comparison confirms that the significant rise in Cu oxidation state primarily originates from NO_3^- adsorption rather than OH^- adsorption or surface reconstruction. It indicates partial electron withdrawal by surface NO_3^- and enhances Cu electron delocalization. Throughout the reduction process, NO_3^- and water molecules repeatedly adsorb, undergo reduction/cleavage, and desorb at Cu/Co sites, accompanied by the formation and rupture of Cu-N/O and Co-N/O bonds. Such dynamic process induces electronic redistribution among Cu, Co, N, and O atoms, further promoting electron delocalization to maintain well activity towards NO_3RR . Upon further lowering the potential to -0.5 V, both Cu and Co absorption edges shifted back toward lower energy, with their oxidation states decreasing to $+0.20$ and $+1.76$, respectively. This is ascribed to the increased

overpotential accelerating water cleavage on Co, thereby generating more H^* to enhance conversion and desorption of NO_3^- . Concurrently, newly adsorbed water molecules and NO_3^- have not yet fully coordinated with Cu/Co, leading to an overall reduction in oxidation state. During the NO_3RR , the oxidation states of both Cu and Co undergo a reversible process of first increasing, then decreasing, and finally almost returning to their initial OCP level to keep the electron delocalization, which enhances the activity and stability of CoO/Cu-CF.

FT-EXAFS fitting of the Cu K-edge reveals that the Cu-O coordination number increases from 1.86 to 2.10 as the potential was lowered from OCP to -0.1 V, while the Cu-Cu coordination number decreases from 4.84 to 4.10, confirming the formation of Cu- NO_3^- bonding (Fig. 5(f) and Fig. S32 and Table S6 in the ESM). Further lowering the potential progressively reduces the adsorbed NO_3^- , resulting in a decreased Cu-O coordination number and an increased Cu-Cu coordination number. The observation suggests that the reduced intermediates do not immediately re-coordinate with newly adsorbed NO_3^- . In the Co K-edge EXAFS spectra, the Co-O peak shifted from $1.50\text{ \AA}$ at OCP to $1.34\text{ \AA}$ (Fig. 5(h)), signaling distortion of the coordination environment due to water molecules adsorption and cleavage [38]. Additionally, both Co-O and Co-Co coordination numbers exhibited an initial increase followed by a decrease (Fig. S33 and Table S7 in the ESM). Such trend likely reflects the sequential dissociation of adsorbed molecules into hydroxyl species, which initially oxidize surface Co to higher valence states and are subsequently converted into water or hydrogen, thereby reducing the cobalt oxide.

3.4 Theoretical Calculations Study

To further comprehend the intricate process of NO_3RR , we performed density functional theory (DFT) calculations on the CoO/Cu-CF system. Based on the above structural analysis results, we used the Cu (111) and CoO (111) planes to construct the CoO/Cu, Cu and CoO models (Fig. S34 in the ESM). As shown in Figs. 6(a) and 6(b), the work functions of Cu and CoO models are respectively found to be 4.416 and 5.919 eV, resulting in a significant 1.503 eV energy gap that promotes electron transfer from Cu to CoO [39]. Such electron transfer induced electron delocalization can optimize the adsorption and activation of reaction intermediates, while the generated built-in electric field supplies sufficient electrons to enhance overall reaction kinetics. Differential charge density analysis in Fig. 6(c) displays interfacial Cu atoms lose electron density while regions adjacent to CoO gain it, further indicating electron donation from Cu to CoO. The d-band density of states (D-band) is illustrated in Fig. 6(d), CoO/Cu, Cu, and CoO models show d-band centers at -2.505 , -2.583 and -1.391 eV, respectively. A d-band center closer to the Fermi level increases the adsorption energy of reaction intermediate, while Sabatier's principle dictates that optimal adsorption strength maximizes catalytic performance [40,41]. Consequently, the intermediate d-band center of CoO/Cu-CF strikes a balanced adsorption-desorption profile, enhancing its electrocatalytic activity. As illustrated in Fig. 6(e), the CoO/Cu model exhibits a water splitting activation energy of 2.41 eV, notably lower than that of Cu model (2.79 eV) and CoO (2.66 eV) model. We further assessed HER activity by calculating the Gibbs free energy of H^* adsorption,

namely ΔG_{H^*} , on CoO/Cu, Cu, and CoO models (Fig. 6(f)). On Cu model, ΔG_{H^*} is -0.15 eV, shifting to -0.30 eV after CoO incorporating. The more negative ΔG_{H^*} indicates enhanced water dissociation during the NO_3RR protonation step and suppression of HER via inhibited H^* dimerization [42], in agreement with EPR and CV measurements.

Building on the mechanistic insights, we simulated the reaction pathways and corresponding ΔG profiles for the optimized adsorption configurations (Fig. 6(g)). The CoO/Cu model not only lowers the barrier for the initial conversion of NO_3^- to NO_3^* but also generates and capture abundant H^* species for subsequent hydrogenation and deoxygenation processes. In the Cu model, the rate-determining step (RDS) is the hydrogenation of NOH^* to NHOH^* ($\Delta G = 1.33$ eV), which reflects its limited capability for surface hydrogenation. In contrast, the CoO/CC model significantly enhances this conversion ($\Delta G = -0.31$ eV), shifting its RDS to the conversion

of NO_3^* to NO_2^* ($\Delta G = 0.86$ eV). Meanwhile, the Cu model readily reduces the energy barrier for NO_3^* conversion to negative values ($\Delta G = -0.34$ eV), identifying the Cu site as the primary active site for NO_3^- reduction. Notably, the CoO/Cu model exhibits low barriers for both NOH^* to NHOH^* ($\Delta G = 0.14$ eV) and NO_3^* to NO_2^* ($\Delta G = -0.37$ eV). This is attributed to the superior activity of CoO in water dissociation, which provides a plentiful supply of H^* . For the CoO/Cu model, the RDS shifts to the conversion of NO^* to NOH^* ($\Delta G = 0.61$ eV), which are 0.72 eV and 0.25 eV lower than the respective barriers for the standalone Cu and CoO/CC models. Therefore, in the CoO/Cu-CF system, the CoO component facilitates water dissociation to generate H^* , while the Cu component plays a crucial role in the hydrogenation of NO_3^- to produce NH_3 . The electron delocalization and built-in electric field within the heterostructure accelerates the reaction kinetic of NO_3RR (Fig. 6(h)).

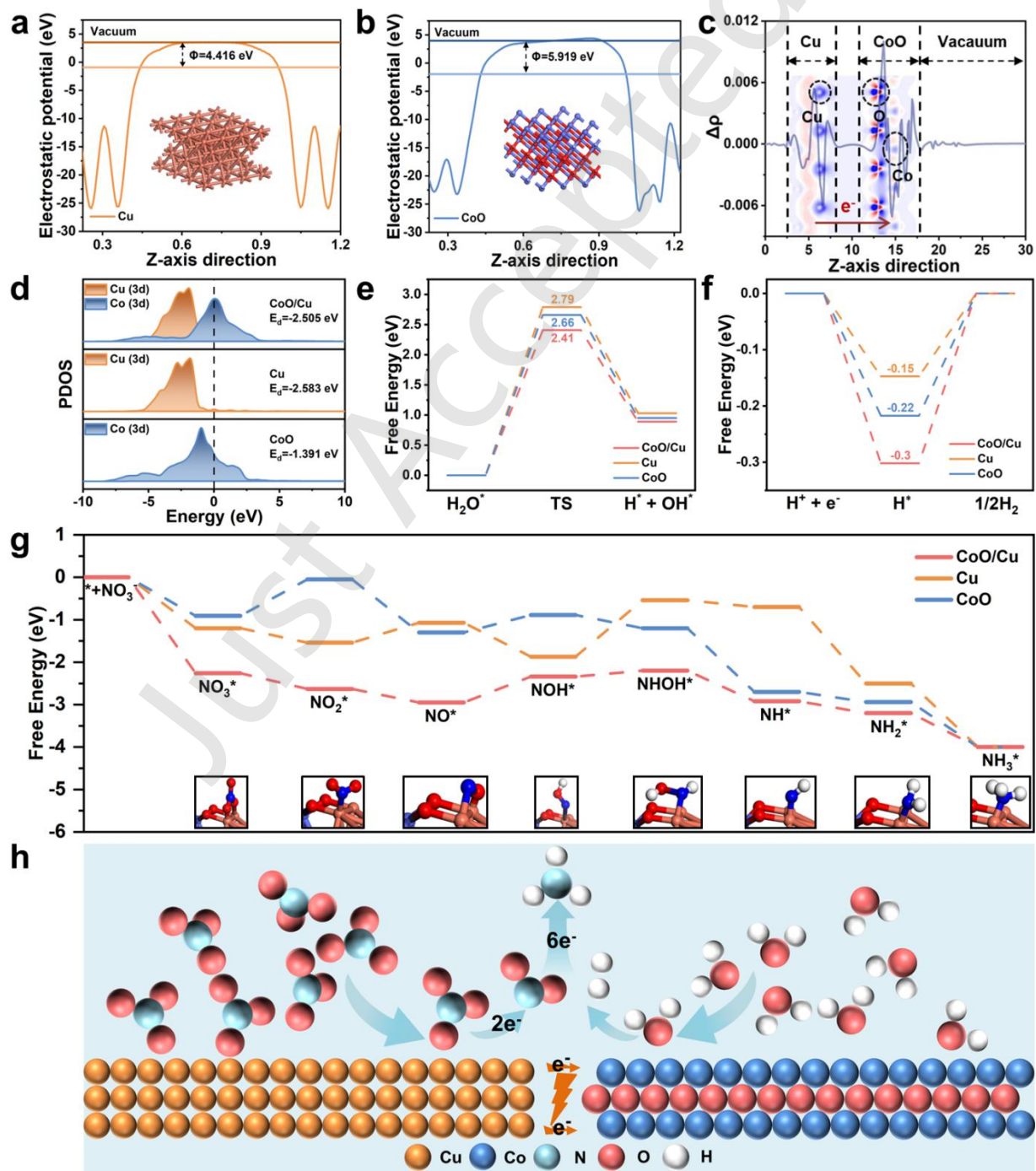


Figure 6 Theoretical insight on electrocatalytic nitrate reduction. Work function of (a) Cu and (b) CoO models. (c) Planar-averaged charge density difference on the Cu-CoO heterointerface as a function of the z-axis. (d) D-band center calculated for various catalysts. Gibbs free energy diagrams of (e) H⁺ generation and (f) NO₃RR processes on CoO/Cu, CoO and Cu models. (g) Schematic illustration of the NO₃RR mechanism on CoO/Cu model.

4 Conclusions

We have developed a CoO/Cu - CF featuring dual-site synergy that significantly accelerates ammonia - generation kinetics. It achieves a FE_{NH₃} of 95% and a high production rate of 14,321 μg h⁻¹ cm⁻² at an overpotential of -0.4 V vs. RHE. It also maintains stable operation for 220 h at an industrial current density of 200 mA cm⁻² in a flow cell for NO₃RR. The NH₄Cl recovered from the post-reaction electrolyte was successfully applied as a nitrogen fertilizer in lettuce cultivation, yielding a 3.1-fold increase in crop biomass and a 1.5-fold improvement in survival rate compared to unfertilized controls. *In situ* XAFS analyses reveal that dynamic modulation of the oxidation states and coordination environments of Cu and Co to keep the electron delocalization under reaction conditions underpins the enhanced activity and durability of CoO/Cu-CF. Complementary *in situ* DEMS coupled with ATR-FTIR shows that electron transfer from Cu to CoO promotes an initial two-electron reduction of NO₃⁻ to NO₂⁻, followed by a six-electron conversion of NO₂⁻ to NH₃. DFT calculations further demonstrate that the induced electron delocalization facilitates the rapid reduction of NO₃⁻ to NO₂⁻ on the Cu, after which H⁺ species generated and captured on CoO drive successive hydrogenation and deoxygenation steps toward NH₃ formation. Our study provides a blueprint for the rational design of dual-site electrocatalysts for efficient nitrate reduction, paving the way toward sustainable, decentralized ammonia synthesis and nutrient recovery from wastewater.

Electronic Supplementary Material: Supplementary material (XAFS measurements, XAFS data processing, TEM images, XPS spectra, XRD patterns, and the relevant test results of CoO/Cu-CF) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909040>.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and the Electronic Supplementary Material. Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Y. Z.: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Writing – original draft. Q. G.: Data curation, Formal analysis, Investigation, Methodology,

Data curation. T. H.: Data curation, Formal analysis, Methodology. B. W.: Investigation, Methodology, Software. Z. L.: Formal analysis, Investigation, Methodology. L. W.: Conceptualization, Formal analysis, Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing.

Use of AI statement

None.

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Electronic Supplementary Material

In situ synchrotron radiation unveils tandem electrocatalytic mechanism in nitrate-to-ammonia conversion enhanced by electron delocalization between cobalt oxide and copper

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Experimental Section

Materials

All chemicals were of reagent grade and used without further purification: Cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, 99%, aladdin), ammonium persulfate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$, 99.9%, aladdin), sodium hydroxide (NaOH, 90%, aladdin), potassium hydroxide (KOH, 90%, aladdin), potassium nitrate (KNO_3 , 99.9%, aladdin), ethanol (> 99.5%, Sinopharm), sulfuric acid (98%, Sinopharm), hydrochloric acid (36%, Tongguang), nessler reagent (99%, pingen technology), potassium sodium tartrate solution (99%, pingen technology).

Characterizations

X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer using $\text{Cu } K_\alpha$ radiation. Scanning electron microscopy (SEM) images were acquired with a Hitachi S-4800 microscope at an accelerating voltage of 15 kV. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and energy-dispersive X-ray spectroscopy (EDS) elemental mapping images were obtained on a JEOL JEM-2100 microscope operating at 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG ESCALAB MK II system with $\text{Mg } K_\alpha$ radiation (1253.6 eV), and all binding energies were calibrated to the C 1s peak at 284.6 eV. X-ray absorption fine structure (XAFS) measurements were performed at the BL14W1 beamline of the Shanghai Synchrotron Radiation Facility (SSRF), China, utilizing a Si (111) double-crystal monochromator via transmission mode.

Electron Paramagnetic Resonance (EPR) Experiments

Electron paramagnetic resonance (EPR) measurements were performed on a Bruker EMXplus spectrometer. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) was employed as a spin-trap to capture the transient hydrogen radical ($\cdot\text{H}$), forming the DMPO-H adduct for EPR detection. During the test, 0.1 mL of electrolyte was mixed with 100 μL of DMPO and deoxygenated by bubbling with argon. Constant-current electrolysis was then carried out for 10 min in an H-type cell under an argon atmosphere.

In Situ Raman Spectroscopy Experiments

The CoO/Cu-CF measuring 1 cm by 1 cm served as the substrate for the working electrode, while Pt wire and Ag/AgCl were employed as the counter and reference electrodes, respectively. The time-dependent Raman spectroscopy measurement towards electrocatalysis process were under programmed applied potentials in 0.1 M KNO_3 +1.0 M KOH. The electrocatalyst is held for 300 s at the applied potential to reach steady state conditions before recording each spectrum. Each spectrum was acquired over 15 sweeps, spanning the range of 175 to 1900 cm^{-1} .

In Situ Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) Experiments

In situ attenuated total reflection Fourier transform infrared (ATR-FTIR) spectra were recorded on a PE Spectrum One B spectrometer using KBr - pellet samples. The light source was operated at a beam current above 400 mA, and each spectrum was obtained by averaging 128 scans at a resolution of 4 cm^{-1} . Prior to data acquisition, a background spectrum of the catalyst-coated electrode was collected at open-circuit potential (OCP). The instrument software automatically subtracted this OCP background from the measured spectra.

Online Differential Electrochemical Mass Spectrometry (DEMS) Experiments

Online differential electrochemical mass spectrometry (DEMS) measurements were carried out on a Shanghai LingLu QAS100. Mass signals were recorded over 600 s at -0.4 V vs. RHE in an argon-saturated aqueous solution of 1.0 M KOH + 0.1 M KNO_3 . A custom-built electrochemical cell was used, with CoO/Cu-CF as the working electrode, a Pt

wire as the counter electrode, and a Hg/HgO electrode as the reference. A polytetrafluoroethylene membrane separated the gas phase from the liquid electrolyte.

In Situ XAFS measurements

A catalyst CoO/Cu-CF was used as the working electrode, graphite rod as the counter electrode and Ag/AgCl electrode as the reference electrode. An organic glass electrochemical cell was employed for the in-situ experiments. The working cell has flat walls with a single circular hole of 1.5 cm in diameter. The solution was poured into the cell. The solutions were not stirred during the experiment. The cell was connected to an electrochemical station by making electrical contact with the copper tape slip that protruded from the side of the working cell. An organic glass cap fitted with a reference electrode was used to cover the cell and to ensure a fixed distance between the working and reference electrodes for all experiments. The XAFS spectra were recorded at different positions on the electrode to check the homogeneity of the catalyst.

Product Detection

Ammonia concentrations were determined by ultraviolet-visible (UV-Vis) spectroscopy spectrophotometric colorimetry using Nessler's reagent. The sample was diluted to a final volume of 5.0 mL to fall within the instrument's detection range. A 0.1 mL aliquot of potassium sodium tartrate solution (500 mg·mL⁻¹) was added and mixed thoroughly, followed by 0.15 mL of Nessler's reagent. After a 20 min incubation at room temperature, the absorbance was measured at 420 nm. Ammonia concentrations were then determined from a calibration curve prepared with standard NH₄Cl solution.

Nitrate concentrations were also measured by UV-Vis spectroscopy. Samples were collected and diluted to fall within the instrument's detection range. Before test, 0.1 mL of 1.0 M hydrochloric acid and 0.01 mL of 0.8 wt% sulfamic acid solution were added to 5.0 mL of diluted sample. After 30 min placing at room temperature, absorption intensities at 220 nm and 275 nm were recorded. Absorbance (A) was then calculated using the following equation:

$$A = A_{220\text{nm}} - A_{275\text{nm}} \quad (2)$$

A calibration curve was established using standard potassium nitrate solutions spanning the analytical range, establishing a linear relationship between absorbance and nitrate concentration for sample quantification.

Nitrite concentrations were measured by UV-Vis spectroscopy after colorimetric derivatization. The reagent was prepared by dissolving 4.0 g p-aminobenzenesulfonamide and 0.20 g N-(1-naphthyl)ethylenediamine dihydrochloride in 50 mL ultrapure water, then adding 10 mL phosphoric acid ($\rho = 1.70 \text{ g}\cdot\text{mL}^{-1}$). Sample aliquots were diluted to 5.00 mL to fall within the detection range, and 0.10 mL of the color reagent was added. After homogenization and a 20 min reaction at room temperature, the absorbance at 540 nm was recorded. A calibration curve prepared from standard sodium nitrite solutions enabled calculation of nitrite concentrations in the samples.

Electrochemical NO₃RR Performance Indicators

The Faradaic efficiency (FE) for ammonia production, the energy efficiency (EE) of the flow - cell reactor, and the ammonia yield rate (Y_{NH_3}) were calculated as follows:

$$\text{FE} = \frac{n \times c \times V \times F \times 10^{-6}}{M_{\text{N}} \times Q} \quad (3)$$

$$\text{EE} = \frac{1.23 - U_0}{1.23 - U} \times \text{FE} \quad (4)$$

$$Y_{\text{NH}_3} = \frac{c \times V \times M_{\text{NH}_3} \times 10^{-6}}{t \times A \times M_{\text{N}}} \quad (5)$$

where n is the electron transfer number of the reaction to form ammonia ($n = 8$ for NO₃RR); c is the concentration of the product (ug mL⁻¹); M_{N} is 14; M_{NH_3} is 17; t is the reaction time (h); A is area of working electrode (cm²); F is the Faraday constant ($F = 96485 \text{ C mol}^{-1}$); V is the volume of cathode electrolyte in H-cell reactor (mL); Q is the total consumed amount of charge (C); U is the voltage of the reactor and U_0 is the theoretical voltage (V).

Computational Methods

Density functional theory (DFT) calculations were carried out with the Cambridge Sequential Total Energy Package (CASTEP) module in Materials Studio. Electronic exchange and correlation effects were described by the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA). The CoO(111) and Cu(111) surfaces were each represented by a four-layer slab in a $3 \times 3 \times 1$ supercell, separated by a vacuum region exceeding 15 Å. The bottom two layers were fixed to their bulk positions, while the top two layers were relaxed. The Cu/CoO interface was constructed by joining the Cu(111) and CoO(111) slabs. Mulliken population analysis was performed, and a plane-wave cutoff energy of 400 eV was used. Brillouin zone integration employed a $2 \times 3 \times 6$ Monkhorst–Pack k-point mesh. Geometry optimizations proceeded until the total energy change was below $1 \times 10^{-5} \text{ eV}$ and the residual forces on all atoms were under 0.03 eV Å^{-1} .

The Gibbs free energy (ΔG) can be expressed as following equation:

$$\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S \quad (6)$$

where ΔE is the reaction energy calculated by the DFT methods. ΔZPE and $T\Delta S$ are the thermodynamic corrections of

zero-point-energy (ZPE) and entropy (S) derived from the vibrational partitions function at 298.15 K, respectively. As the entropy of hydrogen in the absorbed state is negligible, ΔS can be calculated as $-1/2S_0 \text{ H}_2$. Therefore, the Gibbs free energy of H^* can be calculated as follows:

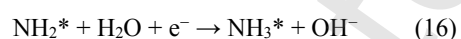
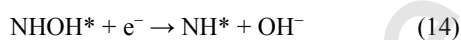
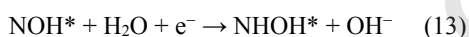
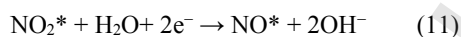
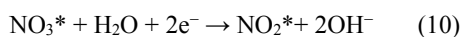
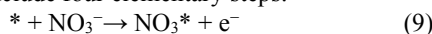
$$\Delta G_{\text{H}^*} = \Delta E_{\text{H}^*} + 0.24 \text{ eV} \quad (7)$$

The adsorption energy ($E_{\text{adsorbate}}$) of an adsorbate on a catalyst surface was calculated using the following equation:

$$\Delta E = E_{\text{total}} - E_{\text{surface}} - E_{\text{adsorbate}} \quad (8)$$

where E_{total} , E_{surface} , and $E_{\text{adsorbate}}$ are the total energy of the adsorption state system, the total energy of the pure surface, and the total adsorption energy of intermediate, respectively.

The NO_3RR process could occur include four elementary steps:



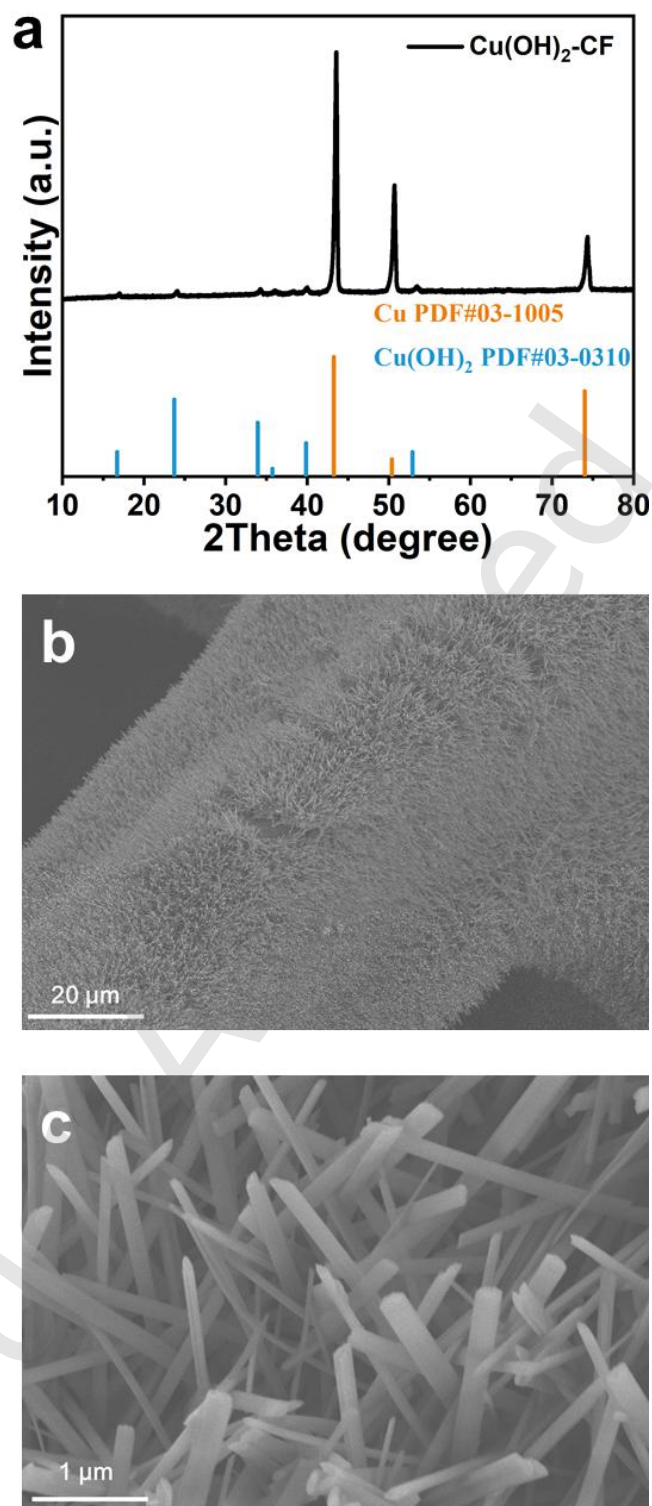


Figure S1. (a) XRD pattern and (b, c) SEM images of Cu(OH)₂-CF.

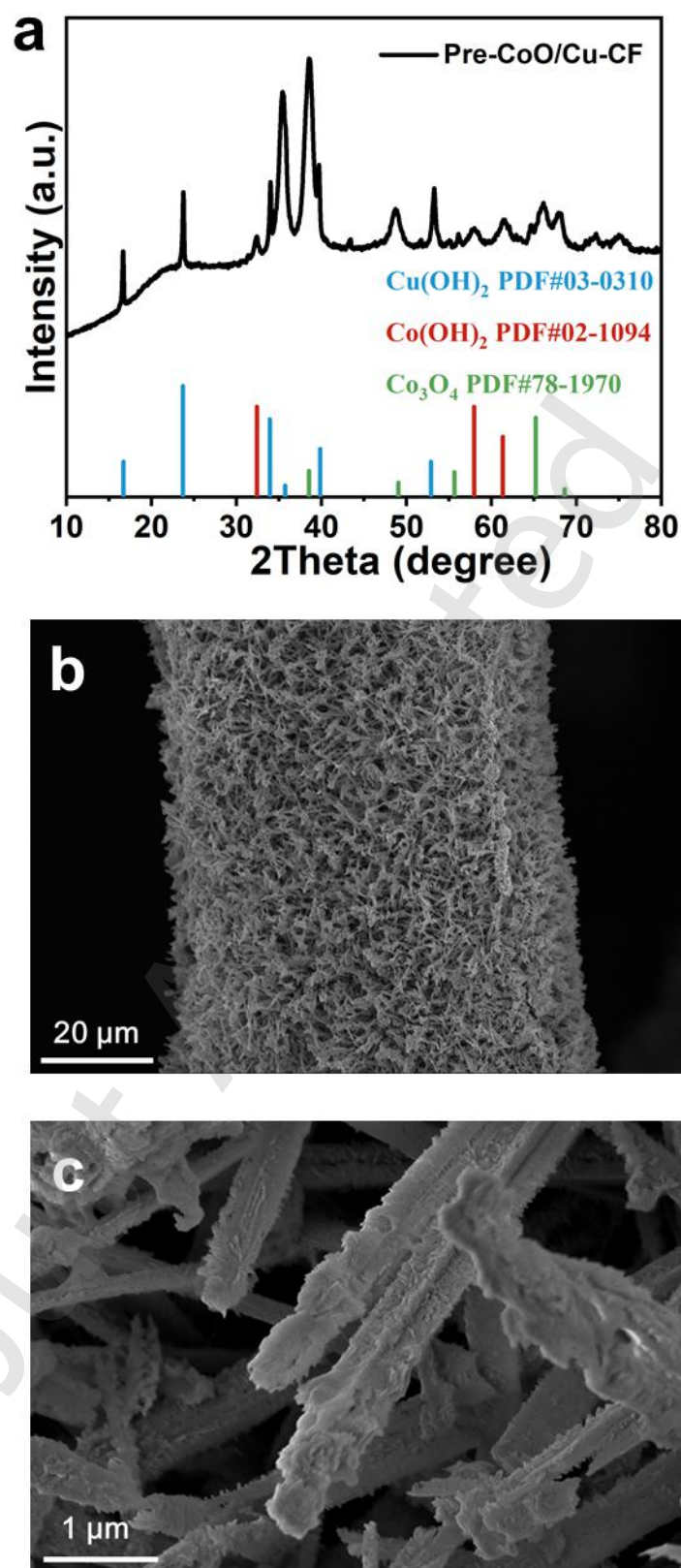


Figure S2. (a) XRD pattern and (b, c) SEM images of pre-CoO/Cu-CF.

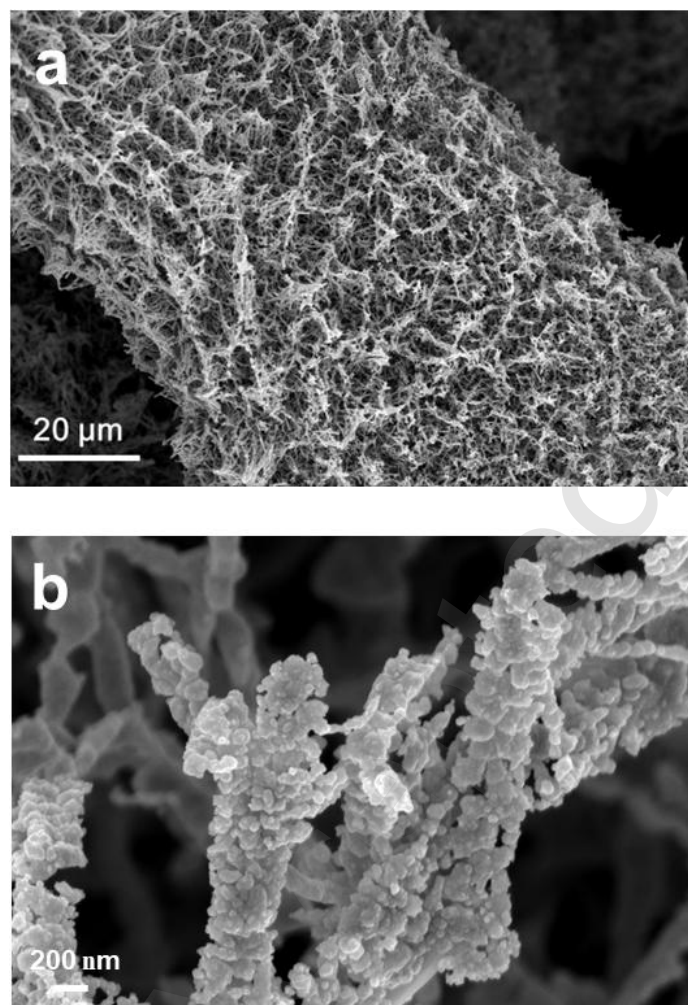


Figure S3. SEM images of CoO/Cu-CF.

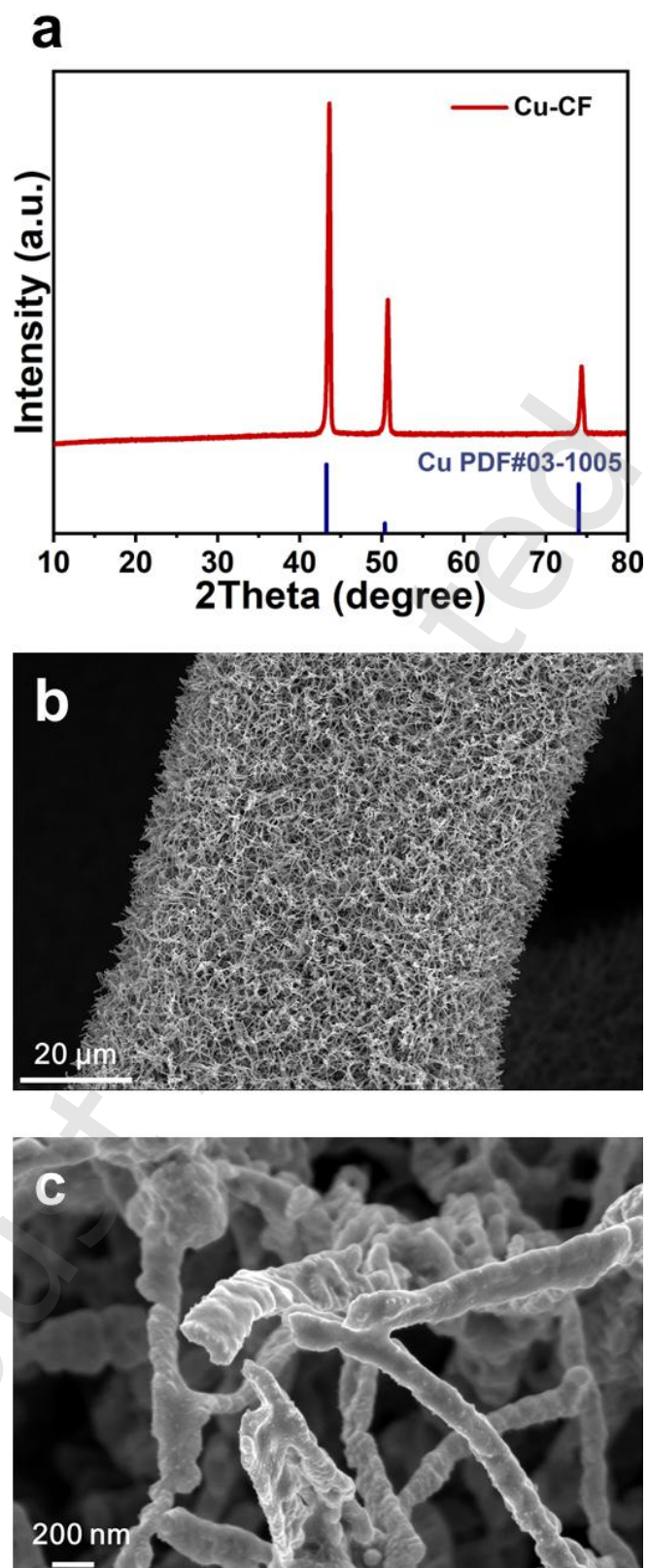


Figure S4. (a) XRD pattern and (b, c) SEM images of Cu-CF.

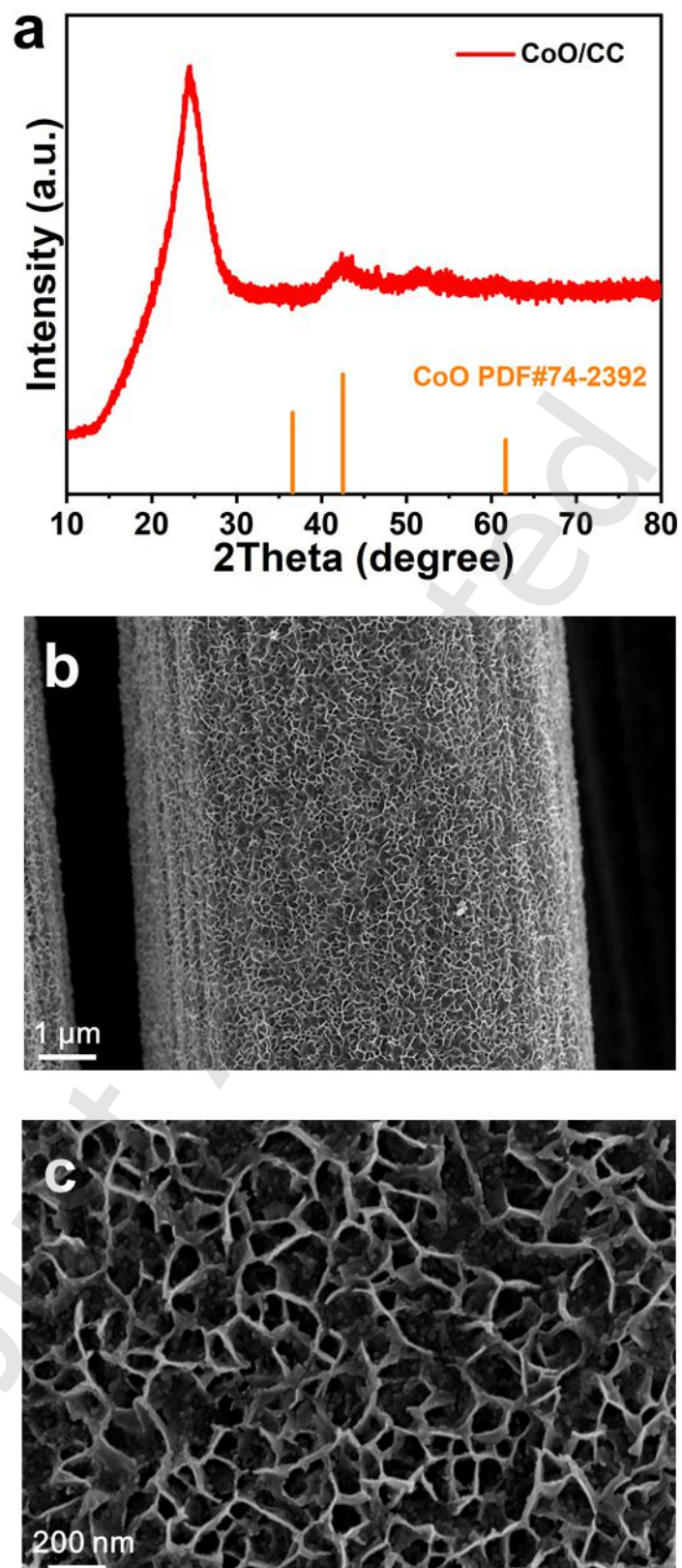


Figure S5. (a) XRD pattern and (b, c) SEM images of CoO/CC.

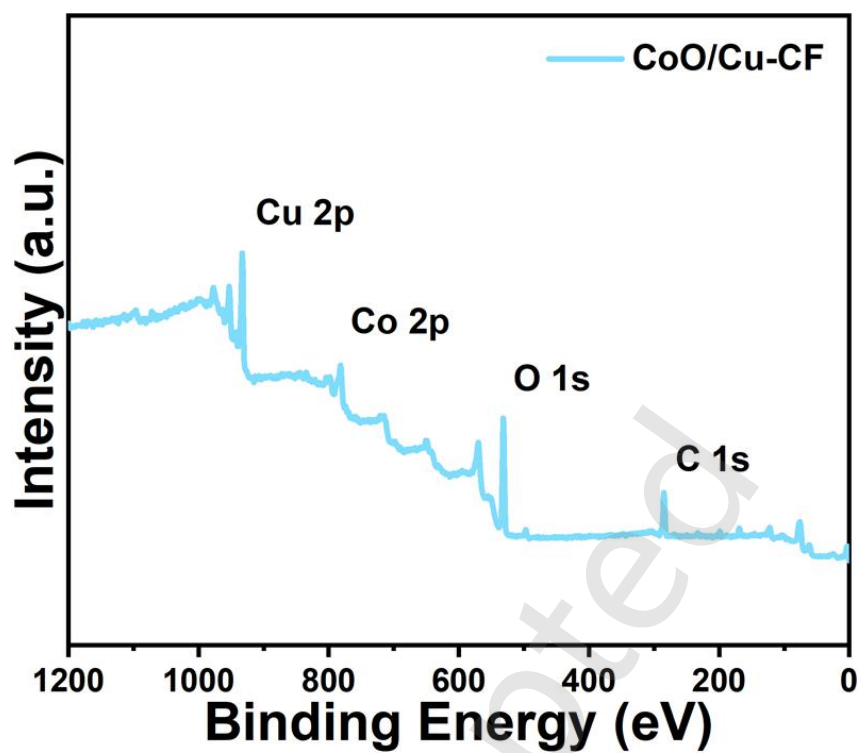


Figure S6. XPS survey spectrum of CoO/Cu-CF.

The XPS survey spectrum of CoO/Cu-CF is displayed in Figure S6, indicating that the elemental compositions of Cu, Co, and O elements are approximately 62.4 wt%, 33.1 wt%, and 4.5 wt%, respectively.

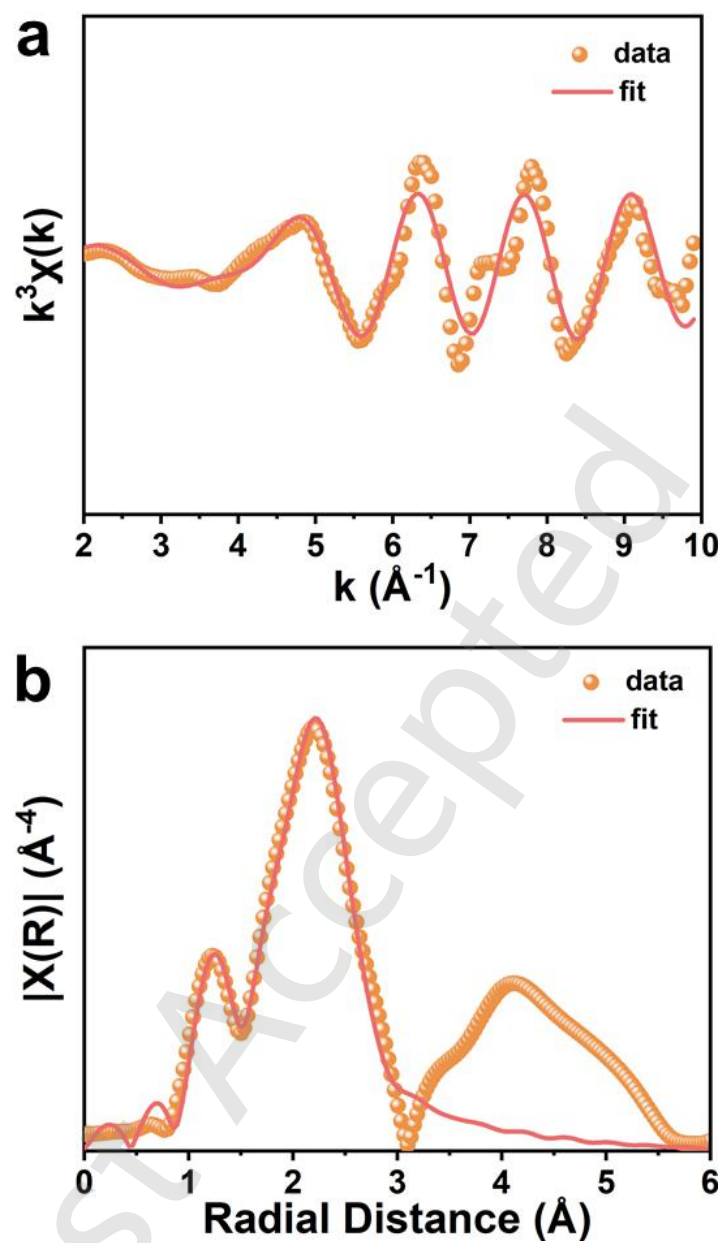


Figure S7. (a) k_3 -weight FT-EXAFS fitting curves of Cu K-edge for CoO/Cu-CF at k -space. (b) k_3 -weight FT-EXAFS fitting curves of Cu K-edge for CoO/Cu-CF at R -space.

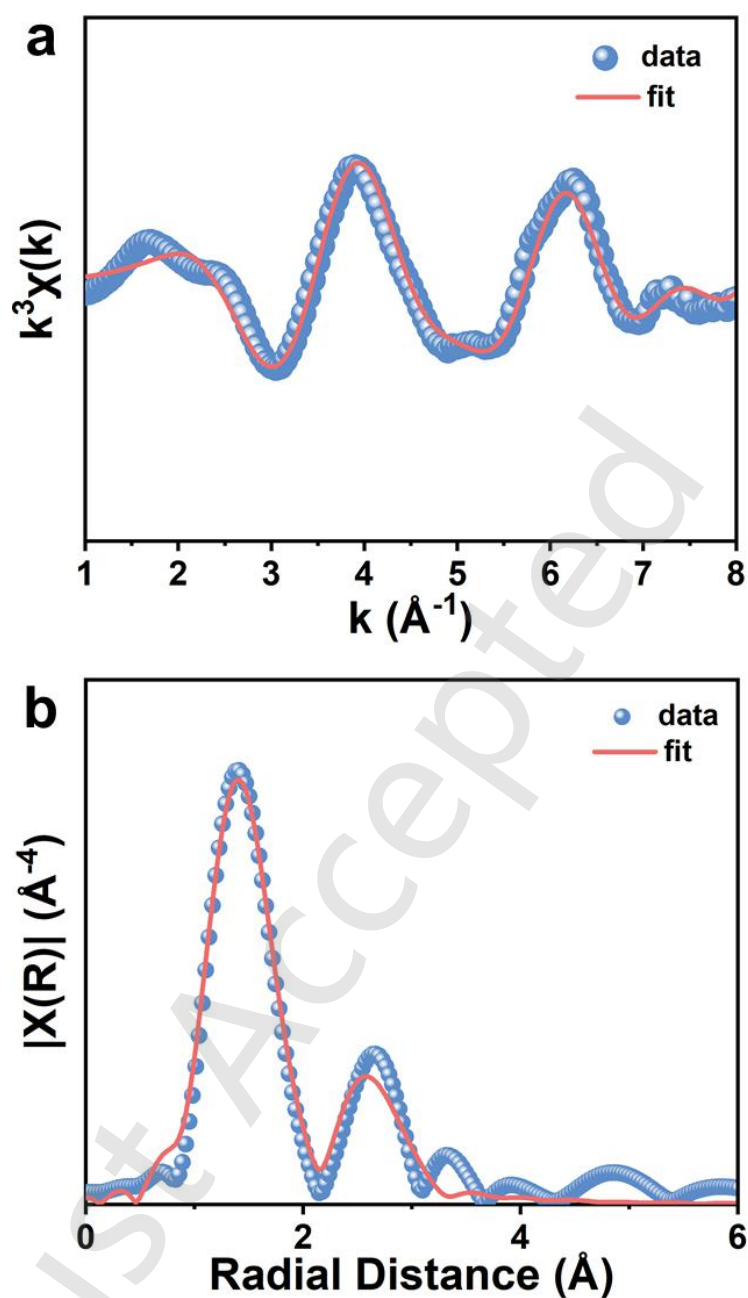


Figure S8. (a) k_3 -weight FT-EXAFS fitting curves of Co K-edge for CoO/Cu-CF at k -space. (b) k_3 -weight FT-EXAFS fitting curves of Co K-edge for CoO/Cu-CF at R -space.

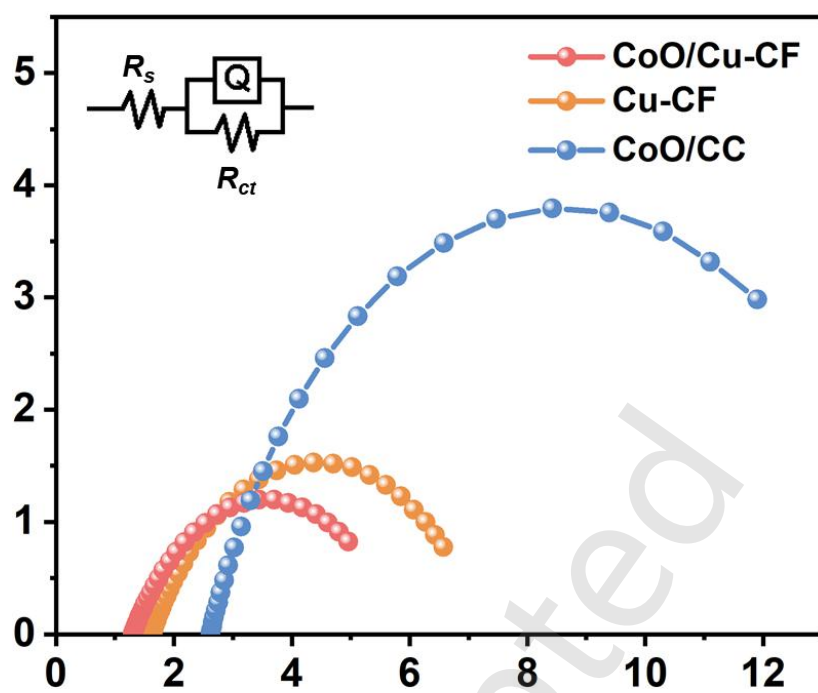


Figure S9. Nyquist plots of all compared samples at -0.4 V vs. RHE.

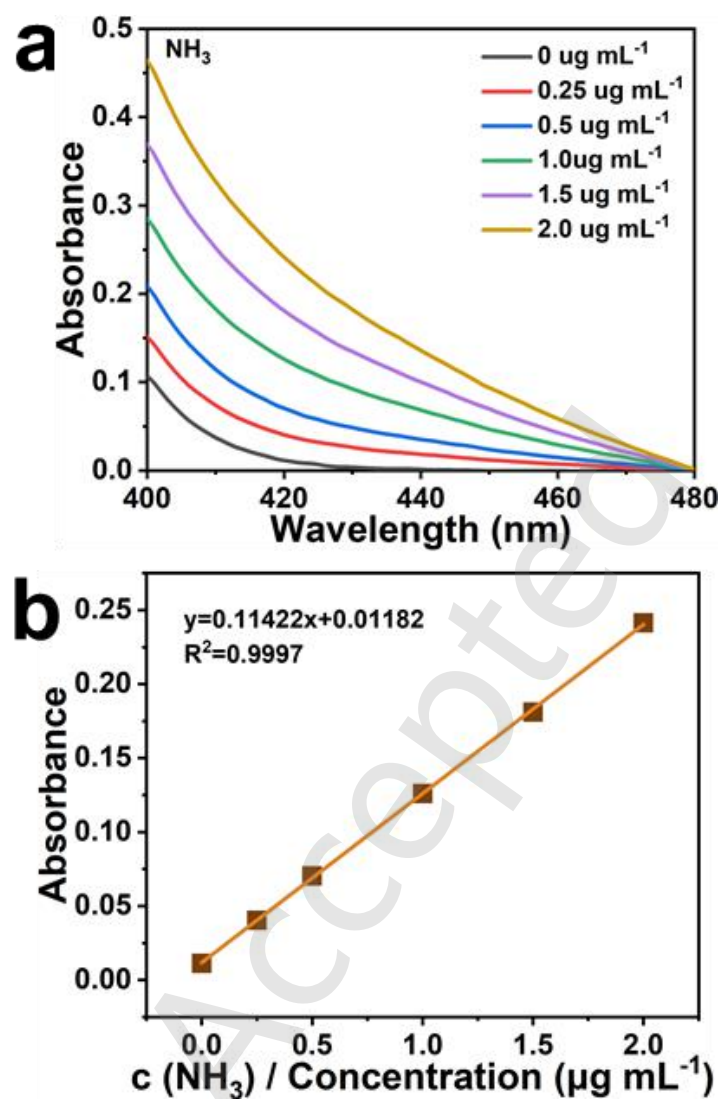


Figure S10. Determination of NH_3 . (a) UV-vis spectra and (b) concentration versus absorbance curve of NH_3 solution with a series of standard concentrations

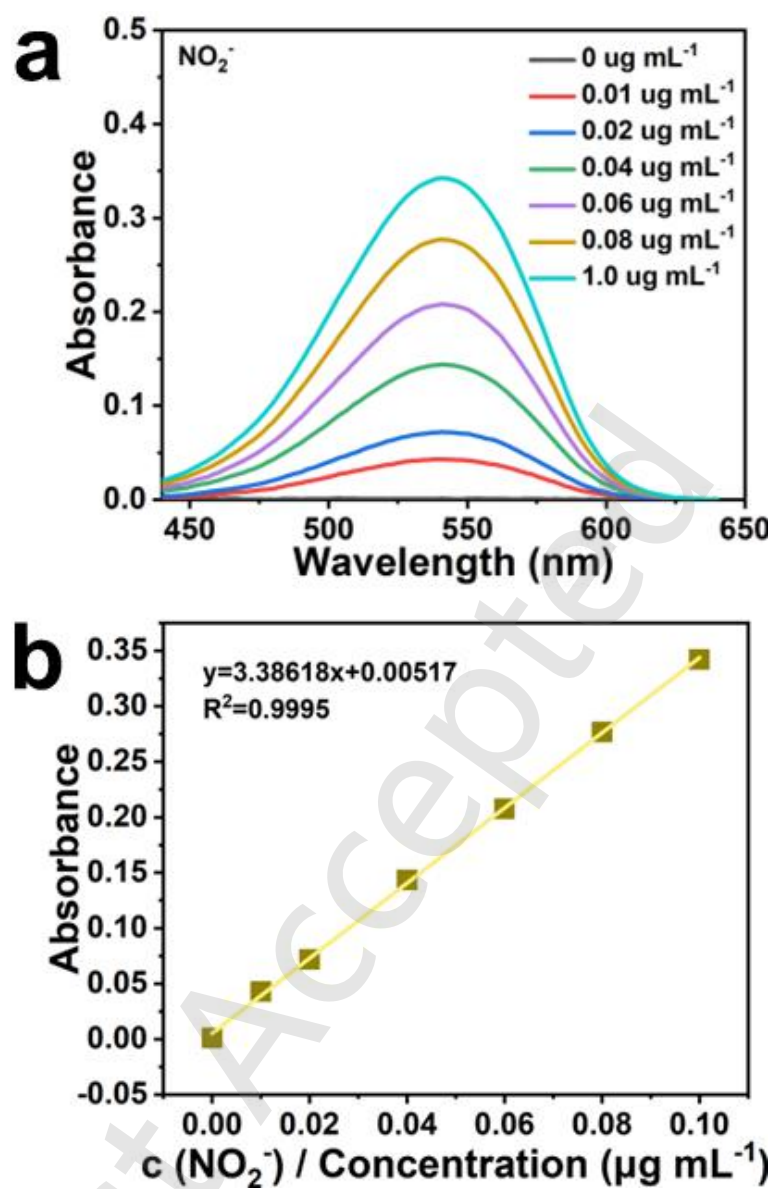


Figure S11. Determination of NO_2^- . (a) UV-vis spectra and (b) concentration versus absorbance curve of NO_2^- solution with a series of standard concentrations.

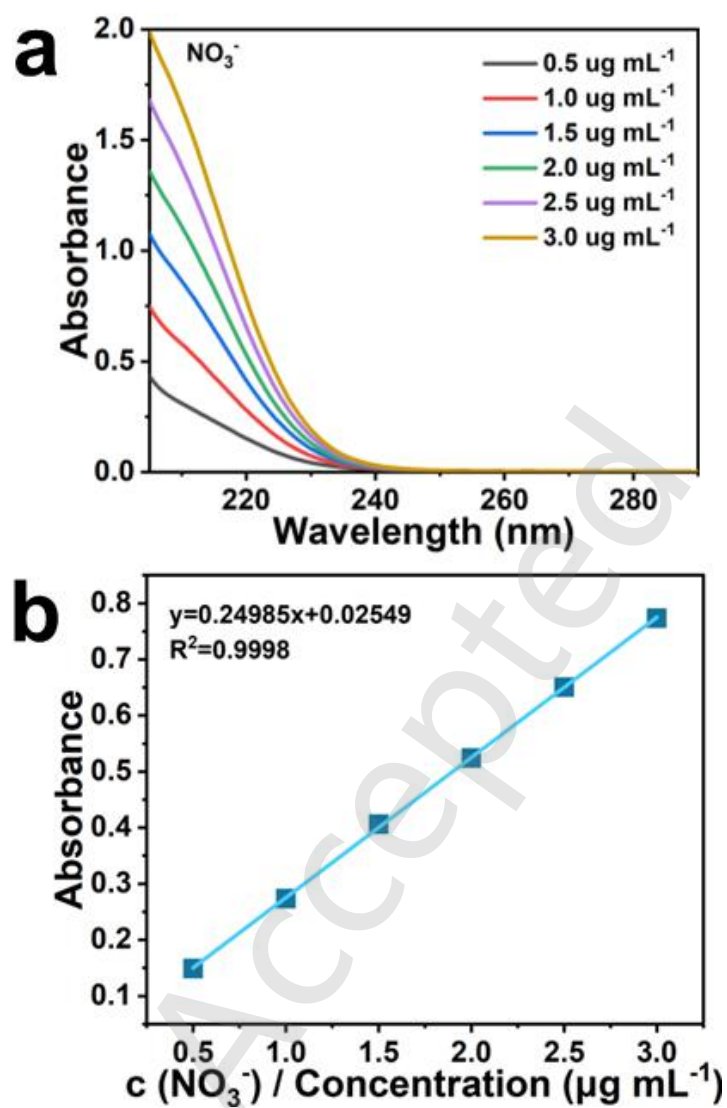


Figure S12. Determination of NO_3^- . (a) UV-vis spectra and (b) concentration versus absorbance curve of NO_3^- solution with a series of standard concentrations.

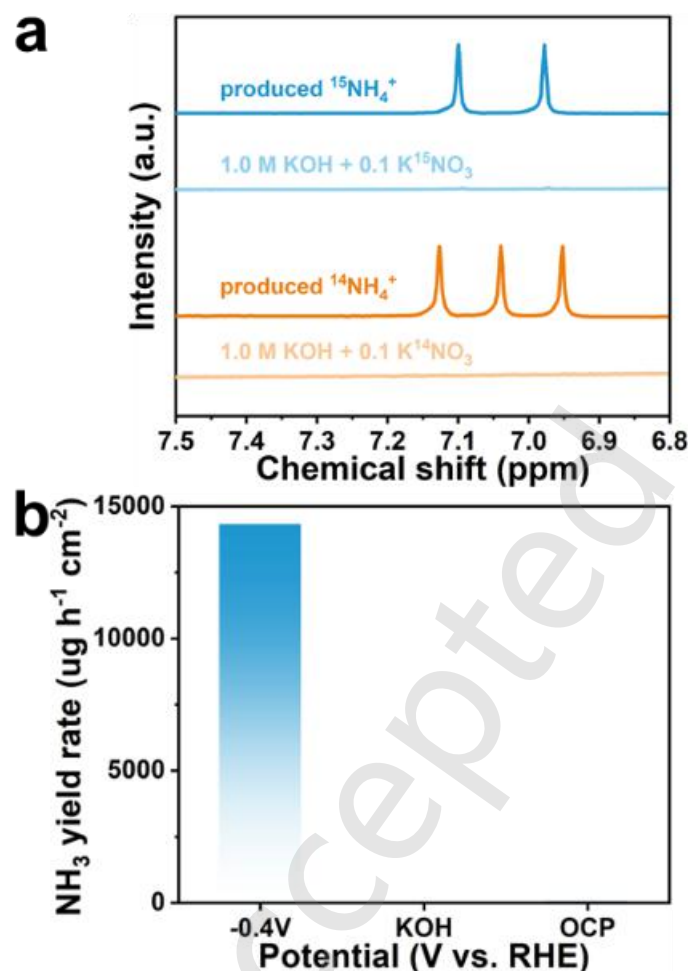


Figure S13. (a) ^1H NMR spectra of the electrolyte before/after NO_3RR at -0.4 V vs. RHE using $^{15}\text{NO}_3^-$ or $^{14}\text{NO}_3^-$ as the feedstock. (b) Control condition test of NO_3RR .

To confirm the nitrogen source of the produced ammonia, the isotope labeling experiments using K^{15}NO_3 and K^{14}NO_3 as parallel nitrogen sources have been supplemented. As shown in Fig. S13a, after electrolysis, the ^1H NMR spectrum displays a characteristic doublet for $^{15}\text{NH}_4^+$ and a triplet for $^{14}\text{NH}_4^+$, corresponding to the respective nitrogen sources. Furthermore, control experiments conducted at -0.4 V vs. RHE in NO_3^- -free 1.0 M KOH, or at OCP in 1.0 M KOH containing 0.1 M KNO_3 , yielded negligible ammonia (Fig. S13b). Since the post-reaction solution is acidified prior to NMR measurement, the detected species corresponds to $^{15}\text{NH}_4^+$ and $^{14}\text{NH}_4^+$ rather than $^{15}\text{NH}_3$ and $^{14}\text{NH}_3$. These results conclusively demonstrate that the detected ammonia originates solely from the electroreduction of nitrate in the electrolyte, ruling out contributions from the catalyst, nitrogen-containing impurities, or environmental N_2/NH_3 contamination.

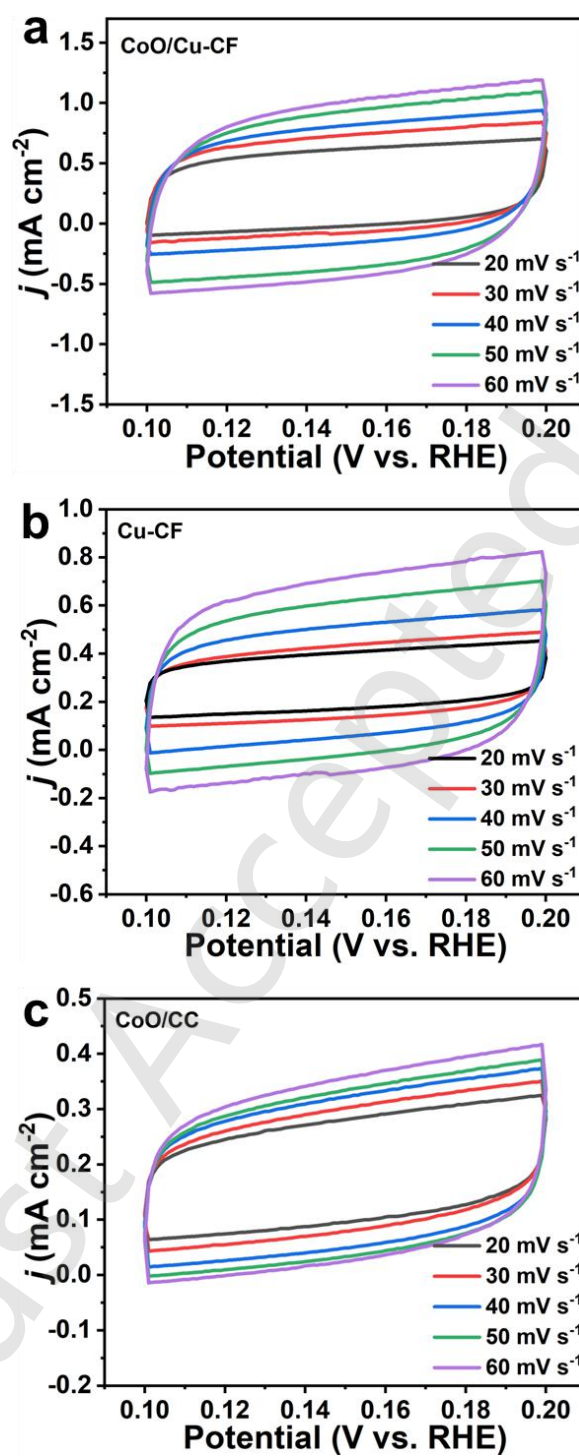


Figure S14. CV curves of (a) CoO/Cu-CF, (b) Cu-CF, and (c) CoO/CC at different scan rates from 20 to 60 mV s⁻¹.

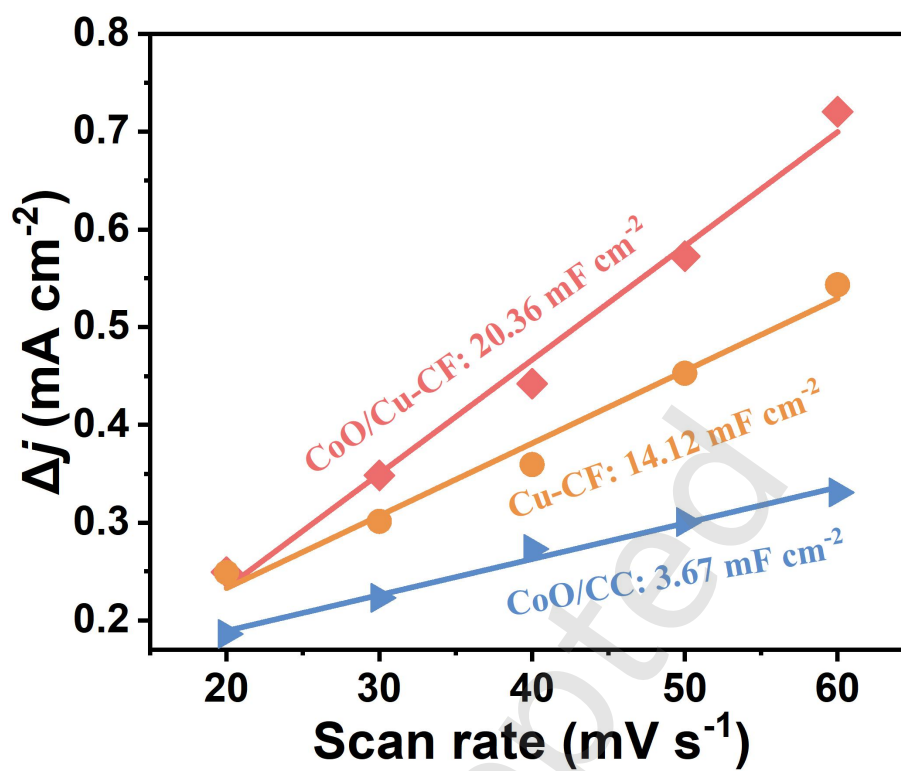


Figure S15. Calculated C_{dl} values of CoO/Cu-CF, Cu-CF and CoO/CC derived from Figure S14.

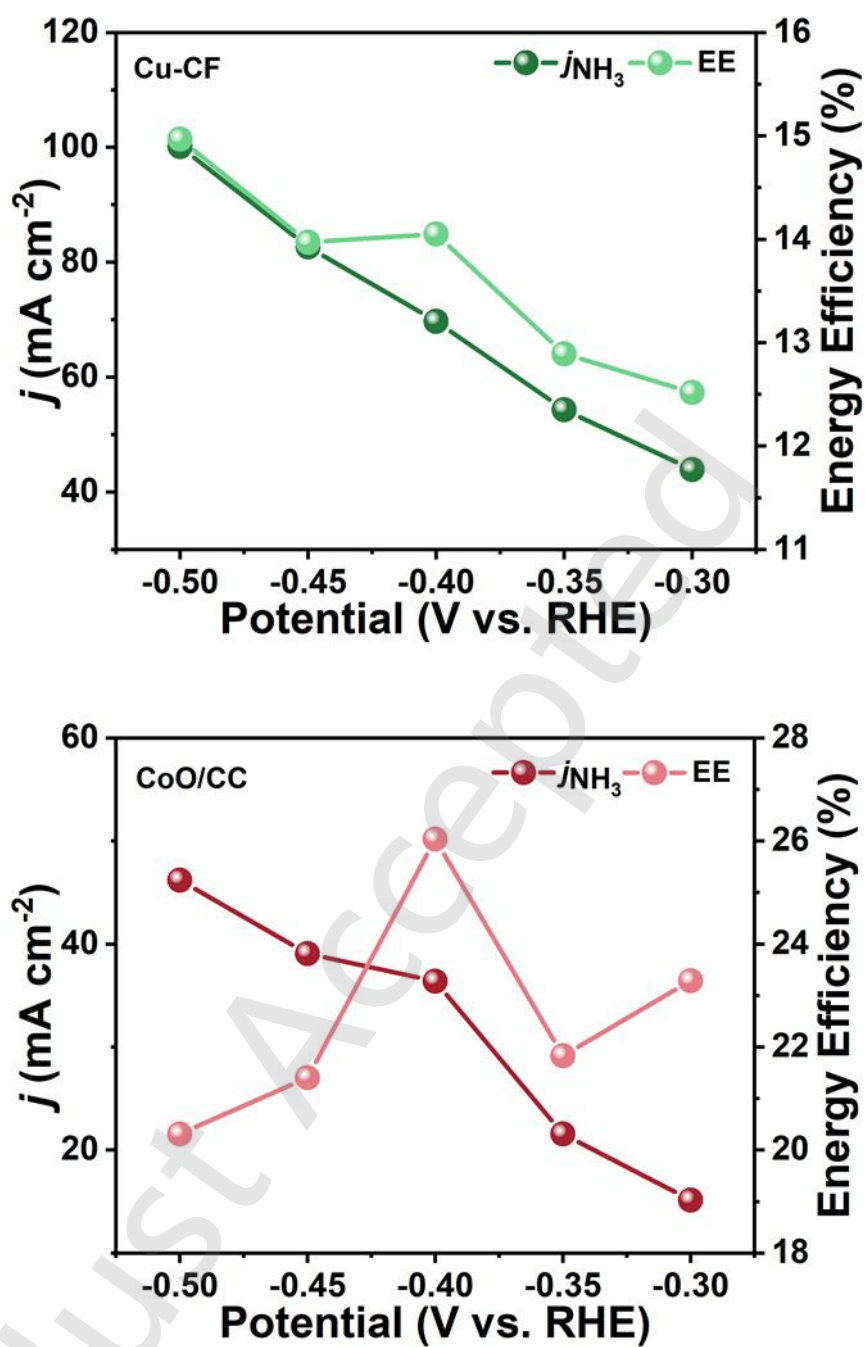


Figure S16. EE and j_{NH_3} of Cu-CF and CoO/CC under different potentials.

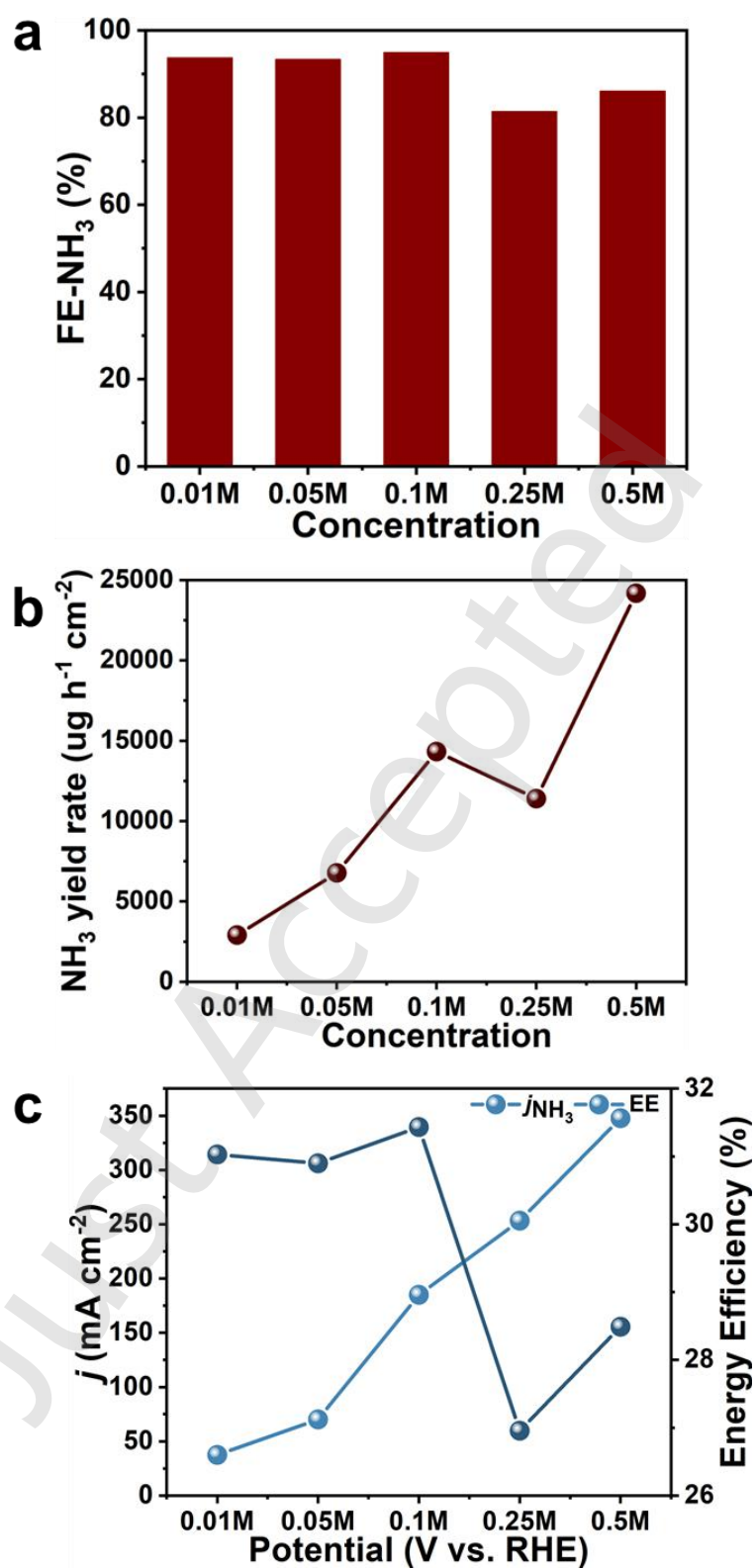


Figure S17. (a) NH₃ FE, (b) yield rate and (c) EE and j_{NH_3} of CoO/Cu-CF at -0.4 V vs. RHE in difference NO₃⁻ concentrations.

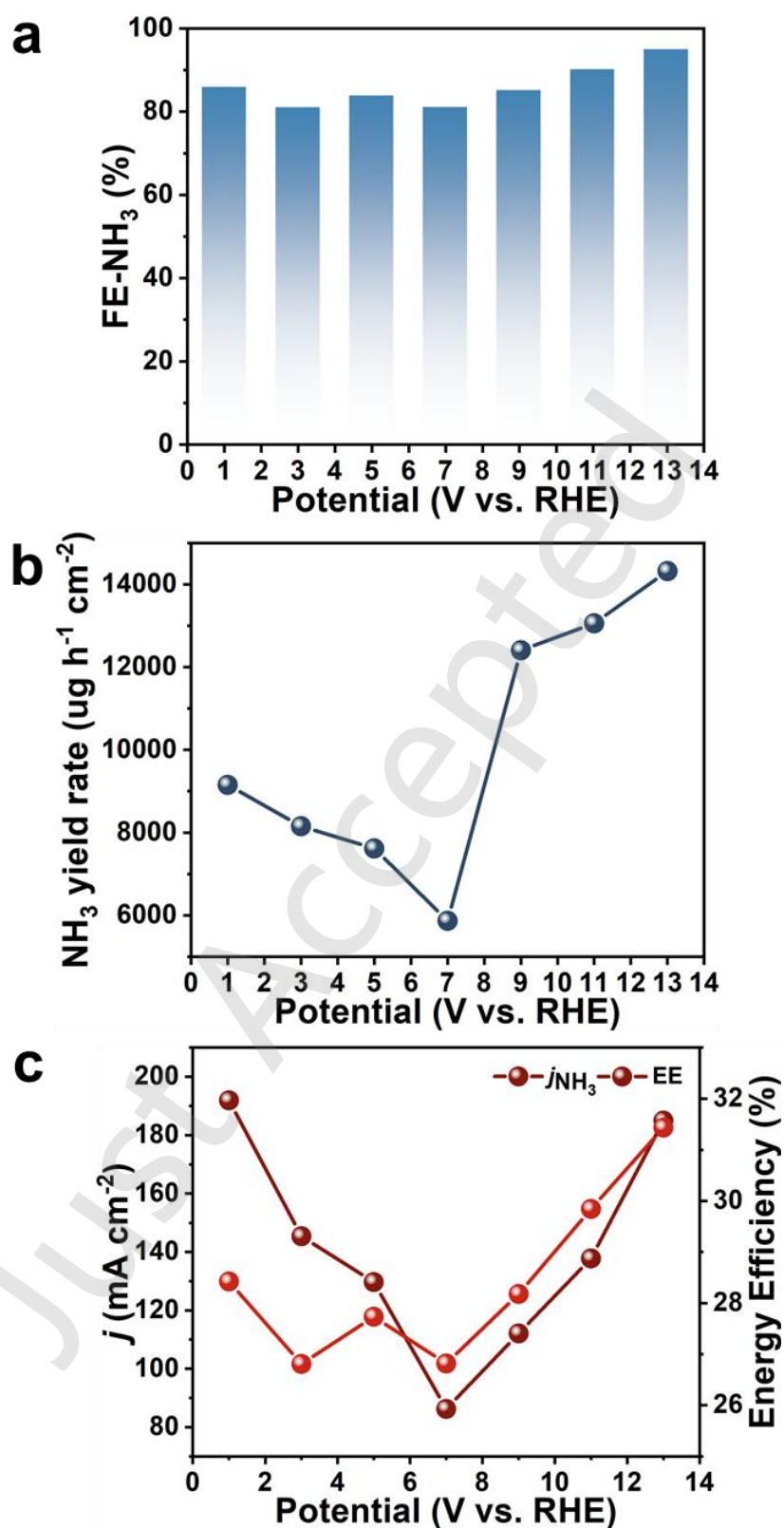


Figure S18. (a) NH₃ FE, (b) yield rate and (c) EE and j_{NH_3} of CoO/Cu-CF at -0.4 V vs. RHE in difference initial pH value.

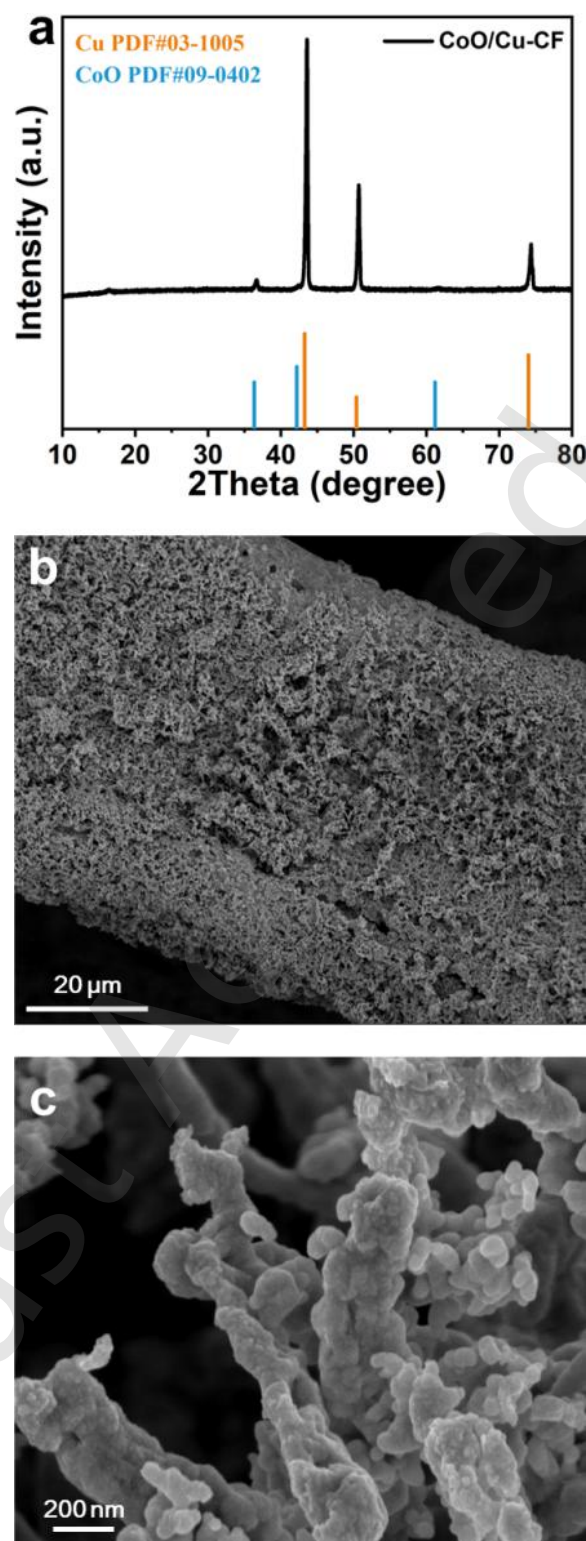


Figure S19. (a) XRD pattern and (b, c) SEM images of post-reaction CoO/Cu-CF.

The XRD pattern in Fig. S19a retains characteristic diffraction peaks of both Cu and CoO with no other new additional phases detected. Furthermore, the SEM image in Fig. (S19(b, c)) show that the well one-dimensional nanorods structure of CoO/Cu-CF after reaction.

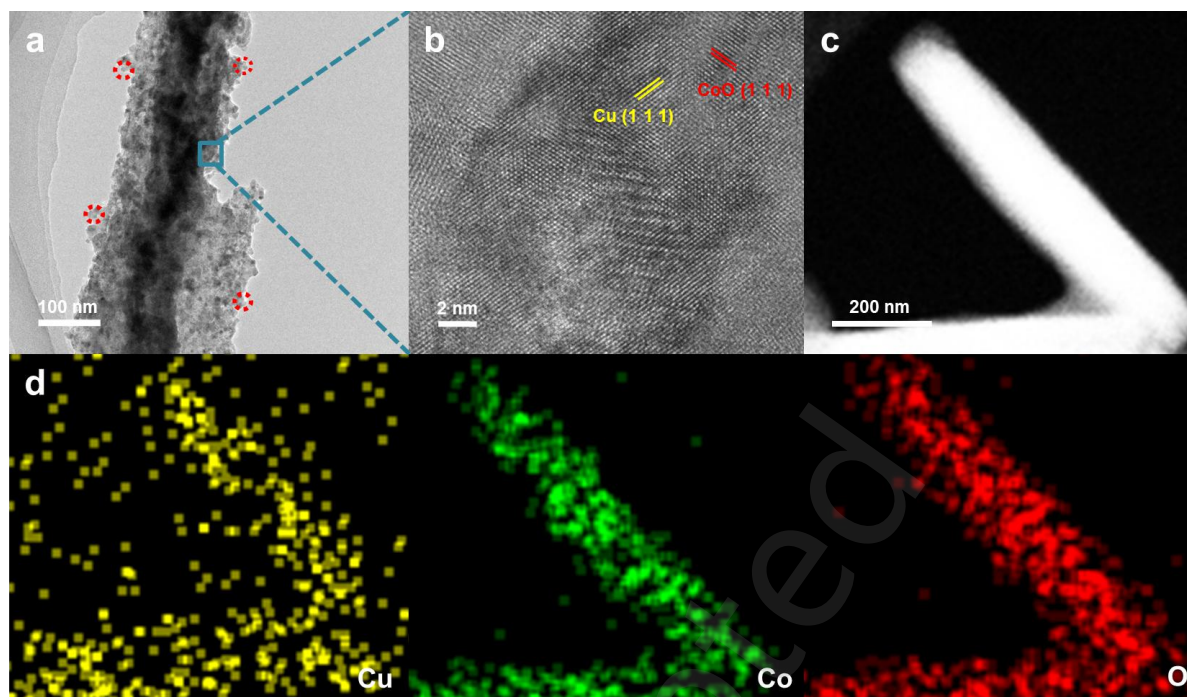


Figure S20. (a) TEM, (b) HRTEM and (c,d) EDS element mapping images of post-reaction CoO/Cu-CF.

TEM image reveals that CoO clusters/nanoparticles remain uniformly distributed on the Cu nanowire surface after the reaction (Fig. S20a). Correspondingly, HRTEM (Fig. S20b) resolves distinct lattice fringes corresponding to the Cu (111) and CoO (111) planes, while elemental mapping shows the uniform distribution of Cu, Co, and O. These results collectively confirm the preservation of the CoO/Cu heterostructure.

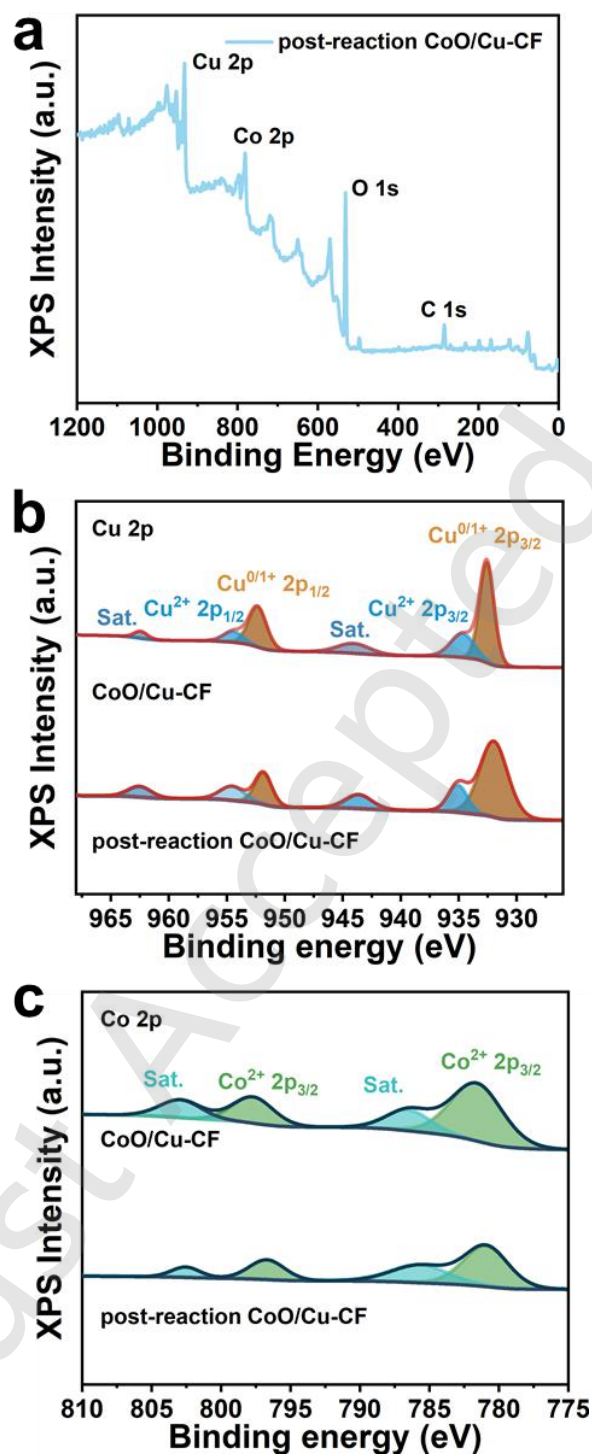


Figure S21. (a) XPS spectra of wide spectra of post-reaction CoO/Cu-CF. (b) Cu 2p and (c) Co 2p XPS spectra of CoO/Cu-CF and post-reaction CoO/Cu - CF.

XPS analysis in Fig. S21 reveals no noticeable shift in Cu or Co peaks, indicating that Cu is not oxidized, and the elemental composition remains comparable to the fresh catalyst. ICP-OES of the post-reaction electrolyte shows a Co concentration below 0.1 ppm, confirming negligible Co leaching.



Figure S22. Photos of test device by a two-electrode flow cell.

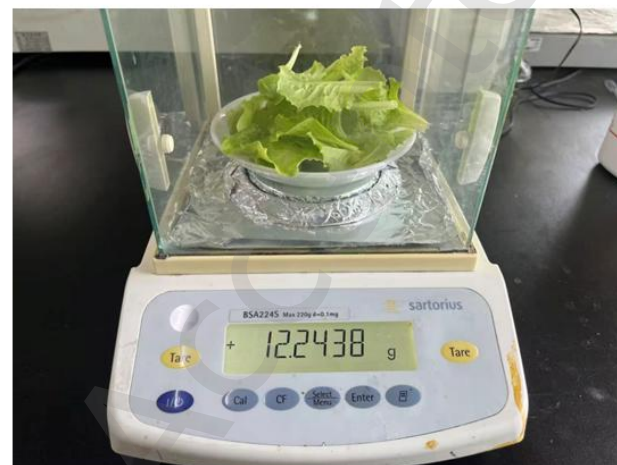
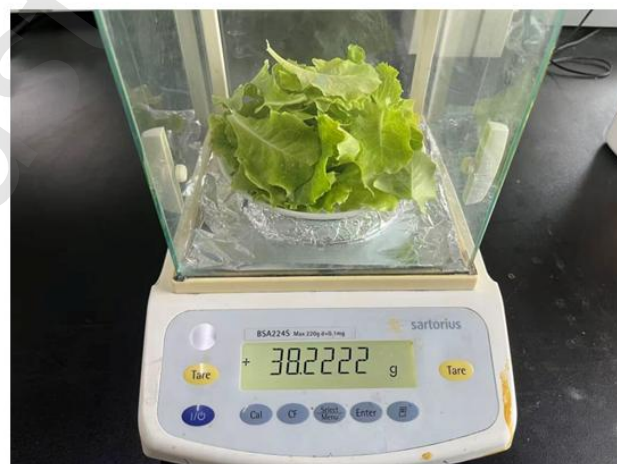
a**b****c**

Figure S23. Photos of (a) reset, (b) unfertilized and (c) fertilized Lettuce weight.

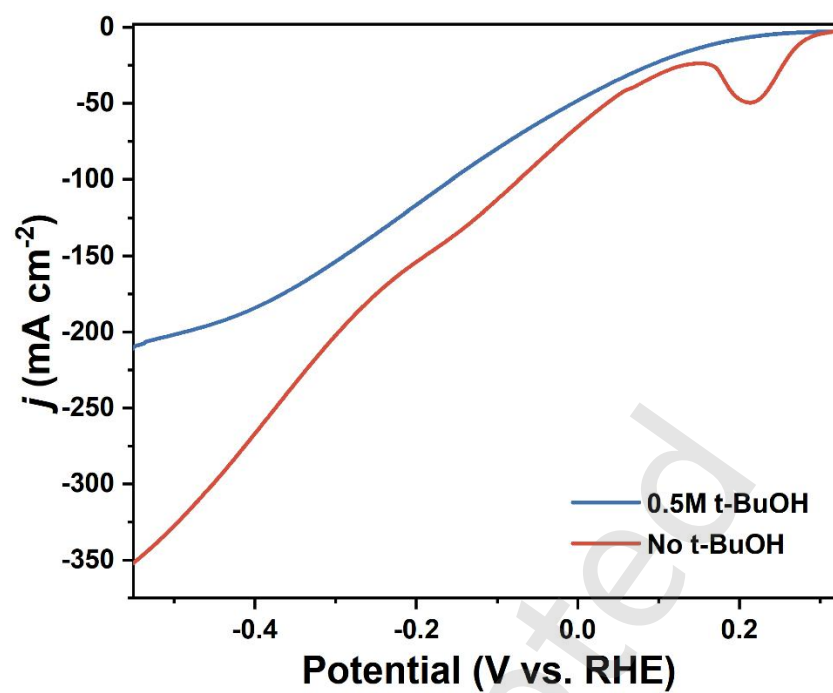


Figure S24. The LSV curves of CoO/Cu-CF in 1.0 M KOH with or without t-BuOH.

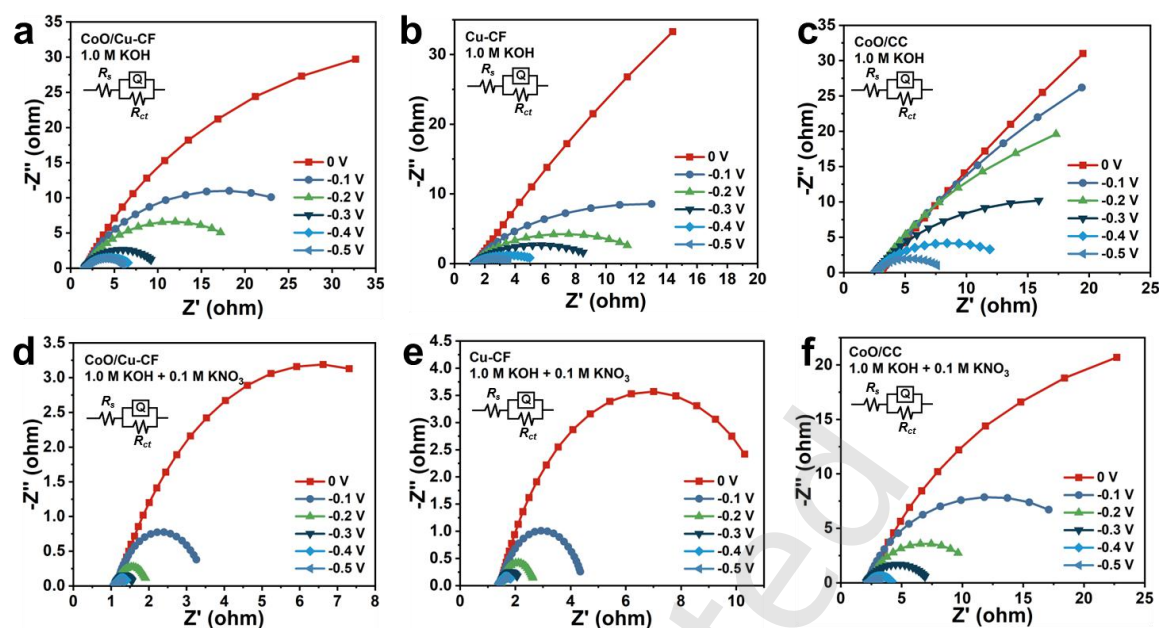


Figure S25. *In situ* Nyquist plots of (a) CoO/Cu-CF, (b) Cu-CF, and (c) CoO/CC under different applied potentials in 1.0 M KOH electrolyte. *In situ* Nyquist plots of (a) CoO/Cu-CF, (b) Cu-CF, and (c) CoO/CC under different applied potentials in 1.0 M KOH + 0.1 M KNO₃ electrolyte.

Nyquist plots in Fig. S25 show that CoO/Cu-CF exhibits the smallest charge transfer resistance (R_{ct}) in both KOH and KOH+KNO₃ electrolytes, indicating the fastest charge transfer kinetics.

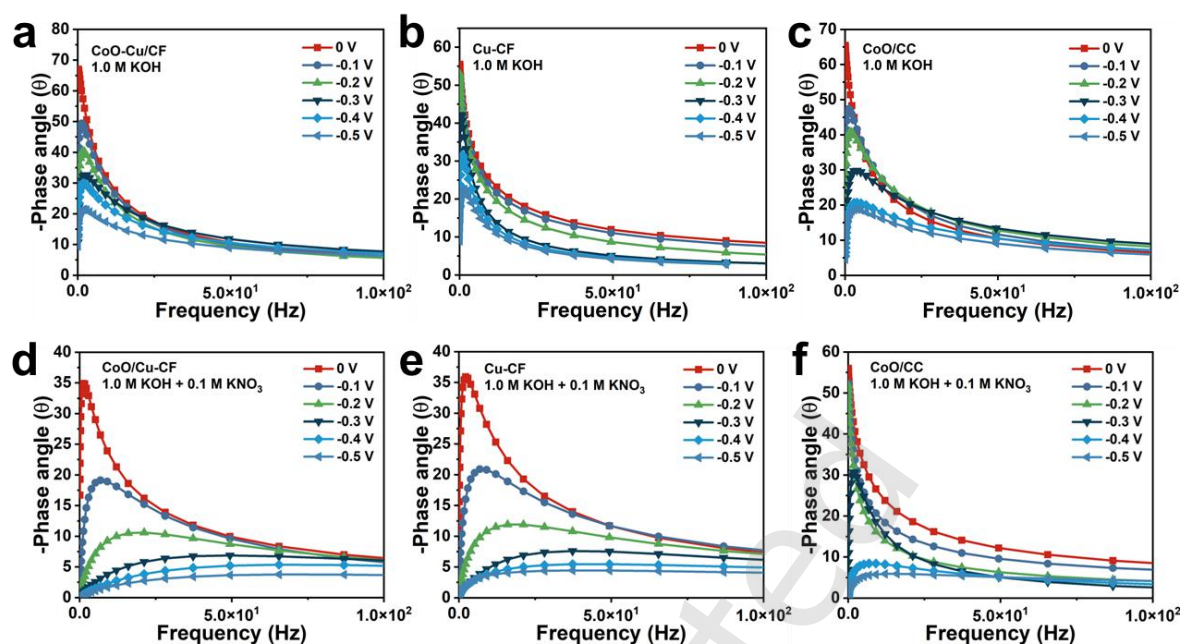


Figure S26. *In situ* bode plots of (a) CoO/Cu-CF, (b) Cu-CF, and (c) CoO/CC under different applied potentials in 1.0 M KOH electrolyte. *In situ* bode plots of (a) CoO/Cu-CF, (b) Cu-CF, and (c) CoO/CC under different applied potentials in 1.0 M KOH + 0.1 M KNO₃ electrolyte.

Bode phase angle analysis in Fig. S26 reveals that in 1.0 M KOH, CoO/Cu-CF and CoO/CC display relatively high phase angles in the mid-frequency region, reflecting strong H⁺ generation capability, consistent with the CV results in Fig. 5c. Upon nitrate addition, the phase angle of CoO/Cu-CF decreases more rapidly and reaches a lower value compared to Cu-CF and CoO/CC, indicating that the electron delocalization effect facilitates the rapid transfer of H⁺ to NO₃⁻ intermediates during hydrogenation, thereby suppressing HER.

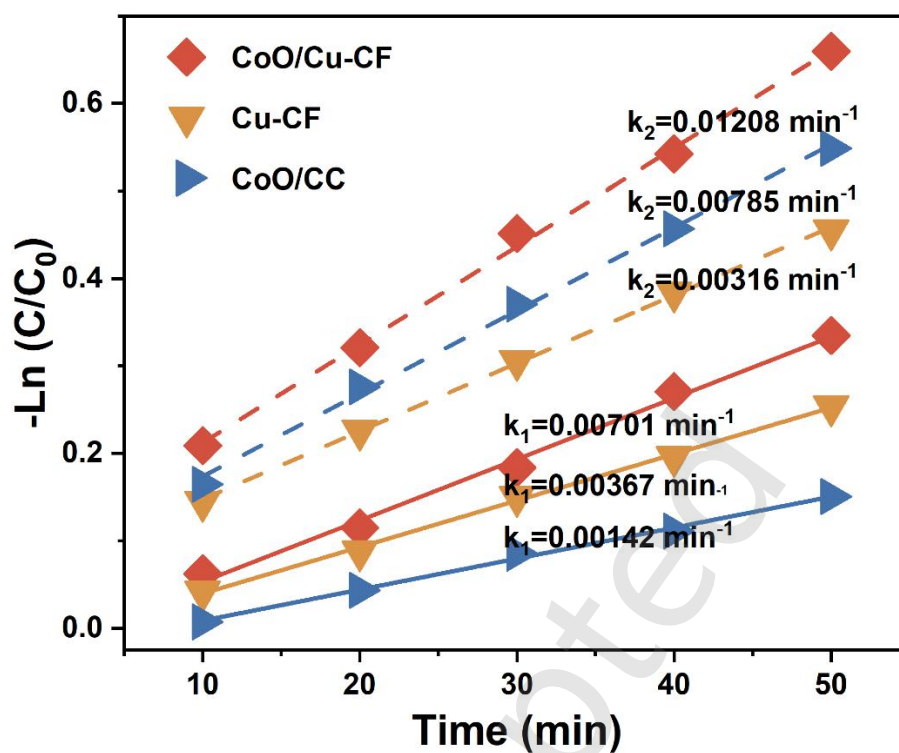


Figure S27. Linearized pseudo-first-order kinetic profiles of CoO/Cu-CF, Cu-CF, and CoO/CC in 0.1 M NO_3^- (k_1) or 0.1 M NO_2^- (k_2).

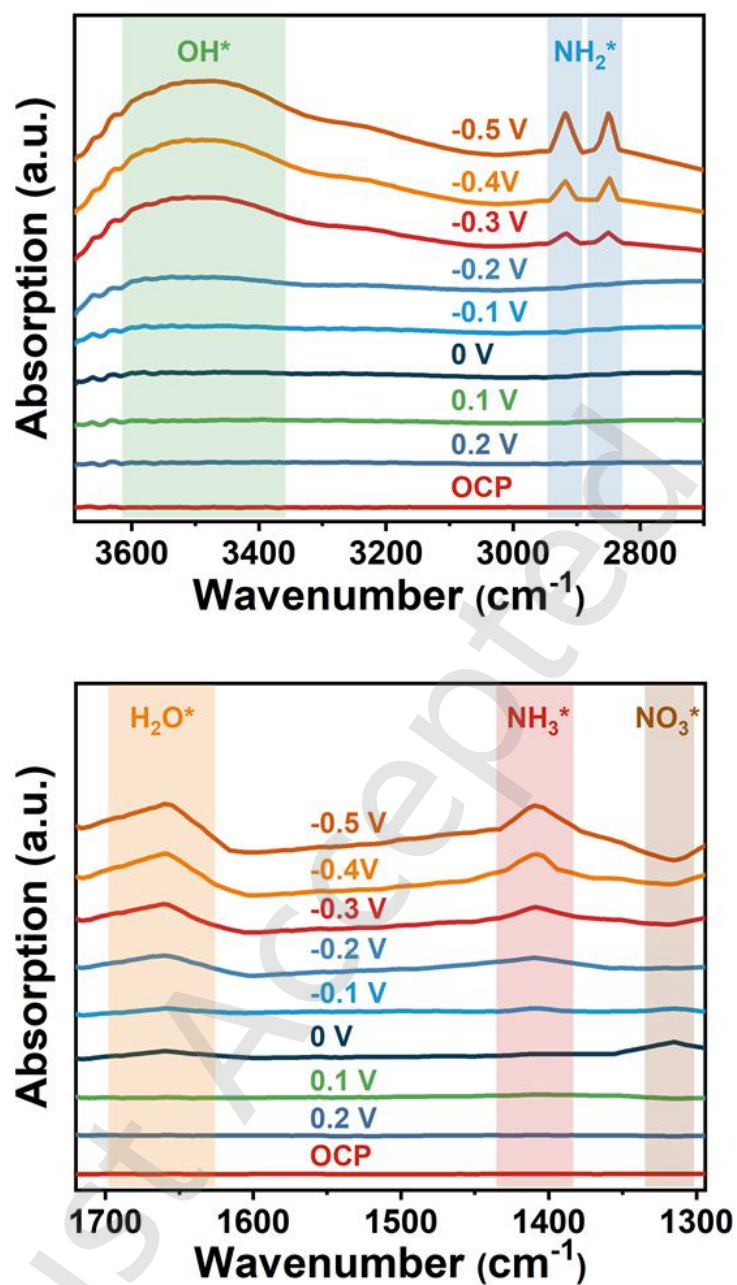


Figure S28. *In situ* ATR-FTIR spectra of CoO/Cu-CF recorded at different potentials.

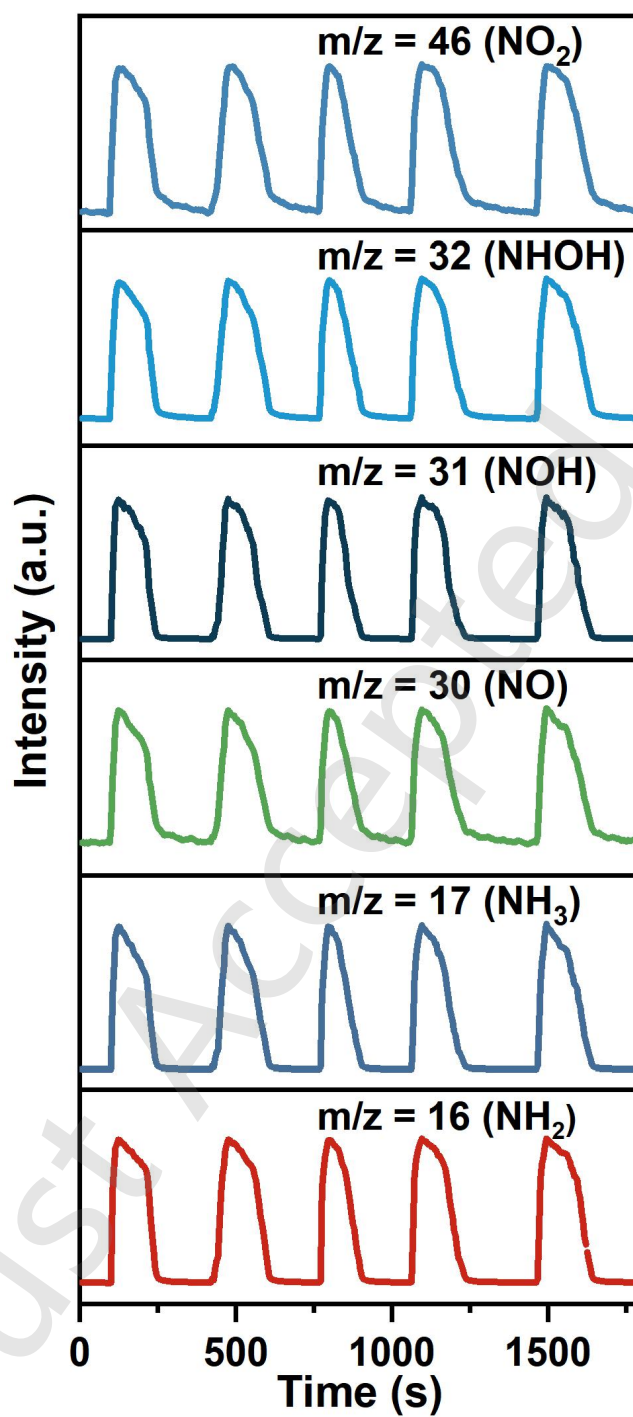


Figure S29. Online DEMS of CoO/Cu-CF during electrochemical NO_3RR .

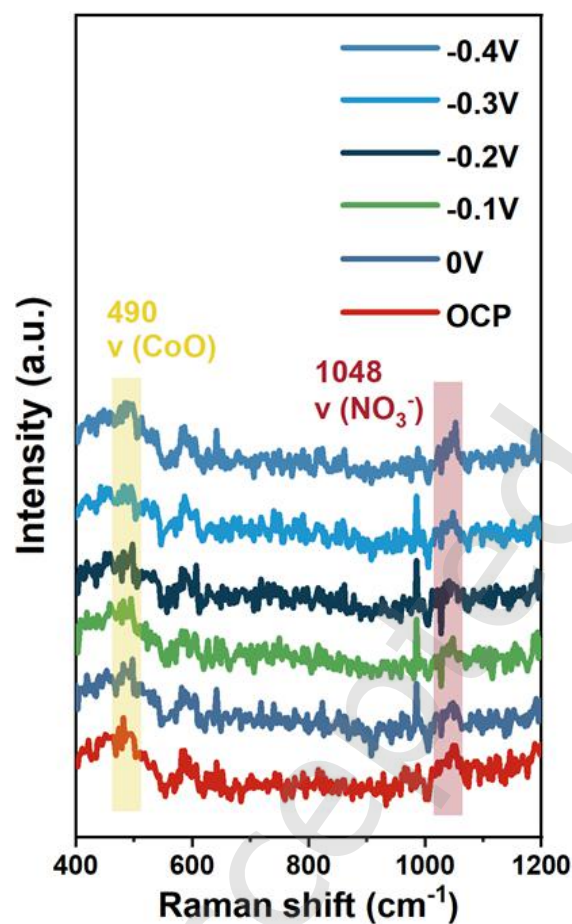


Figure S30. *In situ* Raman spectra of CoO/Cu from OCP to -0.4 V vs. RHE.

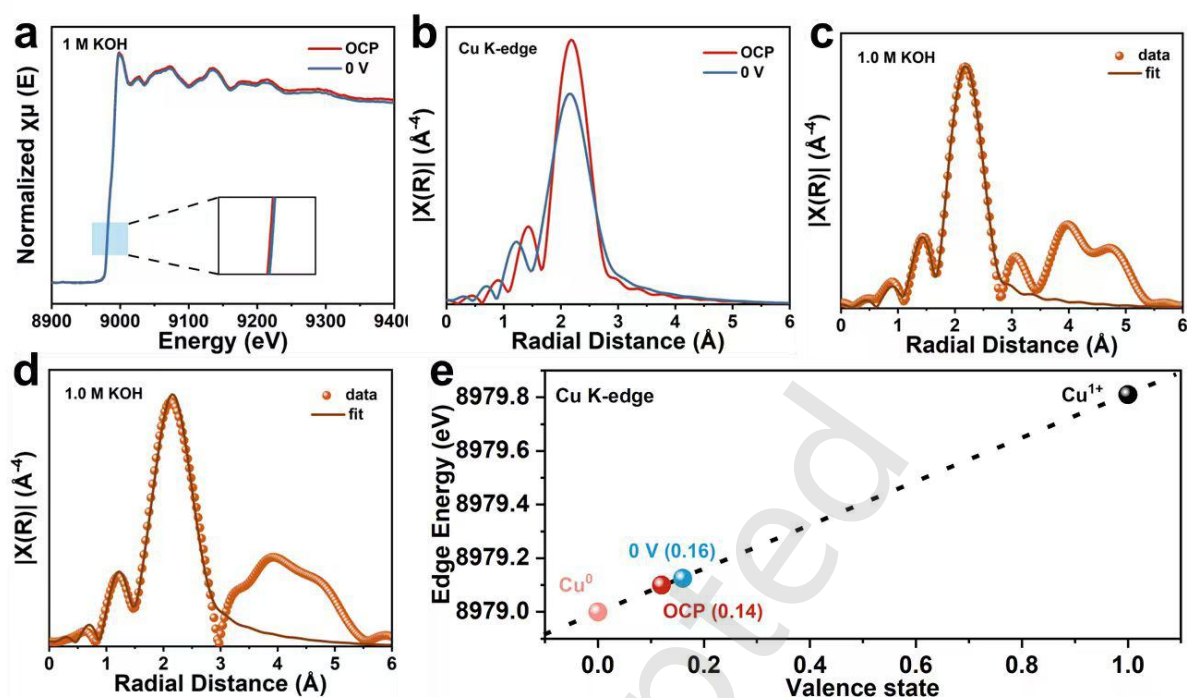


Figure S31. (a) Normalized in situ XANES spectra at the Cu K-edge of CoO/Cu-CF, (b) FT-EXAFS spectra, and corresponding fitting curves of the FT-EXAFS at (c) OCP and (d) 0 V vs. RHE recorded in 1.0 M KOH. (e) The average oxidation state of Cu derived from the Cu K-edge XANES at OCP and 0 V.

As shown in Figure S31 and Table S5, the coordination numbers of Cu–Cu and Cu–O bonds exhibit negligible changes, and no obvious shift in the Cu absorption edge is observed. Quantitatively, the Cu oxidation state increases by only 0.06 in the absence of NO_3^- , which is merely one-seventh of the increase observed in the presence of NO_3^- . The results confirm that the significant rise in Cu oxidation state of CoO/Cu-CF primarily originates from NO_3^- adsorption, with only a minor contribution from OH^- adsorption or surface reconstruction.

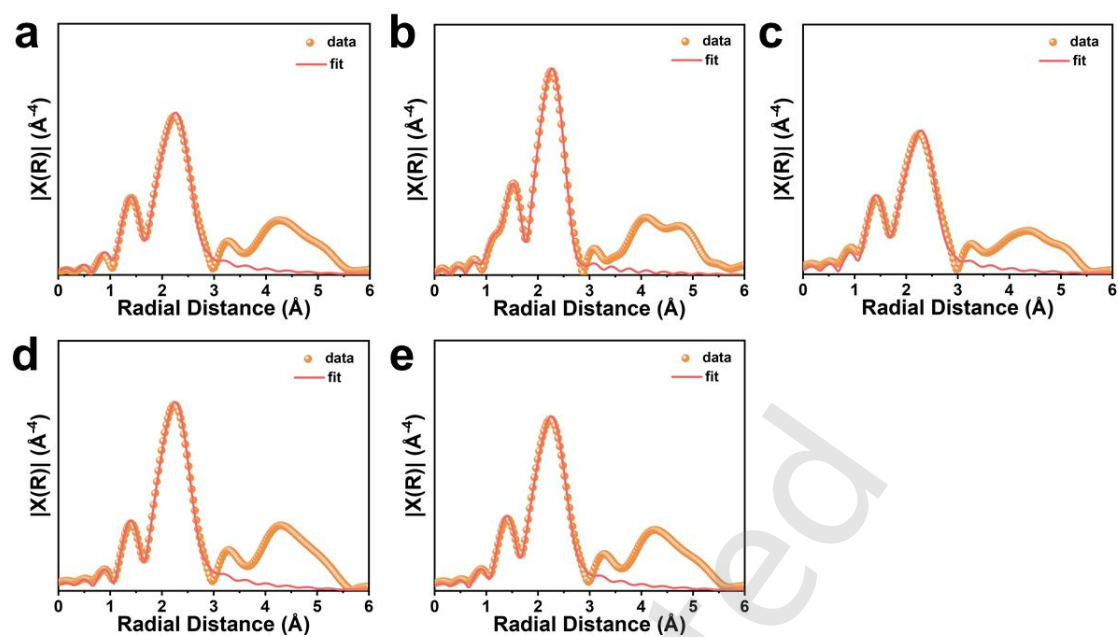


Figure S32. Fitting FT-EXAFS curves of Cu K-edge at the applied potentials of (a) OCP, (b) 0 V, (c) -0.3 V, (d) -0.4 V and (e) -0.5 V derived from Figure 5f.

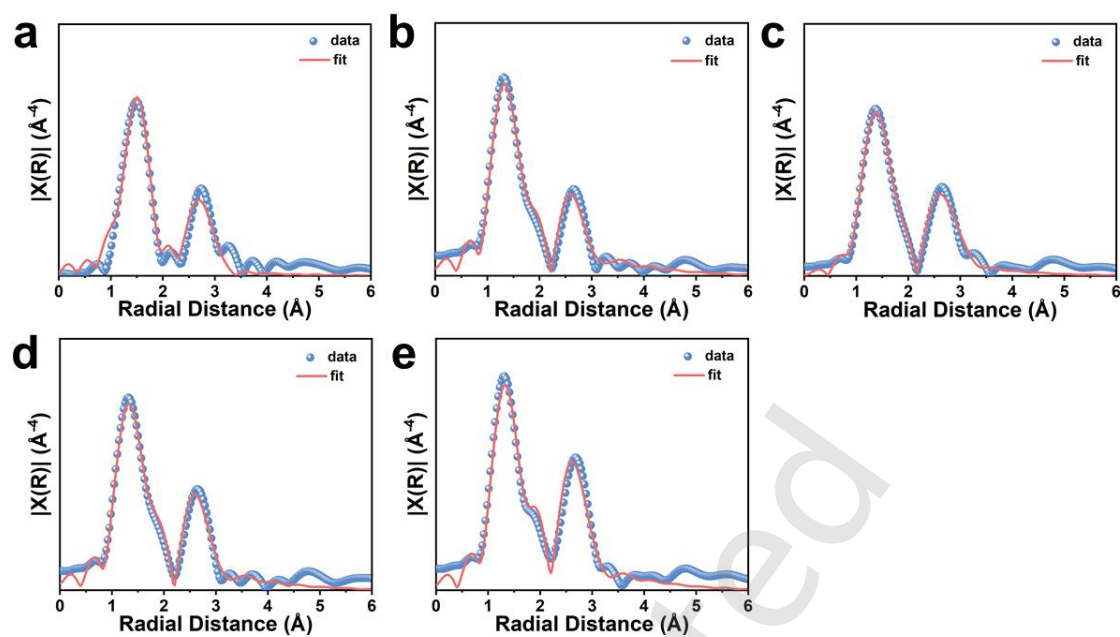


Figure S33. Fitting FT-EXAFS curves of Co K-edge at the applied potentials of (a) OCP, (b) 0 V, (c) -0.3 V, (d) -0.4 V and (e) -0.5 V derived from Figure 5h.

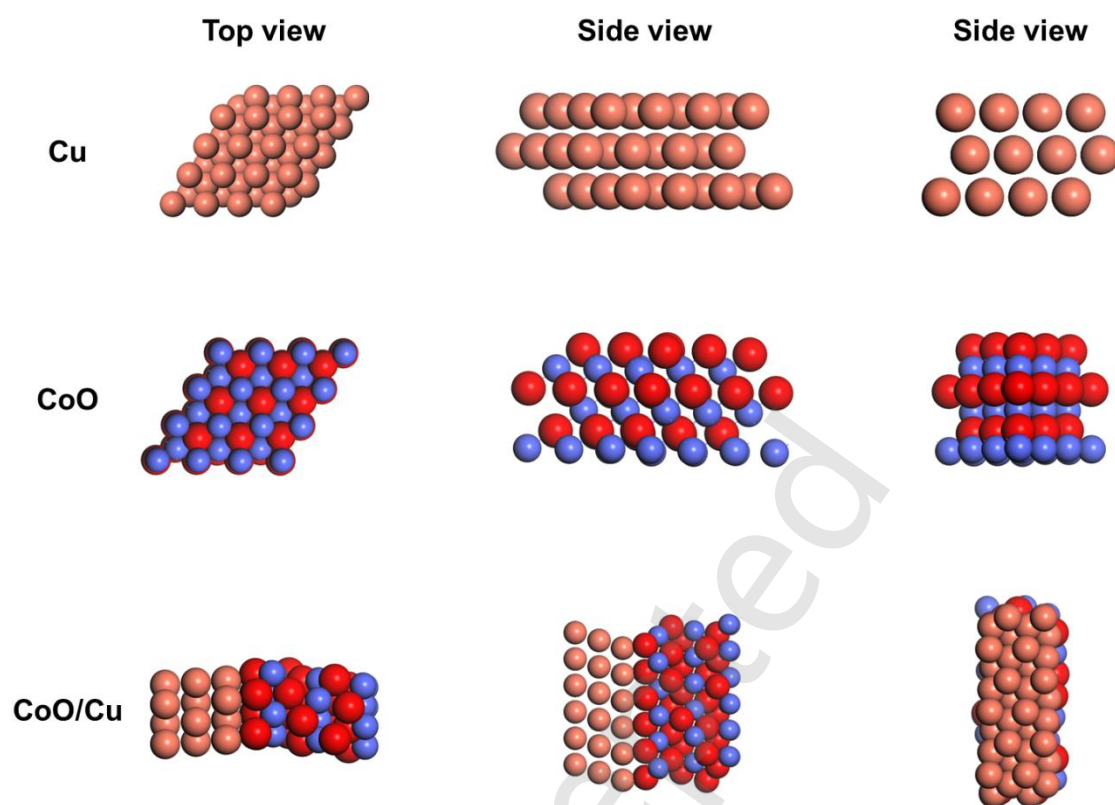


Figure S34. Calculated models of Cu, CoO and CoO/Cu presented from different views.

Table S1. FT-EXAFS fitting parameters of Cu K-edge for CoO/Cu-CF and Cu-CF from Figure S7.

Samples	Shell	CN	R($\text{\AA}$)	σ^2 (10^{-3})	ΔE_0 (eV)	R factor (10^{-1})
CoO/Cu-CF	Cu–O	2.44	1.82	13.41	2.66	0.06
	Cu–Cu	4.91	2.49	7.92		
Cu-CF	Cu–Cu	1.21	2.48	0.99	-3.45	0.11

Note: CN: coordination number; R: distance between absorber and backscatter atoms; σ^2 : Debye-Waller factors; ΔE_0 : inner potential correction; R factor: indicative of fitting goodness.

Table S2. FT-EXAFS fitting parameters of Co K-edge for CoO/Cu-CF and CoO/CC from Figure S8.

Samples	Shell	CN	R(Å)	σ ² (10 ^{−3})	ΔE ₀ (eV)	R factor (10 ^{−1})
CoO/Cu-CF	Co–O	2.93	1.93	6.63	−5.60	0.13
	Co–Co	6.22	3.00	20.34		
	(Co–O–Co)					
CoO/CC	Co–O	3.24	2.04	8.69	−1.32	0.06
	Co–Co	6.03	3.03	21.96		
	(Co–O–Co)					

Note: CN: coordination number; R: distance between absorber and backscatter atoms; σ^2 : Debye-Waller factors; ΔE_0 : inner potential correction; R factor: indicative of fitting goodness.

Table S3. Assignment of equivalent circuit components from Figure S9.

Samples	R_s	R_{ct}	Q(CPE)
CoO/Cu-CF	1.355	0.4812	0.03947
Cu-CF	1.329	0.5929	0.08772
CoO/CC	1.769	0.7398	0.02386

Table S4. Comparison of the NO_3^- RR performance of CoO/Cu with reported electrocatalysts.

Catalysts	Electrolyte	FE_{NH_3} (%)	Current density ($\text{mA}\cdot\text{cm}^{-2}$)	Potential (vs. RHE, V)	NH_3 Yield ($\text{mg}\cdot\text{h}^{-1}\cdot\text{cm}^{-2}$)	Ref.
CoO/Cu-CF	1 M KOH+ 0.1 M KNO_3	95	330	−0.4	16.7	This work
Cu- CoO/Co(OH) ₂	1 M KOH + 0.1 M KNO_3	94.7	120	−0.5	6.0	1
NiMoO ₄ /CuO NW/CF	1 M KOH + 0.1 M NaNO_3	98.8	210	−0.2	11.5	2
Cu@ZnO	0.1 M KOH + 0.05 M KNO_3	89.1	60	−0.6	3.4	3
Cu-SNC-2- SAC	1 M KOH + 0.1 M KNO_3	94.6	60	−0.6	16.5	4
Co@Cu	0.5 M Na_2SO_4 + 0.1 M KNO_3	88.6	250	−0.4	5.1	5
CuCo-SNC	0.5 M Na_2SO_4 + 0.1 M KNO_3	83.5	25	−0.6	12.3	6
OD-Cu	1 M KOH + 0.1 M KNO_3	90.6	230	−0.48	4.7	7
Ag _{SA} -Cu NWs	0.1 M KOH + 5 mM KNO_3	95.4	80	−0.6	2.5	8
V-Cu	0.5 M K_2SO_4 + 0.1 M KNO_3	97.2	210	−0.3	7.8	9

Table S5. *In situ* FT-EXAFS fitting parameters of Cu K-edge for CoO/Cu-CF from Figure S31.

Potentials	Shell	CN	R(Å)	σ^2 (10^{-3})	ΔE_0 (eV)	R factor (10^{-1})
OCP	Cu–O	1.46	1.90	9.83	–5.03	0.09
	Cu–Cu	6.03	2.55	9.12		
0 V	Cu–O	1.48	1.89	9.74	–4.14	0.06
	Cu–Cu	5.99	2.55	9.18		

Note: CN: coordination number; R: distance between absorber and backscatter atoms; σ^2 : Debye-Waller factors; ΔE_0 : inner potential correction; R factor: indicative of fitting goodness.

Table S6. *In situ* FT-EXAFS fitting parameters of Cu K-edge for CoO/Cu-C from Figure S32.

Potentials	Shell	CN	R(Å)	σ^2 (10^{-3})	ΔE_0 (eV)	R factor (10^{-1})
OCP	Cu–O	1.86	1.89	8.18	3.88	0.03
	Cu–Cu	4.84	2.54	8.31		
0 V	Cu–O	2.10	1.90	8.49	6.13	0.03
	Cu–Cu	4.10	2.54	7.68		
–0.3 V	Cu–O	1.87	1.90	7.69	5.61	0.07
	Cu–Cu	4.77	2.55	7.83		
–0.4 V	Cu–O	1.65	1.90	6.23	4.15	0.02
	Cu–Cu	5.16	2.54	7.95		
–0.5 V	Cu–O	1.35	1.90	7.37	4.01	0.02
	Cu–Cu	5.4	2.54	8.24		

Note: CN: coordination number; R: distance between absorber and backscatter atoms; σ^2 : Debye-Waller factors; ΔE_0 : inner potential correction; R factor: indicative of fitting goodness.

Table S7. *In situ* FT-EXAFS fitting parameters of Co K-edge for CoO/Cu-CF from Figure S33.

Potentials	Shell	CN	<i>R</i> (Å)	σ^2 (10^{-3})	ΔE_0 (eV)	<i>R</i> factor(10^{-1})
OCP	Co–O	1.27	2.03	10.94	1.78	0.14
	Co–Co	1.57	3.09	20.30		
	(Co–O–Co)	1.33	1.96	9.42		
0 V	Co–O	1.33	1.96	9.42	–2.01	0.16
	Co–Co	3.13	2.99	11.7		
	(Co–O–Co)	1.34	1.95	5.93		
–0.3 V	Co–O	1.34	1.95	5.93	–4.20	0.11
	Co–Co	2.85	3.03	20.53		
	(Co–O–Co)	1.57	1.96	9.32		
–0.4 V	Co–O	1.57	1.96	9.32	–2.20	0.14
	Co–Co	2.55	3.00	12.98		
	(Co–O–Co)	1.03	1.97	10.77		
–0.5 V	Co–O	1.03	1.97	10.77	–2.18	0.18
	Co–Co	2.10	3.02	12.1		
	(Co–O–Co)					

Note: CN: coordination number; *R*: distance between absorber and backscatter atoms; σ^2 : Debye-Waller factors; ΔE_0 : inner potential correction; *R* factor: indicative of fitting goodness.

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