



# Optimizing local electronic structure of Co nanoparticles in N-doped carbon for efficient electrochemical nitrate reduction to ammonia

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## ABSTRACT

The electrocatalytic nitrate reduction reaction (eNO<sub>3</sub>RR) is generally hindered by sluggish reaction kinetics and insufficient active-site stability, which severely limit the achievement of high NH<sub>3</sub> Faradaic efficiency (FE) and NH<sub>3</sub> yield. Herein, a facile nitrogen-doping strategy was developed to precisely confine cobalt nanoparticles (Co NPs) within an N-doped carbon matrix, yielding an active-site-tailored Co-NC catalyst (the optimized catalyst is denoted as Co-NC-10). Density functional theory (DFT) calculations combined with in situ characterization reveal that an N-doped carbon matrix modulates the local electronic structure of Co NPs, thereby facilitating the formation of key \*H species and lowering the energy barrier for the rate-determining step in nitrate reduction to ammonia. The optimized Co-NC-10 catalyst delivers a high NH<sub>3</sub> FE of 95.82% and an NH<sub>3</sub> yield of 0.989 mmol h<sup>-1</sup> cm<sup>-2</sup> at -0.4 V vs. RHE. Moreover, after six consecutive electrolysis cycles, both the NH<sub>3</sub> FE and NH<sub>3</sub> yield remain nearly unchanged, demonstrating excellent stability. Benefiting from its outstanding catalytic activity and durability, a Zn-NO<sub>3</sub> battery with Co-NC-10 as the cathode catalyst delivers a peak power density of 9.25 mW cm<sup>-2</sup> and demonstrates excellent operational stability.

## 1. Introduction

Ammonia (NH<sub>3</sub>) is a vital chemical feedstock and hydrogen-rich energy carrier, widely used in fertilizer production and energy storage [1,2]. Presently, industrial ammonia production mainly relies on the energy- and carbon-intensive Haber-Bosch process, which requires huge amounts of fossil fuels and produces massive CO<sub>2</sub> emissions [3–5]. Therefore, developing energy-saving, green, and low-carbon methods for NH<sub>3</sub> synthesis is of great importance. The electrocatalytic nitrate reduction reaction (eNO<sub>3</sub>RR), which can be coupled with renewable electricity and conducted under ambient conditions, is considered one of the most promising alternatives to the conventional Haber-Bosch

process [6–8]. Furthermore, nitrate (NO<sub>3</sub><sup>-</sup>) possesses a lower bond dissociation energy (204 kJ mol<sup>-1</sup>), higher solubility, and faster interfacial reaction kinetics than molecular nitrogen, making it more suitable for ammonia production under moderate conditions [9–11]. On the other hand, NO<sub>3</sub><sup>-</sup> exists in large amounts in industrial wastewater, contaminated groundwater, and nuclear effluents and can thus seriously disrupt the natural nitrogen cycle and threaten human health when accumulated excessively [12–14]. Therefore, utilizing eNO<sub>3</sub>RR to convert nitrate-containing wastewater into valuable NH<sub>3</sub> provides an economical and sustainable strategy for environmental remediation and resource recovery [15–17].

Currently, eNO<sub>3</sub>RR still faces significant challenges in achieving high

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NH<sub>3</sub> yield and NH<sub>3</sub> Faradaic efficiency (FE) [18]. This is mainly attributed to the complex eight-electron and nine-proton transfer pathway involved in the conversion of NO<sub>3</sub><sup>-</sup> to NH<sub>3</sub> ( $\text{NO}_3^- + 8\text{e}^- + 9\text{H}^+ \rightarrow \text{NH}_3 + 3\text{H}_2\text{O}$ ) and the tendency to generate undesired byproducts such as NO<sub>2</sub>, NO, and N<sub>2</sub>. In addition, the eNO<sub>3</sub>RR process is often accompanied by the competitive hydrogen evolution reaction (HER), which reduces both the selectivity and yield of NH<sub>3</sub> [19–22]. Therefore, the development of suitable catalysts is crucial for controlling NH<sub>3</sub> selectivity and enhancing both NH<sub>3</sub> yield and NH<sub>3</sub> FE. Among various non-noble-metal systems, cobalt-based catalysts have attracted widespread attention due to their low cost and high NH<sub>3</sub> selectivity [23–25]. Furthermore, the abundance of unoccupied d orbitals in cobalt facilitates the adsorption and activation of NO<sub>3</sub><sup>-</sup> [26]. However, cobalt-based catalysts still face high reaction energy barriers in the critical hydrogenation steps, limiting the reaction kinetics and NH<sub>3</sub> yield [27–30]. In addition, highly dispersed cobalt nanoparticles (Co NPs) are prone to migration and aggregation under practical reaction conditions, resulting in compromised structural stability [31,32]. Therefore, it is necessary to develop cobalt-based catalysts that combine high activity with high stability to enhance their overall performance in electrocatalytic reactions. Metal-organic frameworks (MOFs) are regarded as ideal precursors for the preparation of highly dispersed metals and porous carbon materials due to their ordered structures and tunable metal nodes [33]. During pyrolysis, the ordered frameworks of MOFs can be converted into metal-doped porous carbon structures with high porosity and well-defined skeletons, which facilitate the anchoring and stabilization of Co NPs. Furthermore, surface modification is considered an effective strategy for tuning the catalytic performance [34]. Introducing nonmetal atoms such as P, B, or S into carbon frameworks can modulate the local electronic structure and create synergistic interfaces, thereby optimizing the adsorption energies of nitrogen-containing intermediates during NO<sub>3</sub><sup>-</sup> reduction and improving electrochemical stability [35–37]. However, studies on the regulatory role of nitrogen doping in nitrate reduction and the underlying mechanisms remain relatively limited, providing an important opportunity for the rational design of efficient eNO<sub>3</sub>RR catalysts.

Herein, a Co-NC site-enriched catalyst (Co-NC–10) was synthesized via a one-step pyrolysis method using ZIF–67 as the precursor. Co-NC–10 achieves an NH<sub>3</sub> FE of 95.82% and an NH<sub>3</sub> yield of 0.989 mmol h<sup>-1</sup> cm<sup>-2</sup> at –0.4 V vs. RHE. In situ electrochemical Fourier transform infrared (FTIR) spectroscopy, in situ Raman spectroscopy, and density functional theory (DFT) calculations collectively confirm that nitrogen doping enables the precise modulation of the local electronic structure of Co NPs, which not only efficiently promotes the generation of key \*H species during the reaction but also significantly lowers the energy barrier of the rate-determining step. Furthermore, a zinc-nitrate (Zn-NO<sub>3</sub>) battery with Co-NC–10 as the cathode exhibits a high power density of 9.25 mW cm<sup>-2</sup> along with excellent cycling stability. Through the synergistic combination of the spatial confinement and protective effects of the carbon matrix with the precise modulation of the local electronic structure of Co NPs, this strategy provides valuable insights into the design of high-performance eNO<sub>3</sub>RR catalysts and opens new opportunities for sustainable energy conversion.

## 2. Experimental section

### 2.1. Synthesis of ZIF–67

ZIF–67 powder was prepared according to the reported procedure. In a typical synthesis, 5.248 g of 2-methylimidazole and 1.164 g of Co (NO<sub>3</sub>)<sub>2</sub>·6 H<sub>2</sub>O were separately dissolved in 50 mL of methanol. After magnetic stirring for 30 min, solutions A and B were formed. Solution A was then rapidly poured into solution B and stirred at 700 rpm at room temperature for 24 h. Finally, the stirred solution was centrifuged at 8000 rpm in a centrifuge tube. The resulting precipitate was washed several times with methanol, collected as a purple solid, and dried at

60°C for 12 h to yield the final precipitate.

### 2.2. Synthesis of catalyst Co-NC-X (X = 0, 5, 10 and 15)

0.2 g of ZIF–67 powder and 2.0 g of melamine (corresponding to a mass ratio of 1:10) were placed in a tubular furnace, with melamine positioned upstream and ZIF–67 downstream along the direction of N<sub>2</sub> flow. The furnace temperature was then increased to 800 °C at a constant heating rate and maintained for 2 h under a continuous N<sub>2</sub> atmosphere. After naturally cooling to room temperature, the obtained sample was denoted as Co-NC–10. For comparison, Co-NC–0, Co-NC–5, and Co-NC–15 were synthesized under identical conditions, except that the mass ratios of ZIF–67 to melamine were adjusted to 1:0, 1:5, and 1:15, respectively.

### 2.3. Electrochemical measurements

Electrochemical measurements were performed using a CHI–760E electrochemical workstation with a standard three-electrode sealed H-type cell. The working electrode, reference electrode, and counter electrode consisted of catalyst-loaded carbon paper, a Hg/HgO electrode, and a commercial Pt sheet, respectively. Preparation of the working electrode: 10 mg of electrocatalyst powder and 50 μL of 5% Nafion solution were dispersed into a microcentrifuge tube containing 450 μL of ultrapure water and 500 μL of ethanol. The mixture was then sonicated for 1 h to obtain a uniform dispersion. Fifty microliters of the electrocatalyst ink was loaded onto carbon paper with an area of 1 × 2 cm<sup>2</sup>, resulting in an effective reaction area of 1 × 1 cm<sup>2</sup>. Finally, the carbon paper was air-dried to obtain the working electrode. In this work, a conventional three-electrode system employing an H-type cell was utilized. Nitrate reduction was evaluated by chronoamperometric measurements at different applied potentials or nitrate concentrations for 3 h. The electrolyte consisted of 40 mL of 1 M KOH solution, while the catholyte comprised 40 mL of 1 M KOH containing 0.1 M KNO<sub>3</sub>. All potentials recorded during testing were converted to the reversible hydrogen electrode (RHE) scale using the Nernst equation ( $E(\text{V vs. RHE}) = E(\text{Hg/HgO}) + 0.059 \times \text{pH} + 0.098$ ). Linear sweep voltammetry (LSV) measurements were performed at room temperature with a scan rate of 5 mV s<sup>-1</sup> over the potential range from –0.7 to –1.4 V vs. RHE. More details are described in the [Supporting Information](#).

## 3. Results and discussion

### 3.1. Synthesis and characterization of materials

Under the same conditions, we prepared a series of Co-NC catalysts with different mass ratios of ZIF–67 to melamine (1:5, 1:10 and 1:15), and we marked the obtained Co-NC samples as Co-NC–5, Co-NC–10 and Co-NC–15, respectively. A schematic illustration of the synthesis of the representative Co-NC–10 catalyst is shown in [Fig. 1a](#). Briefly, ZIF–67 was first synthesized from cobalt(II) nitrate hexahydrate and 2-methylimidazole, followed by co-pyrolysis with melamine under a nitrogen atmosphere in a tubular furnace to obtain the final catalyst. For comparison, Co-NC–0 was prepared by directly pyrolyzing ZIF–67 in the absence of melamine. [Fig. 1b](#) shows the XRD patterns of the Co-NC–0 and Co-NC–10 catalysts. The patterns exhibit diffraction peaks at 2θ = 44.37°, 51.59°, and 76.08° for both samples, corresponding to the (111), (200), and (220) crystal planes of metallic cobalt, which are in good agreement with the standard data for the cubic Co phase (PDF#15–0806) [38]. The XRD patterns of Co-NC–0, Co-NC–5, and Co-NC–15 are presented in [Fig. S1](#). With increasing melamine content, the intensity of the Co-related diffraction peaks gradually decreases and the peak widths slightly broaden, indicating that the long-range order of the Co species may be reduced, which could be attributed to a decrease in the size of Co NPs [39]. The morphology of Co-NC–0 and Co-NC–10 was examined by SEM. As shown in [Fig. 1c](#) and [S2a](#), both samples

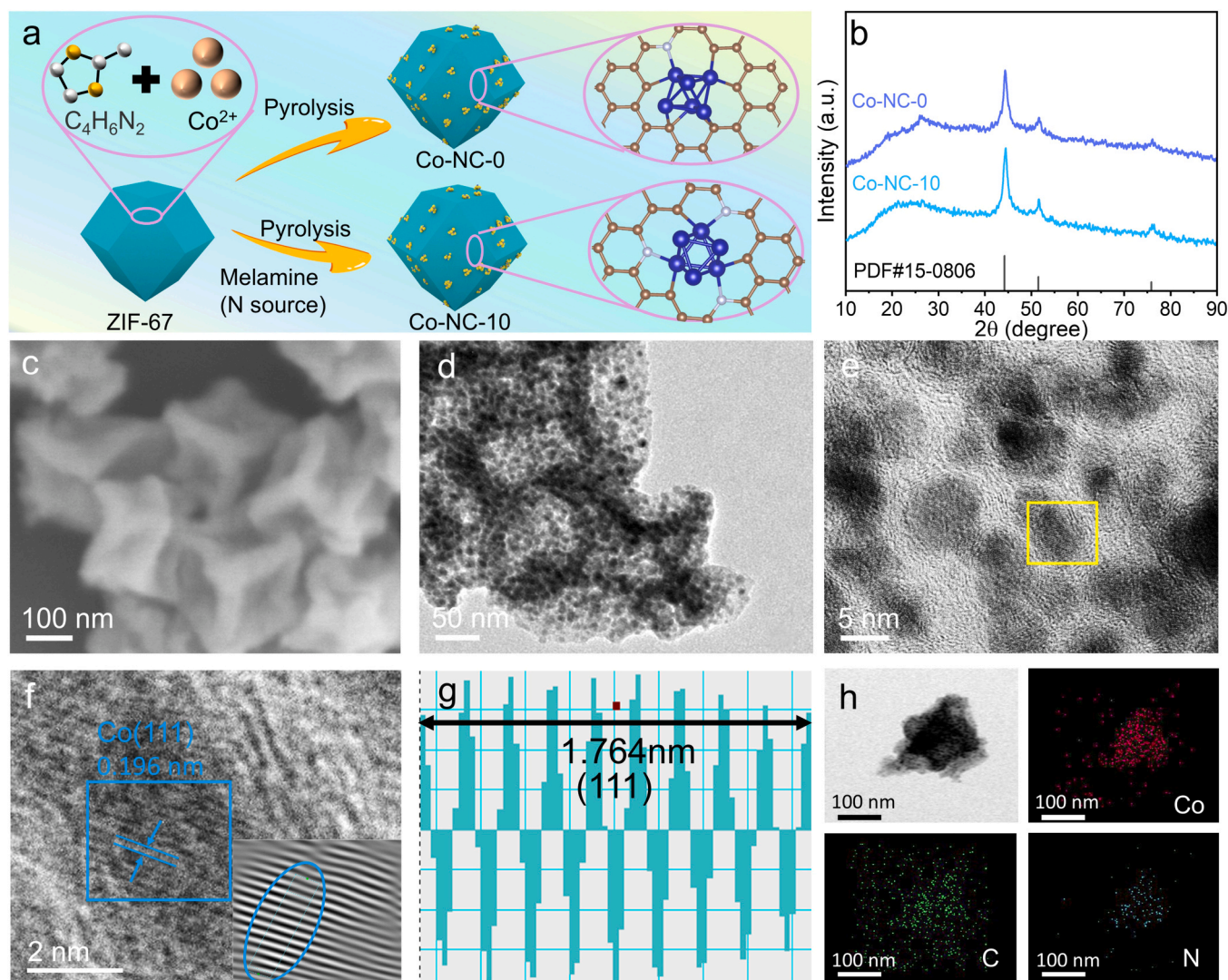


**Fig. 1.** Composition and morphology characterization of the catalyst. (a) Synthesis schematic diagram of Co-NC-0 and Co-NC-10. (b) XRD patterns of Co-NC-0, Co-NC-10, and Co (PDF #15-0806). (c) SEM image of Co-NC-10 after pyrolysis. (d) TEM image of Co-NC-10 after pyrolysis. (e) HRTEM image. (f) Enlarged view of the yellow square in (e), with the inset showing the Co (111) lattice plane. (g) Lattice spacing of the Co (111) plane in Co-NC-10. (h) EDS elemental mapping of Co, C, and N in Co-NC-10.

exhibit a uniform rhombic morphology with an average size of approximately 200 nm, indicating that nitrogen doping has little effect on the overall shape. After pyrolysis, although partial crystal collapse is observed, the overall outlines and edges are largely preserved, demonstrating good structural stability. The SEM and TEM images of Co-NC-0, Co-NC-5 and Co-NC-15 before and after pyrolysis are presented in Fig. S2-S4. TEM further confirms the framework structure of Co-NC-10. As shown in Fig. 1d, Co NPs are uniformly distributed within the carbon framework. In Fig. S5, the Co NPs of Co-NC-10 are marked with yellow circles, while the carbon layers are indicated by white vertical lines. High-resolution TEM (HRTEM) provided an in-depth analysis of the microstructures of Co NPs in Co-NC-0 and Co-NC-10, as shown in Fig. 1e and S6a. The images reveal 5–10 nm Co NPs anchored onto the carbon substrate. Clear lattice fringes can be observed in the enlarged images of the selected regions (Fig. 1f and S6b). Fast Fourier Transform (FFT) analysis reveals that the lattice spacing of the Co NPs in the Co-NC-10 sample is 0.196 nm, corresponding to the (111) crystal plane of Co (Fig. 1f-g). The interplanar spacing in Co-NC-0 is 0.192 nm (Fig. S6b-d). With increasing nitrogen content, the size of the Co NPs formed after pyrolysis gradually decreases, as shown in Fig. S7. Statistical analysis of the Co NP sizes indicates that the average diameters of

Co NPs in Co-NC-0, Co-NC-5, Co-NC-10, and Co-NC-15 are approximately 8.97, 6.59, 6.61, and 6.18 nm, respectively [40]. This demonstrates that increasing the nitrogen content contributes to the stabilization of Co NPs and inhibits their migration and aggregation to some extent [41]. EDS elemental mapping of Co-NC-10 revealed that Co, C and N elements were uniformly distributed throughout the framework, indicating that Co NPs were uniformly distributed on the carbon skeleton substrate (Fig. 1h). The Co and N contents in Co-NC-0, Co-NC-5, Co-NC-10, and Co-NC-15 were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and elemental analysis. As shown in Table S1, the Co content gradually decreased from 19.54 wt% for Co-NC-0–8.69 wt% for Co-NC-15, while the N content increased from 2.18 wt% to 11.07 wt% with increasing melamine dosage.

For more insights into the effect of N doping on the composition and chemical states of Co-NC-10, X-ray photoelectron spectroscopy (XPS) was applied. The XPS survey spectra of Co-NC-0 and Co-NC-10 confirm the presence of Co, C, N and O in both samples. Notably, compared with Co-NC-0, the N signal in the survey spectrum of Co-NC-10 is significantly enhanced, as shown in Fig. S8. The high-resolution XPS spectrum of Co 2p (Fig. 2a) exhibits two main peaks

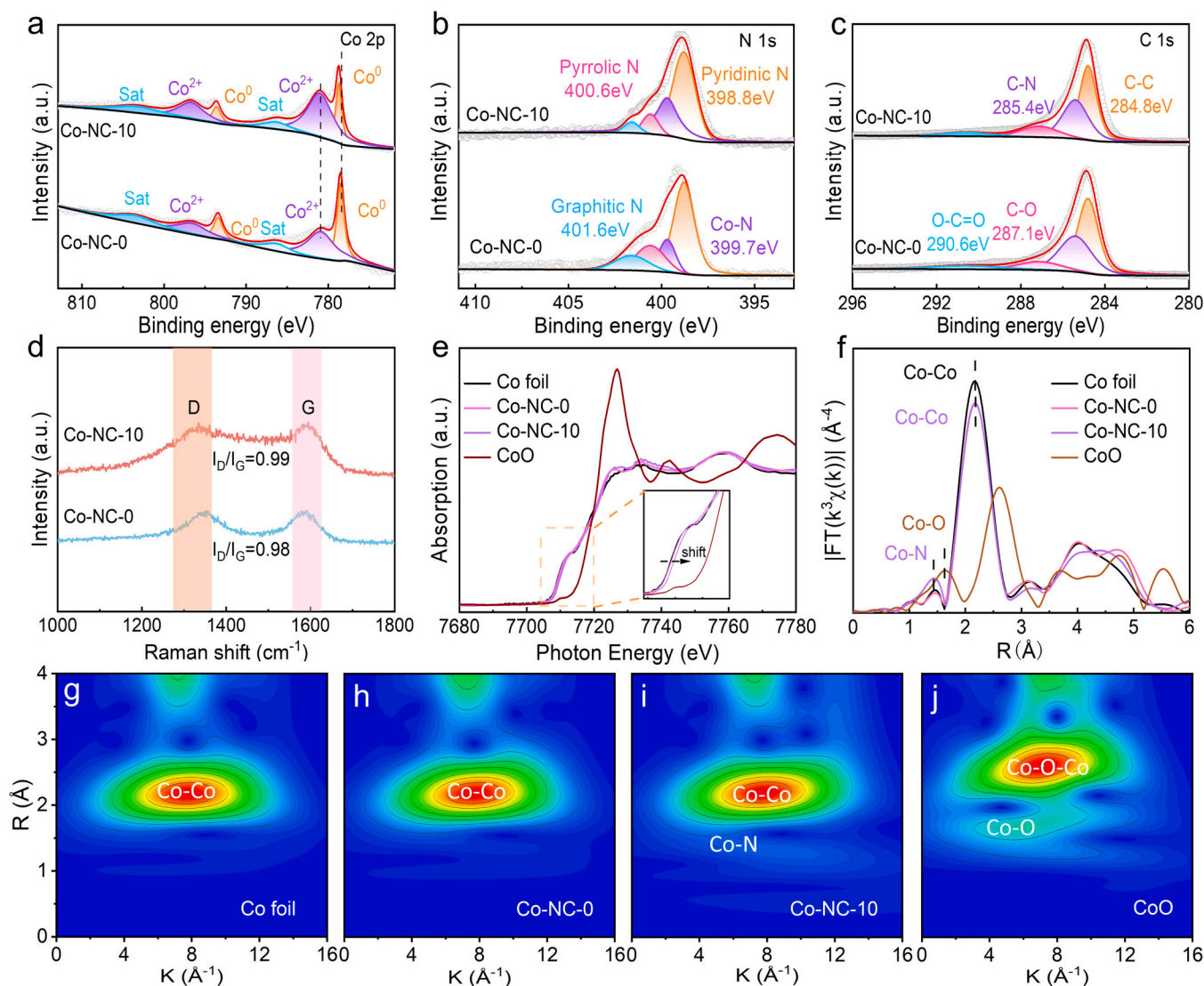


**Fig. 2.** Structural characterization of the catalyst. (a) High-resolution XPS spectra of Co 2p region for Co-NC-0 and Co-NC-10. (b) High-resolution XPS spectra of N 1s region for Co-NC-0 and Co-NC-10. (c) High-resolution XPS spectra of C 1s region for Co-NC-0 and Co-NC-10. (d) Raman spectra of Co-NC-0 and Co-NC-10, with the calculated intensity ratio  $I_D/I_G$  labeled. (e) Normalized Co K-edge XANES spectra; inset shows enlarged edge position. (f) Co K-edge FT-EXAFS spectra in R space for Co foil, Co-NC-0, Co-NC-10 and CoO. (g-j) WT-EXAFS of Co K-edge EXAFS data for Co foil (g), Co-NC-0 (h), Co-NC-10 (i) and CoO (j).

corresponding to Co  $2p_{3/2}$  and Co  $2p_{1/2}$ , along with two broad satellite peaks at approximately 786.5 eV and 803.7 eV. The Co  $2p_{3/2}$  and Co  $2p_{1/2}$  peaks of Co-NC-10 can be deconvoluted into two components, corresponding to metallic Co<sup>0</sup> (778.7/793.6 eV) and Co<sup>2+</sup> species (781.1/796.8 eV). Likewise, the Co  $2p_{3/2}$  and Co  $2p_{1/2}$  peaks of Co-NC-0 can also be fitted with two components, assigned to Co<sup>0</sup> (778.5/793.4 eV) and Co<sup>2+</sup> species (780.9/796.6 eV) [42]. Compared with Co-NC-0, the Co-NC-10 sample exhibits a slight positive shift in binding energy [43]. This observation suggests that the formation of Co-N bonds induces electron withdrawal from the Co centers, leading to a reduced electron density and a higher oxidation state of Co. As shown in Fig. 2b, the N 1s spectra of Co-NC-0 and Co-NC-10 can be fitted with four distinct nitrogen species, namely pyridinic N (398.8 eV), Co-N (399.7 eV), pyrrolic N (400.6 eV), and graphitic N (401.6 eV) [44]. Notably, compared with Co-NC-0, the Co-N content in Co-NC-10 is significantly increased, indicating that nitrogen doping effectively promotes the formation of Co-N bonds. Fig. 2c presents the C 1s spectra of Co-NC-0 and Co-NC-10, which exhibit peaks at 284.8, 285.4, 287.1, and 290.6 eV, corresponding to C-C, C-N, C-O, and O-C=O bonds, respectively [45]. The presence of Co-N and C-N bonds indicates the

successful incorporation of nitrogen at the Co-C interface on the surface of Co NPs, leading to the formation of Co-NC sites. To investigate the degree of graphitization and defect formation, Raman spectra of both pyrolyzed catalysts were collected. As shown in Fig. 2d, two prominent peaks are observed at 1330 and 1592 cm<sup>-1</sup>, corresponding to the D and G bands of carbon, respectively. The D band is typically associated with defects and disordered structures in carbon, whereas the G band arises from the in-plane vibrations of sp<sup>2</sup>-hybridized carbon, characteristic of highly ordered graphite structures [46]. Therefore, the  $I_D/I_G$  ratio can, in most cases, be used to determine the degree of disorder in carbon materials. As shown in Fig. 2d, Co-NC-10 shows a slightly higher  $I_D/I_G$  ratio (0.99) compared with Co-NC-0 (0.98), suggesting a marginal increase in defect density induced by nitrogen doping. These defects can facilitate the anchoring and stabilization of Co NPs and promote the formation of Co-NC active sites, thereby modulating the local electronic structure and interfacial charge distribution [47,48]. Such electronic modulation, in turn, is beneficial for enhancing electronic transport properties and thereby promoting catalytic reactions. To elucidate the local coordination environment and chemical state of Co in Co-NC-0 and Co-NC-10, X-ray absorption near-edge structure (XANES) and

extended X-ray absorption fine structure (EXAFS) analyses were performed. The Co K-edge XANES spectra in Fig. 2e show that the absorption edge of Co-NC-10 lies between those of Co foil and CoO, suggesting that the oxidation state of Co is between 0 and +2. Notably, the absorption edge of Co-NC-10 is closer to that of Co foil, suggesting that the Co species mostly keep metallic characteristics. Compared with that of Co-NC-0, the absorption edge of Co-NC-10 shows a positive shift, which means that nitrogen incorporation imparts electron-deficient Co species and also slightly increases the Co oxidation state [42]. As shown in the Fourier transform EXAFS (FT-EXAFS) spectra (Fig. 2f), Co-NC-10 exhibits a prominent peak at 2.16 Å, which matches the main peak of Co foil and is assigned to Co-Co bonding, along with an additional peak at 1.43 Å attributed to Co-N coordination [49,50]. In contrast, Co-NC-0 exhibits a much weaker Co-N coordination signal at 1.43 Å. This suggests that the enhanced Co-N bonding in Co-NC-10 is likely associated with the incorporation of nitrogen atoms at the Co-C interface of the Co NPs. Wavelet transform (WT) analysis (Fig. 2g-j) clearly shows that Co-NC-10 exhibits distinct contour peaks in k-space at  $\approx 7.7$  and  $\approx 5.9 \text{ \AA}^{-1}$ , corresponding to Co-Co and Co-N coordination, respectively, whereas the Co-N coordination signal in Co-NC-0 is much weaker [10]. Based on the combined XPS and XAS results, the formation of Co-NC sites on the surface of Co NPs induces charge transfer and redistributes the local electronic structure of Co in Co-NC-10.

### 3.2. eNO<sub>3</sub>RR performance measurements

The eNO<sub>3</sub>RR measurements were carried out in a conventional H-type electrolytic cell equipped with a standard three-electrode configuration. Prior to testing, a series of standard solutions with different concentrations of NO<sub>3</sub><sup>-</sup>-N, NO<sub>2</sub><sup>-</sup>-N, and NH<sub>3</sub>-N were prepared, and the corresponding calibration curves were obtained by colorimetry (Fig. S9). Following the electrocatalytic eNO<sub>3</sub>RR, a measured volume of electrolyte was collected from the cathodic chamber and diluted. The concentrations of NO<sub>3</sub><sup>-</sup>-N, NO<sub>2</sub><sup>-</sup>-N, and NH<sub>3</sub>-N were then determined by colorimetry to calculate the NH<sub>3</sub> FE, NH<sub>3</sub> yield, selectivity, and NO<sub>3</sub><sup>-</sup> conversion rate. In addition, a separate set of standard solutions with varying concentrations of NO<sub>3</sub><sup>-</sup>-N, NO<sub>2</sub><sup>-</sup>-N, and NH<sub>3</sub>-N were prepared and analyzed by ion chromatography to establish the corresponding calibration curves (Fig. S10-S12), thereby validating the accuracy of the colorimetric method. Linear sweep voltammetry (LSV) was performed in 1 M KOH electrolyte with and without 0.1 M KNO<sub>3</sub> to evaluate the catalytic activity trends of the Co-NC-0, Co-NC-5, Co-NC-10, and Co-NC-15 catalysts toward nitrate reduction. As shown by the LSV curves in Fig. 3a and S13a, the current densities of all catalysts increase markedly after nitrate addition, indicating that these catalysts exhibit pronounced catalytic activity toward eNO<sub>3</sub>RR. Compared with Co-NC-5 and Co-NC-15, Co-NC-10 requires a lower overpotential to initiate the reaction. In the same potential window, Co-NC-10 exhibits a higher current density, representing faster eNO<sub>3</sub>RR kinetics and a higher nitrate reduction rate. Moreover, the Tafel plots for these catalysts were calculated from the LSV data (Fig. 3b and S13b). The Tafel slopes for Co-NC-0, Co-NC-5, Co-NC-10, and Co-NC-15 are 182.8, 162.3, 122.4, and 169.9 mV dec<sup>-1</sup>, respectively. Co-NC-10 shows the lowest Tafel slope among all catalysts, implying favorable reaction kinetics. The improved eNO<sub>3</sub>RR catalytic performance mainly originates from N-doping, which enhances interfacial charge transfer on the surface of Co NPs to facilitate \*H generation. Cyclic voltammetry (CV) at scan rates ranging from 40 to 120 mV s<sup>-1</sup> was employed to measure the double-layer capacitance (C<sub>dl</sub>), from which the electrochemically active surface area (ECSA) was derived to estimate the number of active sites. As shown in Fig. 3c, S14 and S15a, Co-NC-10 exhibits a C<sub>dl</sub> value of 6.58 mF·cm<sup>-2</sup> and an ECSA value of 164.5 cm<sup>2</sup>, markedly higher than those of Co-NC-0 (3.19 mF·cm<sup>-2</sup>, 79.75 cm<sup>2</sup>), Co-NC-5 (3.43 mF·cm<sup>-2</sup>, 85.75 cm<sup>2</sup>), and Co-NC-15 (3.27 mF·cm<sup>-2</sup>, 81.75 cm<sup>2</sup>). This indicates that a greater number of catalytic active sites are exposed to the electrolyte solution. More importantly, Co-NC-10 maintains a higher ECSA-

normalized current density than all other catalysts, further highlighting its superior intrinsic activity and resulting in an accelerated reaction rate (Fig. S15b). Additionally, electrochemical impedance spectroscopy (EIS) was performed. As shown in Fig. S16, Co-NC-10 exhibits the smallest semicircle diameter in the Nyquist plot compared to Co-NC-0, Co-NC-5, and Co-NC-15, indicating the lowest charge transfer resistance. This facilitates faster reaction kinetics and reduces energy loss [51]. In view of the fact that Co-NC-10 exhibits the best electrochemical performance among Co-NC-0, Co-NC-5, Co-NC-10, and Co-NC-15, Co-NC-0 and Co-NC-10 were selected as the main subjects to discuss their eNO<sub>3</sub>RR performance.

Subsequently, to investigate the catalytic performance of Co-NC-10 at different NO<sub>3</sub><sup>-</sup> concentrations, the catalyst was tested for eNO<sub>3</sub>RR. As can be seen from Fig. S17, the catalyst exhibits relatively low NH<sub>3</sub> FE and NH<sub>3</sub> yield at 0.03 M NO<sub>3</sub><sup>-</sup>, but both NH<sub>3</sub> FE and NH<sub>3</sub> yield increase markedly at 0.1 M. This can be attributed to mass transport efficiency. At low NO<sub>3</sub><sup>-</sup> concentrations, the limited nitrate flux slows the reaction kinetics and promotes the competitive HER (Fig. S18), resulting in an increased H<sub>2</sub> FE.

With increasing NO<sub>3</sub><sup>-</sup> concentration, enhanced mass transport facilitates the delivery and adsorption of NO<sub>3</sub><sup>-</sup> at the catalyst interface, while improving the effective utilization of \*H intermediates during subsequent hydrogenation steps and suppressing H<sub>2</sub> evolution. Consequently, the eNO<sub>3</sub>RR process is promoted, leading to enhanced NH<sub>3</sub> FE and NH<sub>3</sub> yield [52]. To determine its optimal reaction potential, we performed eNO<sub>3</sub>RR tests with the catalyst at different applied potentials and measured the corresponding NH<sub>3</sub> FE and NH<sub>3</sub> yield. As shown in Fig. 3d-e and S19a-b, the NH<sub>3</sub> FE and NH<sub>3</sub> yield of Co-NC-10 first increase and then decrease with increasing potential. The highest NH<sub>3</sub> FE of  $95.82 \pm 1.29\%$  and NH<sub>3</sub> yield of  $0.989 \pm 0.03 \text{ mmol h}^{-1} \text{ cm}^{-2}$  were obtained at -0.4 V vs. RHE. These values are approximately 1.25 and 1.43 times higher, respectively, than those of Co-NC-0. The chronoamperometric (i-t) curves of Co-NC-0 and Co-NC-10, measured at different applied potentials, are shown in Fig. S20. With an increase in the applied cathodic potential from -0.2 V to -0.4 V, the NH<sub>3</sub> FE and NH<sub>3</sub> yield gradually improve, while the H<sub>2</sub> FE gradually decreases. This is because \*H is effectively utilized during the hydrogenation process of the eNO<sub>3</sub>RR, thereby suppressing the HER. With a further increase in potential, however, the competition from HER becomes increasingly significant, resulting in an increased H<sub>2</sub> FE and consequently decreasing both the NH<sub>3</sub> FE and NH<sub>3</sub> yield [50]. The optimal reaction potentials for Co-NC-5 and Co-NC-15 are presented in Fig. S19c-d. In addition, Fig. 3e shows that the NO<sub>3</sub><sup>-</sup> conversion rate follows a volcano-shaped curve, with Co-NC-10 achieving its maximum at -0.4 V vs. RHE, which correlates well with its NH<sub>3</sub> FE. More importantly, Co-NC-10 maintains NH<sub>3</sub> selectivity above 97% at all tested potentials, while the NO<sub>2</sub><sup>-</sup> FE remains negligible, demonstrating its excellent catalytic performance for the eNO<sub>3</sub>RR. Fig. 3f and S21 show the eNO<sub>3</sub>RR performance of different catalysts at the optimal reaction concentration and potential. Co-NC-0 exhibits poor NO<sub>3</sub><sup>-</sup> conversion ( $39.28 \pm 1.53\%$ ) and NH<sub>3</sub> FE ( $52.48 \pm 1.02\%$ ). With increasing N content, the growth and aggregation of Co NPs in Co-NC-5 and Co-NC-10 are inhibited. The C<sub>dl</sub> and ECSA values gradually increase, indicating that more active sites are exposed to the electrolyte. In addition, the increased N content modulates the electronic structure of Co sites, optimizes the adsorption and desorption of nitrogen-containing intermediates during the eNO<sub>3</sub>RR process, and promotes the effective utilization of \*H during the hydrogenation steps, thereby gradually increasing the NO<sub>3</sub><sup>-</sup> conversion ( $63.37 \pm 1.42\%$  and  $90.13 \pm 1.48\%$ ) and NH<sub>3</sub> FE ( $76.58 \pm 1.49\%$  and  $95.82 \pm 1.29\%$ ). However, although the size of Co NPs in Co-NC-15 is further reduced with increasing nitrogen content, excessive nitrogen incorporation may lead to a further decrease in the electron density around Co sites, which is unfavorable for NO<sub>3</sub><sup>-</sup> activation. Meanwhile, the charge-transfer resistance and Tafel slope of Co-NC-15 are not further reduced compared with those of Co-NC-10, indicating that the eNO<sub>3</sub>RR kinetics are not further improved. Consequently, the NO<sub>3</sub><sup>-</sup> conversion

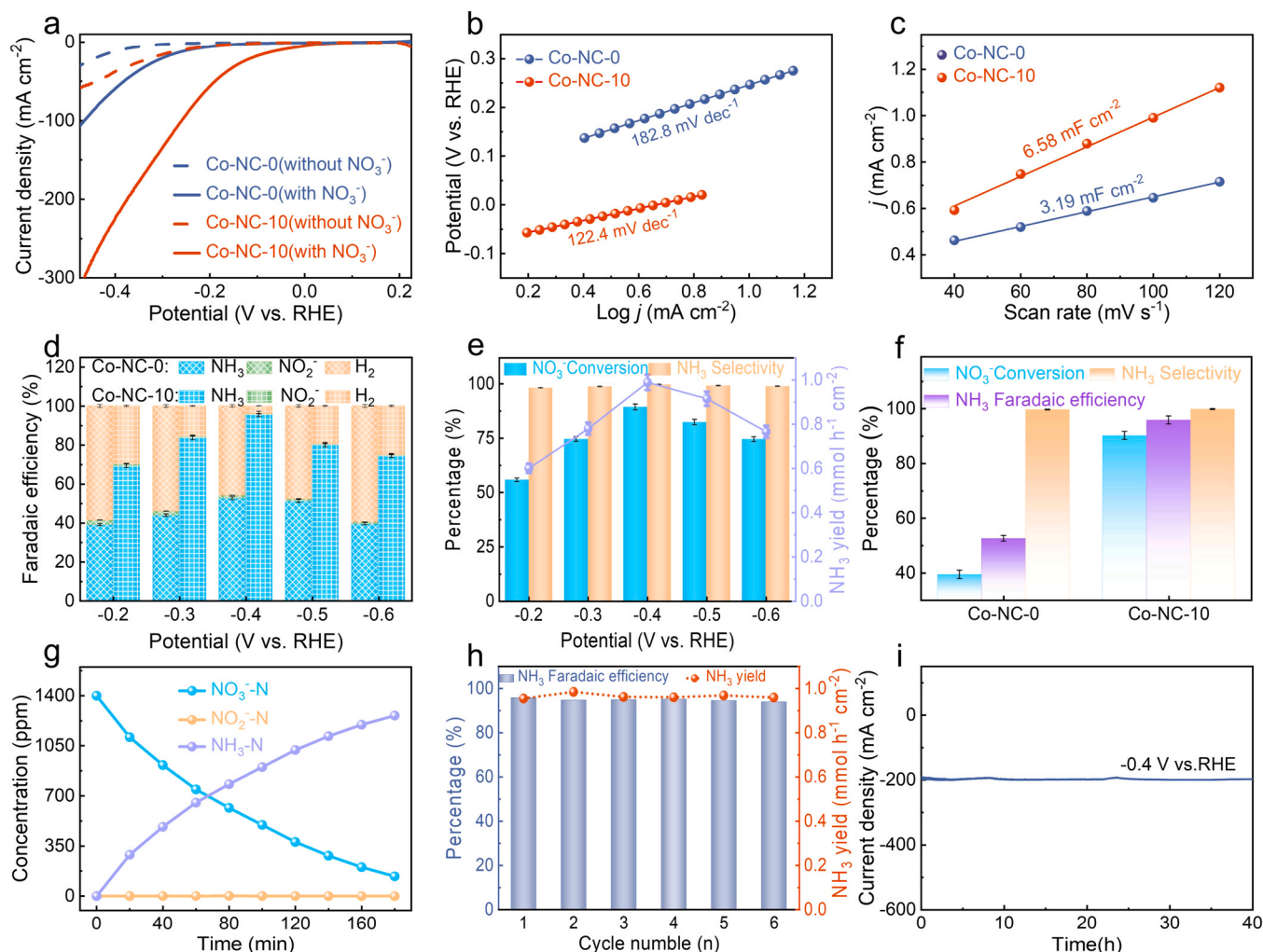


**Fig. 3.** eNO<sub>3</sub>RR performance. (a) LSV curves in 1 M KOH with and without 0.1 M NO<sub>3</sub><sup>-</sup>. (b) Corresponding Tafel plots of Co-NC-0 and Co-NC-10. (c) C<sub>dl</sub> derived from cyclic voltammetry at different scan rates. (d) NH<sub>3</sub> FE, NO<sub>2</sub><sup>-</sup> FE, and H<sub>2</sub> FE of Co-NC-0 and Co-NC-10 at different potentials (vs. RHE). (e) NO<sub>3</sub><sup>-</sup> conversion, NH<sub>3</sub> selectivity and NH<sub>3</sub> yield of Co-NC-10. (f) Comparison of NO<sub>3</sub><sup>-</sup> conversion, NH<sub>3</sub> selectivity and NH<sub>3</sub> FE between Co-NC-0 and Co-NC-10 at -0.4 V vs. RHE. (g) Time-dependent changes of ion concentration on Co-NC-10 at -0.4 V vs. RHE. (h) The NH<sub>3</sub> yield and NH<sub>3</sub> FE of Co-NC-10 at -0.4 V vs. RHE during six cycling tests. (i) Long-term chronoamperometric (i-t) curve of Co-NC-10 during eNO<sub>3</sub>RR electrolysis.

(46.14 ± 1.45%) and NH<sub>3</sub> FE (64.36 ± 1.26%) of Co-NC-15 decrease. During the reaction, the cathodic electrolyte of Co-NC-10 was collected every 20 min for analysis, as shown in Fig. 3g. As the reaction proceeded, the NO<sub>3</sub><sup>-</sup>-N concentration continuously decreased, the NH<sub>3</sub>-N concentration steadily increased, and the NO<sub>2</sub><sup>-</sup>-N concentration remained negligible, indicating that Co-NC-10 effectively prevents the accumulation of NO<sub>2</sub><sup>-</sup>. The dynamic changes in the ion concentrations for Co-NC-0 during the reaction are shown in Fig. S22. Despite maintaining high selectivity, the ammonia yield of Co-NC-0 is still relatively low, which may be attributed to the competitive HER consuming some electrons and protons, thereby weakening the NO<sub>3</sub><sup>-</sup> reduction process.

The stability and durability of Co-NC-10 during eNO<sub>3</sub>RR were evaluated through six consecutive cycles totaling 18 h at -0.4 V vs. RHE. As illustrated in Fig. 3h and S23, both the NH<sub>3</sub> FE and NH<sub>3</sub> yield demonstrate good stability without noticeable decay. The maximum NH<sub>3</sub> FE (95.68%) was observed in the first cycle, while the maximum NH<sub>3</sub> yield (0.979 mmol h<sup>-1</sup> cm<sup>-2</sup>) was observed in the second cycle. To investigate the morphological and structural changes of Co-NC-10 after six consecutive cycles, a series of characterizations were performed. SEM and TEM images obtained after the cycling tests reveal that the diamond-shaped framework structure is well preserved, with no obvious structural collapse or aggregation of Co NPs observed (Fig. S24). The

XRD patterns after six eNO<sub>3</sub>RR cycles (Fig. S25) show that the diffraction peak positions and intensities remain essentially unchanged, indicating the preservation of the crystalline structure. Furthermore, the XPS survey spectrum of Co-NC-10 after cycling exhibits no obvious changes, suggesting that the overall elemental composition of the catalyst remains stable (Fig. S26a). The Co 2p, N 1s, and C 1s XPS spectra after cycling exhibit no significant changes compared with those of the pristine catalyst, suggesting the overall preservation of the surface chemical composition and structure of the catalyst during long-term electrochemical cycling (Fig. S26b-d). ICP-AES analysis further demonstrates that the Co content decreases only slightly from 10.73 wt% to 10.67 wt% after cycling, corresponding to a negligible decrease of 0.06 wt% (Table S2). These results confirm the excellent structural and compositional stability of Co-NC-10 during eNO<sub>3</sub>RR operation. Beyond the cycling stability test, Co-NC-10 was further subjected to a long-term chronoamperometric electrolysis test (Fig. 3i) to evaluate its operational stability during continuous eNO<sub>3</sub>RR. During the 40 h test, the current density remained stable without noticeable decay. Relative to previously reported Co-based catalysts, Co-NC-10 demonstrates comparable or superior NH<sub>3</sub> FE and NH<sub>3</sub> yield, as summarized in Table S3. To exclude any potential influence from the carbon paper substrate or airborne nitrogen-containing species on the eNO<sub>3</sub>RR process, we performed

control experiments under three conditions: with and without nitrate in the electrolyte, and without the catalyst. As shown in Fig. S27, only trace amounts of  $\text{NH}_3$  were detected under the conditions of bare carbon paper or in the presence of the catalyst without nitrate electrolyte. In addition, isotope-labeling experiments were performed using  $^{14}\text{NO}_3^-$  and  $^{15}\text{NO}_3^-$  as nitrogen sources (Fig. S28). The corresponding  $^1\text{H}$  nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra exhibited the characteristic triplet of  $^{14}\text{NH}_4^+$  and the characteristic doublet of  $^{15}\text{NH}_4^+$ , respectively. These results confirm that the generated  $\text{NH}_3$  originates from nitrate reduction catalyzed by Co-NC-10 and exclude the possible contribution of airborne nitrogen-containing species to  $\text{NH}_3$  formation. Furthermore, to verify the accuracy of the colorimetric detection method, ion chromatography (IC) was employed for comparison. As shown in Fig. S29, the  $\text{NH}_3$  FE,  $\text{NH}_3$  yield,  $\text{NO}_3^-$  conversion, and  $\text{NH}_3$  selectivity calculated from the IC data closely match those obtained by the colorimetric method, thus validating the reliability of our measurements.

### 3.3. Mechanism analysis of Co-NC-10 catalyst

In alkaline media, the  $^*\text{H}$  required for  $\text{eNO}_3\text{RR}$  hydrogenation is primarily derived from interfacial water molecules on the catalyst surface. Analysis of the in situ Raman spectra of Co-NC-0 and Co-NC-10 in

the 3000–3700  $\text{cm}^{-1}$  region reveals distinct vibrational features of interfacial water. As shown in Fig. 4a, interfacial water can be categorized into three types: tetra-coordinated hydrogen-bonded water (4-HB- $\text{H}_2\text{O}$ ), bi-coordinated hydrogen-bonded water (2-HB- $\text{H}_2\text{O}$ ), and alkali metal-ion-coordinated water ( $\text{K}^+\text{-H}_2\text{O}$ ) [53,54]. The Raman signal intensities of the three types of interfacial water vary with the applied potential. As the potential decreases, the proportion of  $\text{K}^+\text{-H}_2\text{O}$  in Co-NC-10 increases significantly from 5.85% to 8.15%, whereas the proportion of  $\text{K}^+\text{-H}_2\text{O}$  in Co-NC-0 remains relatively low (Fig. S30). Moreover, the direct comparison of the Raman spectra of Co-NC-0 and Co-NC-10 under identical applied potentials (Fig. S31) reveals that the interfacial water-related Raman signal (3000–3700  $\text{cm}^{-1}$ ) is consistently stronger for Co-NC-10 than for Co-NC-0. This indicates that Co-NC-10 effectively promotes water dissociation and creates an environment rich in  $^*\text{H}$ , thereby facilitating efficient  $\text{eNO}_3\text{RR}$ . To further verify the critical role of a continuous  $^*\text{H}$  supply in the hydrogenation of reaction intermediates toward ammonia formation, CV measurements were also carried out. CV curves show that both Co-NC-0 and Co-NC-10 exhibit  $^*\text{H}$  peaks at approximately 0.3 V vs. RHE, with the  $^*\text{H}$  peak intensity of Co-NC-10 being higher than that of Co-NC-0 (Fig. S32) [51,55]. This observation indicates the formation of  $^*\text{H}$  during  $\text{eNO}_3\text{RR}$  and demonstrates that Co-NC-10 exhibits a significantly

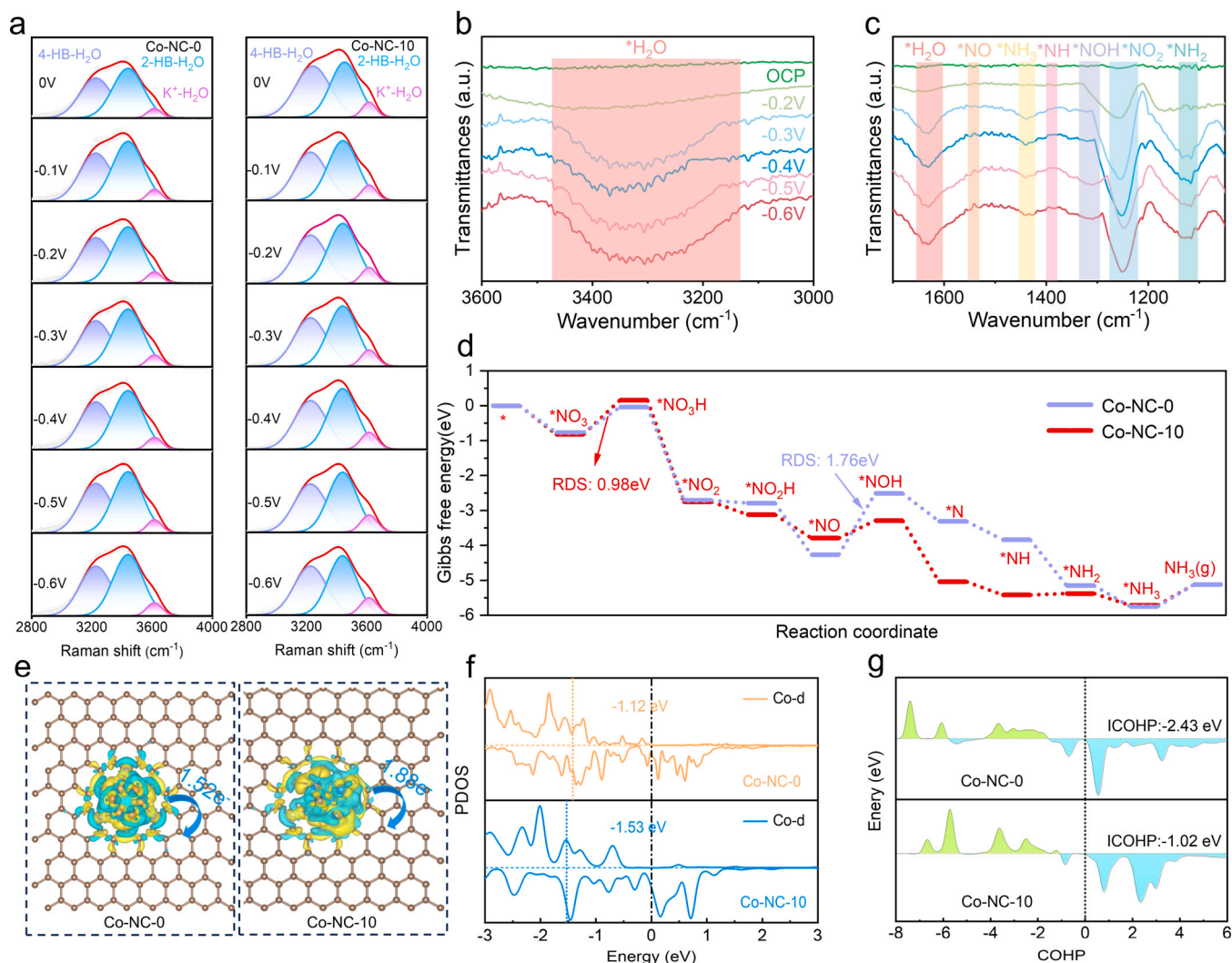


**Fig. 4.** In situ characterization and theoretical calculations. (a) In situ Raman spectra of Co-NC-0 (left) and Co-NC-10 (right) recorded under different applied potentials (vs. RHE). (b, c) In situ FTIR spectra of Co-NC-10 at different potentials (vs. RHE) in the wavenumber ranges of 3000–3600  $\text{cm}^{-1}$  (b) and 1150–1700  $\text{cm}^{-1}$  (c). (d) Gibbs free energy profiles for the  $\text{NO}_3^-$  reduction pathway on Co-NC-0 and Co-NC-10 calculated using DFT. (e) Charge density difference and Bader charge transfer at the interface of Co-NC-0 and Co-NC-10. (f) Calculated Co d-band PDOS of Co-NC-0 and Co-NC-10. (g) COHP analysis of Co-NC-0 and Co-NC-10.

enhanced  $^*H$  generation capability compared to Co-NC-0. Furthermore, as the  $NO_3^-$  concentration increases, the intensity of the  $^*H$  peak for Co-NC-10 gradually decreases, indicating an enhanced utilization efficiency of the generated  $^*H$ . Subsequently,  $^*H$  scavenging tests were conducted by employing tertiary butanol (TBA) at varying concentrations as a trapping agent for  $^*H$  [56]. As shown in Fig. S33, when the TBA concentration increased from 0 to 1000 mM, the  $NO_3^-$  reduction kinetics of Co-NC-10 were progressively inhibited. Concurrently, the  $NH_3$  FE and  $NH_3$  yield decreased rapidly, accompanied by a significant drop in the current density. These experiments confirm the essential role of  $^*H$  in the hydrogenation steps of  $eNO_3RR$ . This indicates that the formation of Co-NC sites on Co NPs, induced by nitrogen incorporation, facilitates the generation of  $^*H$  on the surface of Co NPs, thereby accelerating key hydrogenation steps and improving overall catalytic performance in  $eNO_3RR$ .

To confirm the reaction pathway, the reaction intermediates during the  $eNO_3RR$  were identified using in situ electrochemical Fourier transform infrared (FTIR) spectroscopy. Fig. 4b-c show the appearance of spectral bands associated with reaction intermediates at different applied potentials. The band at  $1250\text{ cm}^{-1}$  is attributed to the asymmetric stretching vibration of  $^*NO_2$ . The band at  $1302\text{ cm}^{-1}$  is associated with the bending vibration of  $^*NOH$ , while the band at  $1540\text{ cm}^{-1}$  is assigned to  $^*NO$  [36,50,57]. These bands correspond to key intermediates in the nitrate reduction process. Absorption peaks at 1112, 1397, and  $1440\text{ cm}^{-1}$  are assigned to  $^*NH_2$ ,  $^*NH$ , and  $^*NH_3$ , respectively, which signify the formation of hydrogenated intermediates and ammonia [49,58,59]. Additionally, the broad spectral features centered at  $1634\text{ cm}^{-1}$  and in the  $3000\text{--}3600\text{ cm}^{-1}$  region are attributed to the vibrational modes of adsorbed water ( $^*H_2O$ ) [54]. With increasing applied potential, the intensities of these spectral features gradually increase, clearly indicating the progressive conversion of  $NO_3^-$  to  $NH_3$  during  $eNO_3RR$ . Therefore, we propose that the conversion of  $NO_3^-$  to  $NH_3$  likely proceeds via the following pathway:  $^*NO_3 \rightarrow ^*NO_2 \rightarrow ^*NO \rightarrow ^*NOH \rightarrow ^*N \rightarrow ^*NH \rightarrow ^*NH_2 \rightarrow ^*NH_3$  [60].

To assess the influence of nitrogen doping on catalytic performance, density functional theory (DFT) calculations were performed to examine the electronic structures of Co-NC-0 and Co-NC-10, as well as the Gibbs free energy changes of each elementary step during the  $eNO_3RR$ . As shown in Fig. 4d, compared with Co-NC-0, the free-energy changes associated with each elementary step of nitrate reduction on Co-NC-10 are significantly more moderate. The optimized structural models of Co-NC-0 and Co-NC-10 and the corresponding adsorption configurations of the reaction intermediates are provided in Fig. S34-S35. The maximum free-energy barrier decreases from 1.76 eV to 0.98 eV, and the rate-determining step (RDS) shifts from the intermediate  $^*NO \rightarrow ^*NOH$  hydrogenation step to the initial  $^*NO_3 \rightarrow ^*NO_3H$  step [27]. This shift indicates that N doping mainly alleviates the energy bottleneck associated with the original  $^*NO$  hydrogenation step, rather than making the initial nitrate hydrogenation process intrinsically unfavorable. Therefore, the overall free-energy profile of Co-NC-10 is more favorable for nitrate-to- $NH_3$  conversion. The differential charge density plot (Fig. 4e) shows that N-doping induces a greater electron transfer around the Co NPs, indicating a charge redistribution in their vicinity. This conclusion is consistent with the analysis of the XPS results. Additionally, the projected density of states (PDOS) and d-band center of the electrocatalysts were calculated. As shown in Fig. 4f, the Co-d states are primarily distributed below the Fermi level, and both systems exhibit characteristic d-electron features of transition metals. Compared with Co-NC-0, the Co-d band center in Co-NC-10 shifted from  $-1.12\text{ eV}$  to  $-1.53\text{ eV}$ . The distance between the d-band center and the Fermi level is widely recognized as a key descriptor of the adsorption properties of reactants. In the  $eNO_3RR$  process, the adsorption strength of reaction intermediates is precisely the critical parameter for predicting electrocatalytic activity. The highest electrocatalytic activity is achieved when reactants exhibit a moderate adsorption strength, which is governed by an optimal adsorption energy [26]. Based on this, it can be inferred that

nitrogen doping enhances the metal-support coupling, shifting the d-band center of Co appropriately away from the Fermi level, thereby moderately weakening the chemisorption strength of Co toward the reaction intermediates. Crystal orbital Hamilton population (COHP) analysis further reveals that nitrogen doping modulates the binding modes of key reaction intermediates (Fig. 4g). For Co-NC-0, the ICOHP value between  $^*NOH$  and Co is  $-2.43\text{ eV}$ , indicating strong  $^*NOH$ -Co bonding, thereby resulting in a high free energy barrier (1.76 eV) for the  $^*NO \rightarrow ^*NOH$  step. In contrast, for Co-NC-10, the ICOHP of the Co-N bond is significantly reduced to  $-1.02\text{ eV}$ , indicating a noticeably weakened adsorption of  $^*NOH$ . This weakened interaction renders the  $^*NOH$  intermediate more prone to subsequent hydrogenation and N-O bond cleavage, thereby avoiding its excessive stabilization and effectively lowering the overall reaction energy barrier.

#### 3.4. Performance evaluation of assembled Zn- $NO_3$ batteries

In this study, a Zn- $NO_3$  battery was assembled using Co-NC-10 as the cathode material and Zn as the anode material to evaluate its electrochemical performance (see Fig. 5a) [61]. As shown in Fig. 5b, the Zn- $NO_3$  battery based on Co-NC-10 exhibits a stable open-circuit voltage of 1.34 V (vs.  $Zn/Zn^{2+}$ ), surpassing that of the battery assembled with Co-NC-0 [51]. Additionally, the discharge polarization curve of the battery reveals that as the potential becomes more negative, the current density gradually increases, reaching a peak power density of  $9.25\text{ mW cm}^{-2}$  at a current density of  $11.6\text{ mA cm}^{-2}$  (Fig. 5c). This performance surpasses that of the Co-NC-0-based battery ( $6.18\text{ mW cm}^{-2}$ ), indicating that the assembled Zn- $NO_3$  battery possesses favorable energy output capability. Fig. 5d displays the stepwise discharge curves tested at different current densities for 1 h each to investigate the discharge performance of the assembled Zn- $NO_3$  battery. It can be observed that the battery maintains a stable initial potential across these varying current densities from 2 to  $10\text{ mA cm}^{-2}$ , and returns to its original potential upon resuming the  $2\text{ mA cm}^{-2}$  current density. This further highlights the battery's potential for practical application. Additionally, the  $NH_3$  yield and  $NH_3$  FE of the battery after 1 h of discharge at different current densities are shown in Fig. 5e. The  $NH_3$  yield gradually increases with current density, reaching a maximum of  $211.45\text{ }\mu\text{mol h}^{-1}\text{ cm}^{-2}$  at  $10\text{ mA cm}^{-2}$ , while the  $NH_3$  FE attains a maximum of 84.58% at a current density of  $8\text{ mA cm}^{-2}$ . Notably, the assembled battery successfully powered an embedded electronic timer for over 24 h (Fig. 5f). Furthermore, at a current density of  $4\text{ mA cm}^{-2}$ , the battery maintained a stable voltage output over 20 h, highlighting its excellent charge-discharge repeatability and durability (Fig. 5g) [49]. During a 15 h discharge test at a constant current density of  $8\text{ mA cm}^{-2}$ , both the  $NH_3$  yield and  $NH_3$  FE were nearly unchanged (Fig. 5h and S36), confirming the battery's exceptional stability and long-term durability. Therefore, the self-assembled Zn- $NO_3$  battery, using Co-NC-10 as the cathode catalyst, successfully integrates nitrate-to-ammonia reduction with chemical-to-electric energy conversion in a single device. This design enables it to function as a self-powered electrochemical reactor, which simultaneously converts pollutants ( $NO_3^-$ ) in nitrate-containing wastewater into valuable chemicals ( $NH_3$ ) while generating usable electricity, thus offering a novel approach for sustainable environmental remediation and energy recovery.

#### 4. Conclusion

In summary, we successfully synthesized a catalyst enriched with Co-NC sites (denoted as Co-NC-10) by using ZIF-67 as a precursor in combination with an N-doping strategy. Benefiting from the interfacial charge polarization induced by nitrogen regulation and the downward shift of the d-band center, the adsorption of key nitrogen-containing intermediates (e.g.,  $^*NOH$ ) is weakened while their hydrogenation is promoted, thereby accelerating the reaction kinetics of  $NO_3^-$  conversion

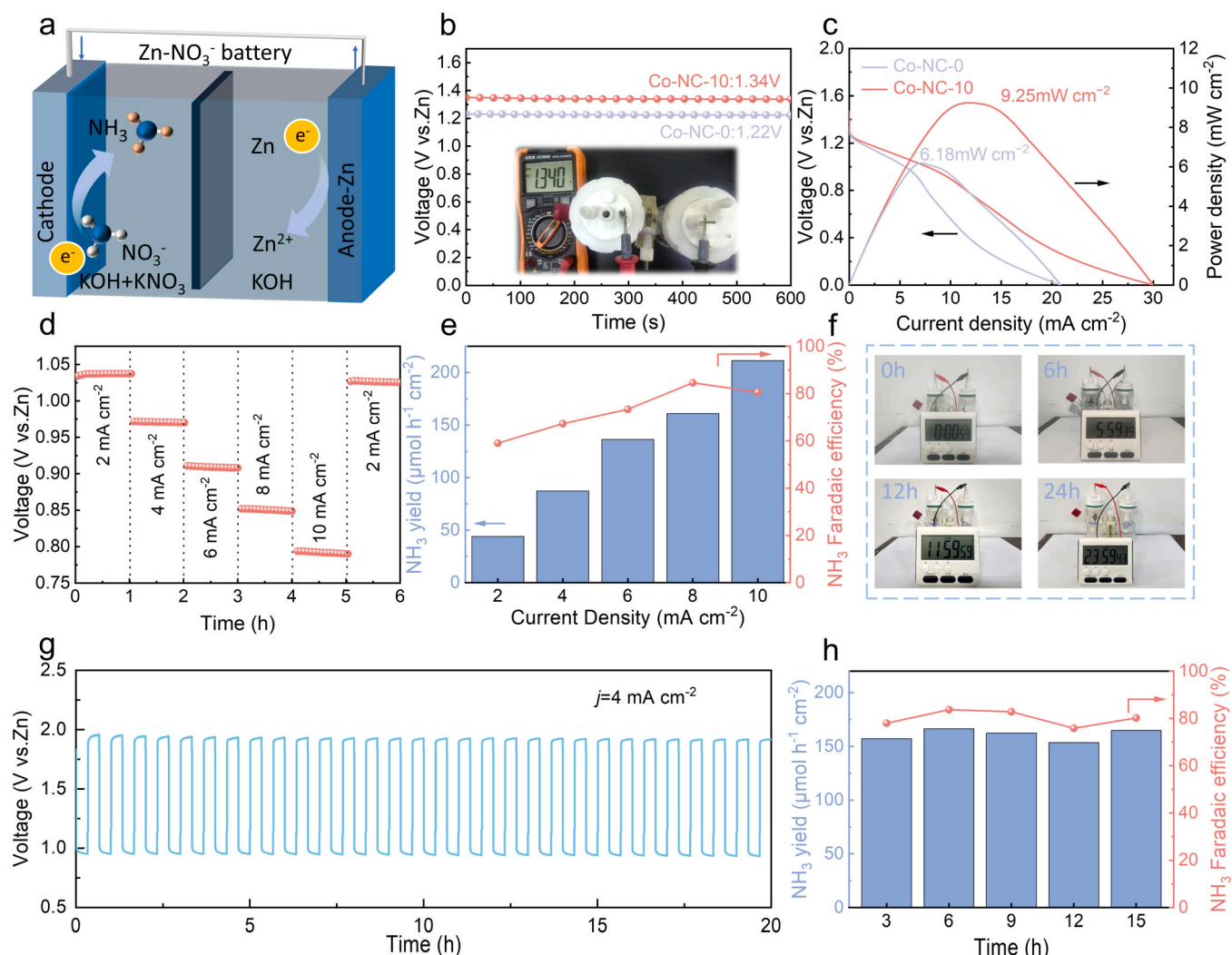


**Fig. 5.** Rechargeable Zn-NO<sub>3</sub> battery applications. (a) Operating schematic of the Zn-NO<sub>3</sub> battery. (b) Open-circuit potential (OCP) of Zn-NO<sub>3</sub> batteries assembled with Co-NC-10 and Co-NC-0 catalysts. (c) Power density versus current density polarization curves of batteries with the two catalysts. (d) Battery voltage stability under different current densities (2, 4, 6, 8, 10 mA cm<sup>-2</sup>). (e) NH<sub>3</sub> yield and NH<sub>3</sub> Faradaic efficiency of Co-NC-10 at varying current densities. (f) Photograph of a timer powered by a Zn-NO<sub>3</sub> battery. (g) Voltage stability of the battery during multiple charge-discharge cycles at a current density of 4 mA cm<sup>-2</sup>. (h) NH<sub>3</sub> yield and NH<sub>3</sub> Faradaic efficiency obtained at different time intervals during continuous discharge at 8 mA cm<sup>-2</sup>.

to NH<sub>3</sub>. As a result, Co-NC-10 achieves a high NH<sub>3</sub> Faradaic efficiency of 95.82% and an NH<sub>3</sub> yield of 0.989 mmol h<sup>-1</sup> cm<sup>-2</sup> at -0.4 V vs. RHE. After six consecutive cycles, both the NH<sub>3</sub> FE and the NH<sub>3</sub> yield show no significant decay, demonstrating excellent stability. Furthermore, a Zn-NO<sub>3</sub> battery using Co-NC-10 as the cathode and a Zn plate as the anode exhibited stable NH<sub>3</sub> production along with a peak power density of 9.25 mW cm<sup>-2</sup>. This work demonstrates that heteroatom doping serves as an effective strategy for constructing highly efficient and durable electrocatalysts, thereby providing a viable pathway to couple pollutant removal, NH<sub>3</sub> synthesis under mild conditions, and energy supply.

#### CRediT authorship contribution statement

**Wei Zhu:** Data curation, Formal analysis, Writing – original draft. **Jie Wang:** Methodology, Validation, Writing – original draft. **Wen Wang:** Supervision, Validation. **Jixin Yao:** Investigation, Methodology, Supervision. **Ying Meng:** Supervision, Visualization. **Xueqin Zu:** Resources, Supervision. **Qun Yang:** Supervision, Validation. **Guang Li:** Funding acquisition, Resources, Writing – review & editing. **Zhong Jin:** Resources, Supervision, Writing – review & editing.

#### Declaration of Competing Interest

We declare that we do not have any commercial or associative interest that represents a conflict of interest in connection with the work submitted. The article is published with the approval of all authors, all authors or groups with the article no conflict of interest or bad effect.

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## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jallcom.2026.190577.

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