

Article

Electrocatalytic Performance of MOF-Derived Cu-Co Bimetallic Electrode for Nitrate Reduction

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Abstract

The massive anthropogenic discharge of nitrate into aquatic environments disrupts the nitrogen cycle, posing threats to both ecosystems and human health. Electrocatalytic nitrate reduction to ammonia (ENRA) enables both nitrate removal and the production of high value-added NH_3 . Developing highly efficient and stable electrode materials, along with overcoming the rate-limiting step of nitrite accumulation, is crucial for enhancing the catalytic reduction of nitrate. In this study, by employing Cu as the core metal, a MOF-derived Cu-Co bimetallic catalytic electrode was fabricated as the cathode for converting nitrate to ammonia, while simultaneously resolving the issue of nitrite accumulation. The preparation parameters of the catalytic electrode were optimized, and the effects of current, initial pH, metal loading sequence, and other factors on ENRA performance were investigated. Experimental results demonstrate that the MOF-derived Cu-Co catalytic electrode achieved NO_3^- removal and NH_4^+ generation efficiencies of 94.26% and 90.58%, respectively, under a current density of 20 mA cm^{-2} for 150 min, with a marked suppression of NO_2^- accumulation. This study provides experimental evidence and technical support for the Cu-catalyzed electroreduction of nitrate to ammonia.

Keywords: electrocatalysis; Cu-Co catalyst; MOF-derived; nitrate reduction

1. Introduction

Nitrate is a ubiquitous inorganic contaminant in aquatic environments. It exhibits high water solubility and mobility, while being poorly immobilized in soil [1]. Excessive nitrate accumulation caused by anthropogenic emissions disrupts the nitrogen cycle, posing risks to both ecosystems and human health. Electrocatalytic reduction converts aqueous NO_3^- into N_2 or NH_4^+ as final products via electron transfer in water. Notably, $\text{NH}_3/\text{NH}_4^+$ serves as a critical chemical feedstock for fertilizer, pharmaceutical, and dye manufacturing, and it also plays a key role in energy storage and carbon-free energy transportation [2,3]. Therefore, electrocatalytic nitrate-to-ammonia conversion, featuring a simple process and low pollutant byproducts, offers a potential alternative route for both nitrate removal and ammonia synthesis.

Significant strides have been made in applying various electrocatalysts toward nitrate reduction [4–6]. The catalysts explored encompass single-metal, bimetallic, and metal-oxide types, commonly supported on nickel foam and nanocarbon [7–9]. Among these, transition metal catalysts, particularly those based on Cu, Fe, Co, Ni, and their alloys, have



Academic Editor: Kug-Seung Lee

Received: 21 June 2026

Revised: 14 July 2026

Accepted: 18 July 2026

Published: 21 July 2026

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been extensively studied due to their availability and economic viability [10,11]. Various coordinating atoms around Cu atoms can effectively regulate the electronic polarity of the catalytic active center. In addition, Cu catalysts are low-cost, possess tunable electronic structures, and can effectively suppress the hydrogen evolution reaction while accelerating the formation of NO_2^- intermediates [1,12,13]. Based on these advantages, Cu catalysts are considered among the most promising catalysts for the electrocatalytic nitrate reduction to ammonia (ENRA). Cu single-atom, copper oxides, and Cu-based alloy catalysts have all been reported to be effective in nitrate reduction [14,15].

Transition metal Cu exhibits a strong affinity for nitrate and can effectively reduce nitrate to nitrite. However, this leads to the undesired accumulation of nitrite, which adversely affects the ammonia selectivity. Previous studies have shown [16] that the introduction of a second metal can effectively overcome the linear scaling relationship of single-type active sites, prevent strong adsorption from inhibiting product desorption, and avoid activity loss. The second type active site primarily serves to further reduce the nitrite generated at Cu sites into the final product ammonia. Co exhibits certain electrocatalytic activity, owing to its various oxidation states that offer abundant active centers and facilitate electron transfer during the reaction [17–19]. Despite exhibiting electrocatalytic activity for nitrate reduction and generating negligible byproducts during the reaction, Co suffers from relatively weak nitrate adsorption and activation [20]. Combining the advantages of Cu and Co in electrocatalytic nitrate reduction, free nitrate in solution is adsorbed and reduced to nitrite at Cu sites, while the nitrite is further reduced to ammonia at Co sites. The synergistic effect of the Cu-Co dual-active sites effectively reduces the accumulation of intermediate byproducts, enhancing the performance of ENRA [21,22].

In addition to the type of active sites in catalysts, the dispersion of active sites is also a critical factor affecting the performance of catalysts. Metal–organic frameworks (MOFs) have attracted considerable attention due to their ordered porous structures and easily tunable pore sizes. Catalysts derived from MOFs can retain the morphological characteristics of MOF precursors, thereby preserving a large surface area that favors active site exposure. Furthermore, MOF materials readily enable the highly dispersed doping of heteroatoms, which can regulate the local electronic structure and thereby further boost the catalytic activity [23–25]. To improve the atomic utilization efficiency of metal catalysts, atomically dispersed metals derived from MOFs have also been employed in nitrate reduction to ammonia [26,27].

In this work, a MOF-derived dual-active-site catalytic electrode (CuCo-MOF-E) was constructed via anodic oxidation and cathodic electrodeposition, which was then employed to investigate its nitrate reduction performance in aqueous solutions. The effects of different current densities, initial pH values, and electrode fabrication conditions on the nitrate reduction performance of the prepared catalytic electrodes were investigated. This work strengthens the experimental foundation for the design of highly efficient electrocatalytic electrodes for the conversion of nitrate to ammonia.

2. Results and Discussion

2.1. Electrocatalytic Reduction Performance

MOF-derived CuCo catalytic electrodes were prepared via anodic oxidation and cathodic reduction methods. The $\text{Co}(\text{OH})_2/\text{Cu}$ electrode was obtained by electrodepositing Co onto a Cu mesh substrate. This electrode was then used as the anode to prepare a MOF-derived CuCo-MOF precursor via an anodic oxidation method [28]. Subsequently, the CuCo-MOF precursor was subjected to in situ electrochemical reconstruction [29] via a cathodic reduction process, forming the CuCo composite catalytic electrode, denoted as CuCo-MOF-E.

The SEM image of the CuCo-MOF-E electrode is shown in Figure 1a. The electrode surface exhibits a mesh-like structure with uniform Cu distribution. No obvious Co signal was detected by EDS scanning. The XRD patterns (Figure 1b) also indicate that the electrode presented a distinct Cu_2O signal and a relatively weak CoO signal. This is attributed to the use of Cu mesh as the electrode substrate and the low Co loading, where the intense Cu signal overshadows the Co signal. Similarly, no obvious Co signals were observed for the precursor catalyst powders CuCo-MOF. Since the electrode underwent electrochemical reconstruction via cathodic reduction, the electrode surface exists as $\text{Cu}_2\text{O}/\text{Cu}$, primarily in the form of low-valence Cu^+ . This serves as the catalytically active species for nitrate reduction, which is consistent with the XRD results. Further compositional analysis by ICP-MS was performed, and the results are shown in Table 1. The Co content in the CuCo-MOF-E electrode was quantitatively analyzed, confirming the successful fabrication of the CuCo-MOF-E bimetallic catalytic electrode. The low Co content (0.24%) may be attributed to the dissolution of Cu^{2+} from the Cu mesh during the anodic oxidation process for MOF precursor formation, which consequently limits the incorporation of Co.

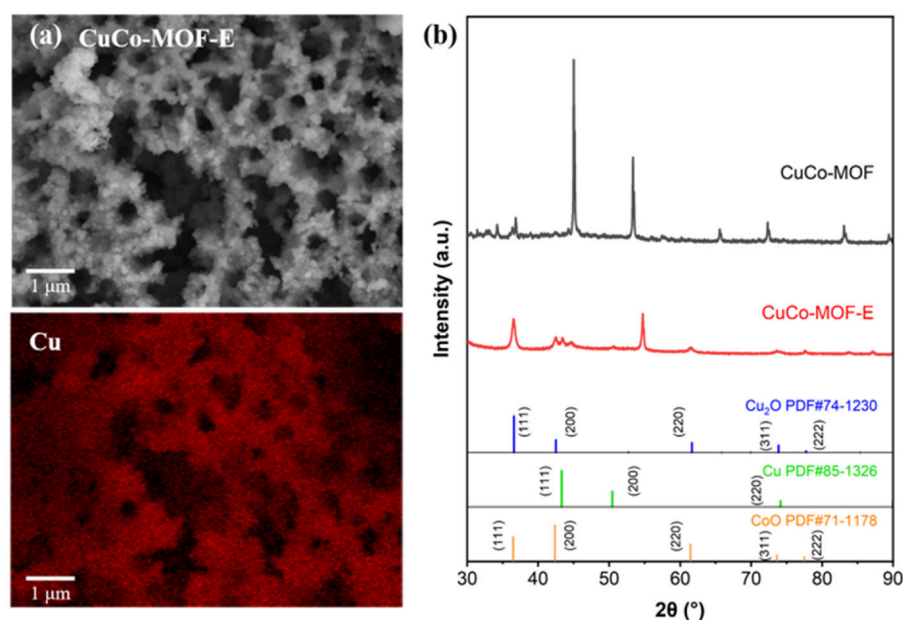


Figure 1. (a) SEM images and elemental distribution characterization of CuCo-MOF-E, (b) XRD patterns of Cu-MOF, CuCo-MOF, and the CuCo-MOF-E electrode.

Table 1. Concentration of Co in the CuCo-MOF-E catalytic electrode by ICP.

Element	Concentration (mg L^{-1})	Content (%)
Co	0.17×10^{-1}	0.24

To comparatively investigate the respective effects of Cu and Co on the reduction performance of the catalytic electrodes, CuCo-MOF-E, Cu-MOF-E (without Co), and $\text{Co}(\text{OH})_2/\text{Cu}$ (without Cu MOF structure) electrodes were prepared as working electrodes. Linear sweep voltammetry (LSV) was employed to investigate the nitrate reduction activity of the electrodes, as shown in Figure 2a. In a three-electrode system, the current densities of the LSV curves for Cu-MOF-E, $\text{Co}(\text{OH})_2/\text{Cu}$, and CuCo-MOF-E catalytic electrodes significantly increased in the presence of NO_3^- , indicating that these catalytic electrodes exhibit good reduction activity toward nitrate. Analysis of the electrochemical impedance spectroscopy (EIS) (Figure 2b) reveals that the charge transfer resistance of CuCo-MOF-

E is significantly lower than those of $\text{Co(OH)}_2/\text{Cu}$ and Cu-MOF-E. This suggests that CuCo-MOF-E has the fastest electron transfer efficiency in the nitrate reduction.

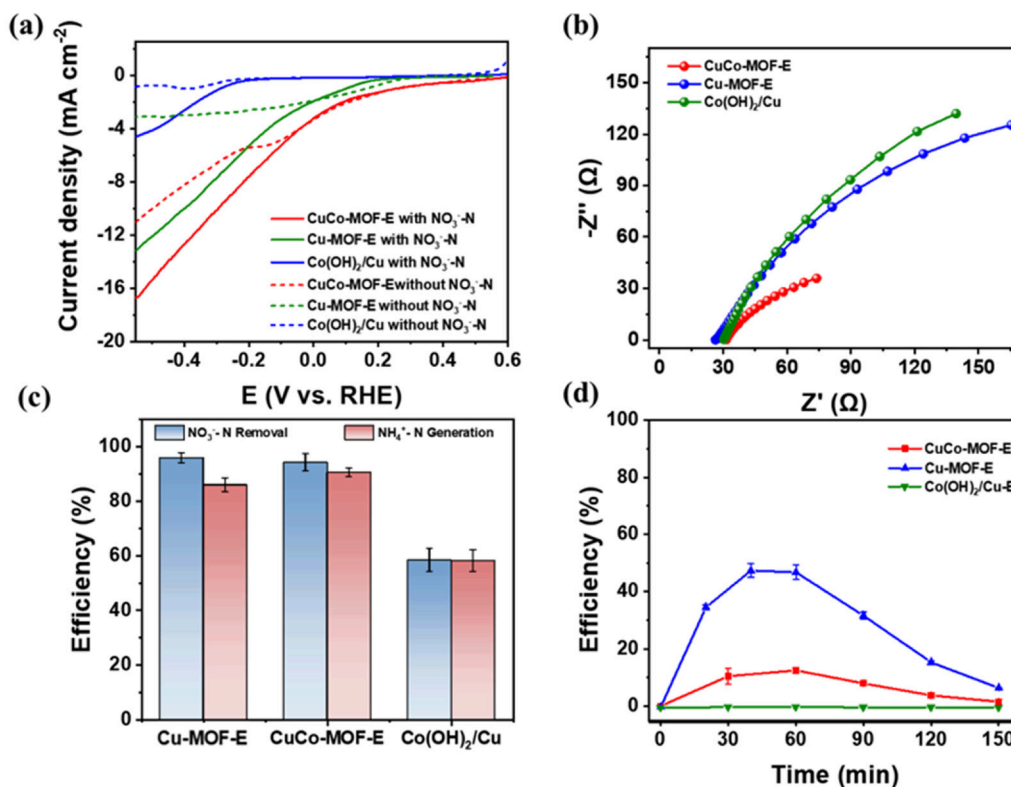


Figure 2. (a) LSV curves, (b) EIS diagram, (c) NO_3^- -N removal efficiency and NH_4^+ -N generation efficiency, and (d) NO_2^- -N generation efficiency of CuCo-MOF-E, Cu-MOF-E, and $\text{Co(OH)}_2/\text{Cu}$.

The NO_3^- removal efficiency (RE), NO_2^- , and NH_4^+ generation efficiency (GE) of the three electrodes under 20 mA cm^{-2} for 150 min are illustrated in Figure 2c,d. Cu-MOF-E benefits from the favorable enrichment and activation of NO_3^- by its porous framework, resulting in a higher NO_3^- RE than that of CuCo-MOF-E. However, its NH_4^+ GE (85.90%) is lower than that of CuCo-MOF-E (90.58%), accompanied by relatively high NO_2^- residue (approximately 50%) during the reaction. This can be ascribed to the limitations of single-type active sites in Cu-MOF-E regarding the adsorption energy and hydrogenation kinetics toward NO_2^- intermediates, which cannot fully match the rapid preceding NO_3^- reduction step. In contrast, no NO_2^- accumulation was observed during the nitrate reduction process by using a $\text{Co(OH)}_2/\text{Cu}$ electrode, indicating that the electrodeposition of $\text{Co(OH)}_2/\text{Cu}$ on Cu mesh facilitates the conversion of NO_2^- to NH_4^+ . Therefore, upon introducing Co to construct CuCo-MOF-E, the bimetallic synergistic effect significantly optimizes the electronic structure. The incorporation of Co not only enhances the electrode's adsorption capability toward nitrogen-containing intermediates and suppresses the desorption of NO_2^- , but also accelerates the subsequent hydrogenation step. Thus, while maintaining high NO_3^- RE, the NH_4^+ GE is also improved and the accumulation of intermediate NO_2^- is avoided. The nitrate reduction performance of the CuCo-MOF-E electrode prepared in this work, along with related materials reported in recent years, is presented in Table S1 in the Supplementary Materials.

The double-layer capacitance (C_{dl}) can reflect the number of active sites on the electrode surface to a certain extent. Figure 3 shows the CV curves and double-layer capacitances of CuCo-MOF-E, Cu-MOF-E, and $\text{Co(OH)}_2/\text{Cu}$ catalytic electrodes obtained at scan rates of 20, 40, 60, 80, and 100 mV s^{-1} in the non-Faradaic region. The C_{dl} of CuCo-

MOF-E (3.59 mF cm^{-2}) is significantly larger than those of Cu-MOF-E (1.46 mF cm^{-2}) and $\text{Co(OH)}_2/\text{Cu}$ (0.20 mF cm^{-2}) (Figure 3d). A high electrochemically active surface area can increase the contact area between the catalyst and electrolyte, thereby enhancing the performance of electrocatalytic nitrate reduction.

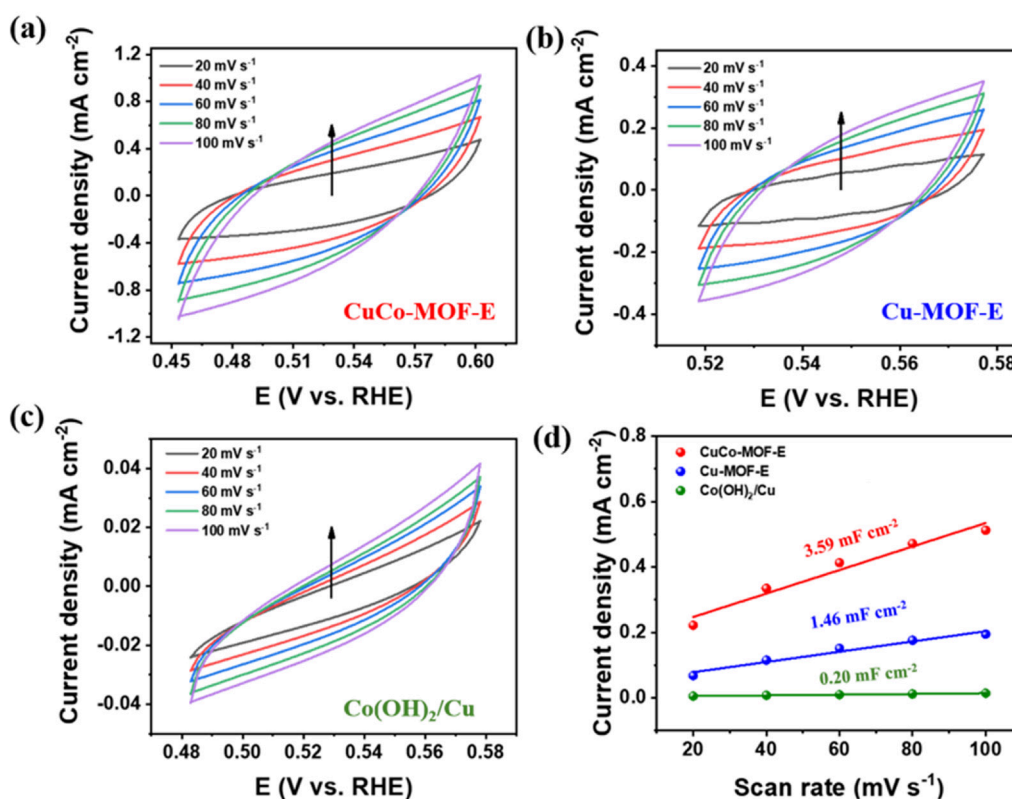


Figure 3. CV curves of (a) CuCo-MOF-E, (b) Cu-MOF-E, (c) $\text{Co(OH)}_2/\text{Cu}$ with different scanning rates, and (d) double-layer capacitance values of the electrodes. The arrows indicate the changing trend of the CV curves.

To investigate the effect of current density on electrocatalytic nitrate reduction, experiments were conducted at current densities of 10, 20, 30, 40, and 50 mA cm^{-2} with the electrode of CuCo-MOF-E, and the results obtained at a reaction time of 150 min are shown in Figure 4a. As the current density increased from 10 to 20 mA cm^{-2} , the NO_3^- RE increased from 74.58% to 94.26%, and the NH_4^+ GE increased from 46.33% to 90.58%. As the current density further increased from 20 to 50 mA cm^{-2} , the NO_3^- RE continued to rise, while the NH_4^+ GE gradually decreased to 81.36%. This is attributed to the occurrence of side reactions such as hydrogen evolution at excessively high current densities. As shown in Figure 4b, when the current density increased from 10 to 20 mA cm^{-2} , the current utilization efficiency exhibited an upward trend. At 10 mA cm^{-2} , the applied current was primarily consumed for the reduction of the catalyst precursor rather than the reduction of nitrate. When the current density increased from 20 to 50 mA cm^{-2} , the current utilization efficiency decreased from 73.29% to 28.78%, following the same trend as the NH_4^+ GE. Considering the efficiency of nitrate conversion, ammonia generation, and current utilization, a current density of 20 mA cm^{-2} was selected.

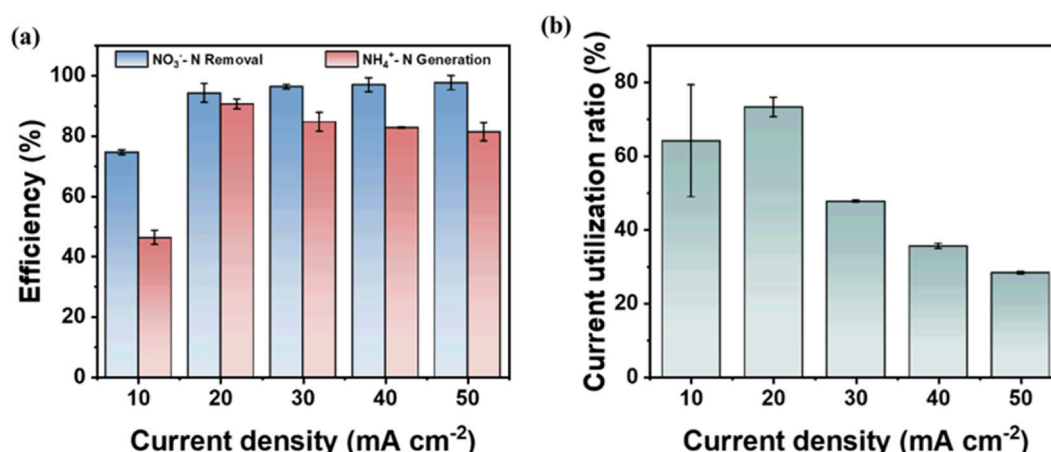


Figure 4. (a) NO_3^- -N removal efficiency, NH_4^+ -N generation efficiency and (b) current utilization efficiency at different current densities with the electrode of CuCo-MOF-E.

2.2. Optimization of CuCo-MOF-E Preparation Parameters

The content of the second active site Co on the CuCo-MOF-E electrode was optimized by controlling the electrodeposition time of $\text{Co}(\text{OH})_2$. Using 25 mL of 20 mM $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ as the electrolyte, with Cu mesh and Pt sheet as the cathode and anode, respectively, a constant current of 10 mA was applied for 100 s, 200 s, 300 s, and 400 s to obtain $\text{Co}(\text{OH})_2/\text{Cu}$ electrodes with different deposition times. A constant current experiment at 20 mA cm^{-2} was then conducted in 25 mL of 100 mg L^{-1} NO_3^- -N aqueous solution (containing 0.05 M Na_2SO_4) for a reaction time of 150 min.

Figure 5a shows the NO_3^- conversion efficiency and NH_4^+ generation efficiency for the electrodeposition time ranging from 0 to 400 s. As the electrodeposition time increased to 300 s, the NH_4^+ generation efficiency increased from 87.86% to 90.58%. When the deposition time was further increased to 400 s, both the NO_3^- conversion efficiency and NH_4^+ generation efficiency exhibited a downward trend. This may be attributed to excessive $\text{Co}(\text{OH})_2$ loading on the Cu mesh caused by prolonged electrodeposition time, leading to detachment issues during subsequent preparation processes. The variation trend of NO_2^- during the nitrate reduction is shown in Figure 5b. The NO_2^- accumulation for catalysts with electrodeposited $\text{Co}(\text{OH})_2$ was significantly lower than that for Cu-MOF-E. Among these, the catalyst prepared under a deposition time of 300 s showed the least NO_2^- accumulation, with a maximum NO_2^- generation efficiency of only 12.44% at 60 min. Additionally, the ammonia selectivity exhibited the same trend as the NH_4^+ generation efficiency (Figure 5c), reaching a maximum of 96.40% at a deposition time of 300 s. Therefore, the CuCo-MOF-E electrode with an electrodeposition time of 300 s demonstrated the best activity in this work, and 300 s $\text{Co}(\text{OH})_2$ deposition was adopted for subsequent experiments.

The reduction time of CuCo-MOF was further optimized, as shown in Figure 6a. When the reduction time of the precursor CuCo-MOF increased from 0 min to 10 min, the NO_3^- RE increased from 50.89% to 94.26%, and the NH_4^+ GE increased from 47.56% to 90.58%. Further extension of the reduction time resulted in essentially unchanged NO_3^- RE and NH_4^+ GE. This indicates that the catalytic electrode reached a stable state after 10 min of reduction, and further increasing the reduction time had little effect on its nitrate reduction performance. Figure 6b shows the variation of NO_2^- GE during the reaction for catalytic electrodes prepared with different reduction times. The maximum NO_2^- GE were all below 20.0%, demonstrating that the prepared catalytic electrodes effectively suppress the accumulation of intermediate byproducts.

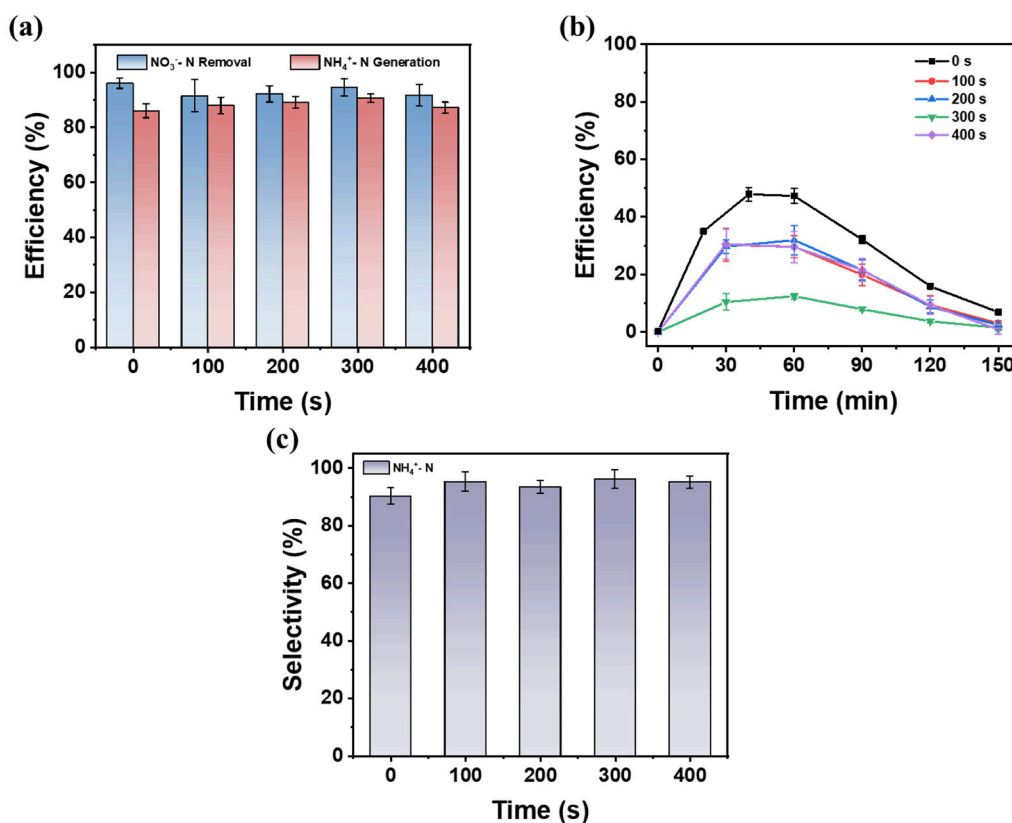


Figure 5. (a) NO_3^- removal efficiency NH_4^+ generation efficiency, (b) NO_2^- generation efficiency, and (c) NH_4^+ selectivity at different electrodeposition times of $\text{Co}(\text{OH})_2$.

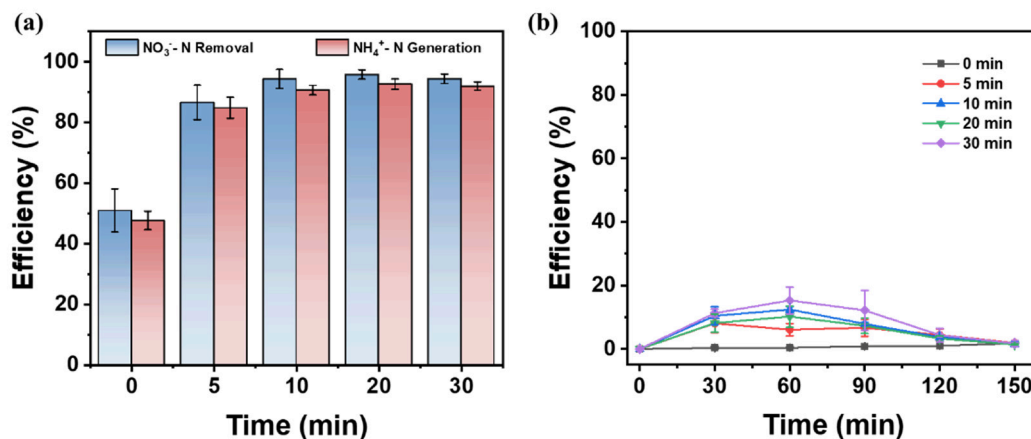


Figure 6. (a) NO_3^- -N removal efficiency, NH_4^+ -N generation efficiency and (b) NO_2^- -N generation efficiency with different reduction times of the precursor CuCo-MOF .

To investigate the effect of Cu-Co loading sequence on the catalytic reduction of nitrate, Cu-MOF precursors were first prepared, then $\text{Co}(\text{OH})_2$ was electrodeposited onto the Cu-MOF precursors, and finally, reduction was carried out for 10 min to obtain the $\text{Co}(\text{OH})_2/\text{Cu-MOF-E}$ catalytic electrode. A constant current experiment at 20 mA cm^{-2} was conducted in 25 mL of 100 mg L^{-1} NO_3^- -N aqueous solution (containing $0.05 \text{ M Na}_2\text{SO}_4$) for a reaction time of 150 min. The NO_3^- RE, NO_2^- GE, and NH_4^+ GE are shown in Figure 7a,c. The NO_3^- RE (89.48%) and NH_4^+ GE (84.94%) of $\text{Co}(\text{OH})_2/\text{Cu-MOF-E}$ were both lower than those of CuCo-MOF-E . This may be attributed to the detachment of some $\text{Co}(\text{OH})_2$ caused by the shedding of organic matter from the electrode surface during the $\text{Co}(\text{OH})_2/\text{Cu-MOF}$ reduction process. In addition, NO_3^- in solution tends to

adsorb on copper sites and undergo subsequent conversion, while the surface $\text{Co}(\text{OH})_2$ layer partially hinders the mass transfer process of nitrate, thereby reducing its reduction efficiency. Furthermore, the trend of NO_2^- during the reaction process was similar to that of CuCo-MOF-E.

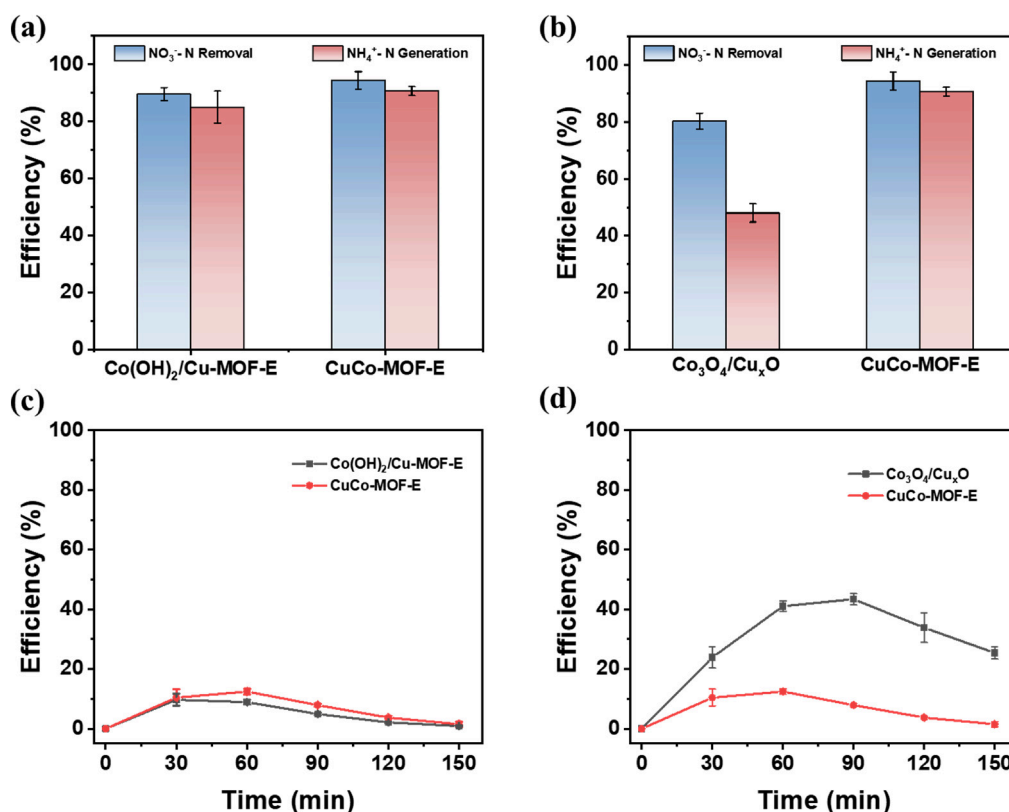


Figure 7. Effects of copper and cobalt loading sequences on (a) NO_3^- -N removal efficiency, NH_4^+ -N generation efficiency, and (c) NO_2^- -N generation efficiency; effects of annealing on (b) NO_3^- -N removal efficiency, NH_4^+ -N generation efficiency, and (d) NO_2^- -N generation efficiency.

The effect of annealing the precursor on its catalytic activity was investigated. The CoCu-MOF was annealed in a tube furnace at 400°C for 2 h with a heating rate of 5°C min^{-1} . The resulting catalyst was subsequently reduced for 10 min to obtain the $\text{Co}_3\text{O}_4/\text{Cu}_x\text{O}$ catalytic electrode. The comparison between $\text{Co}_3\text{O}_4/\text{Cu}_x\text{O}$ and the CuCo-MOF-E electrode is shown in Figure 7b,d. The NO_3^- RE and NH_4^+ GE of $\text{Co}_3\text{O}_4/\text{Cu}_x\text{O}$ were significantly lower than those of CuCo-MOF-E, with the NH_4^+ GE decreasing by approximately 50.00%. This may be attributed to the detachment of Co_3O_4 from the catalytic electrode surface along with carbonized organic matter during the annealing process, leading to the accumulation of NO_2^- during the reaction and thereby reducing the NH_4^+ GE.

2.3. Electrochemical Stability

The effect of initial solution pH on ENRA was investigated, as shown in Figure 8a. When the initial pH increased from 3 to 7, the NO_3^- RE increased from 85.41% to 94.26%, and the NH_4^+ GE increased from 81.03% to 90.58%. When the pH further increased to 11, the NO_3^- RE remained almost unchanged while the NH_4^+ GE gradually decreased to 83.73%. Overall, the catalytic electrode exhibits optimal nitrate removal performance under neutral conditions. Both NO_3^- RE and NH_4^+ GE maintained high levels above 80%, indicating that the catalytic electrode can sustain high efficiency over a wide pH range.

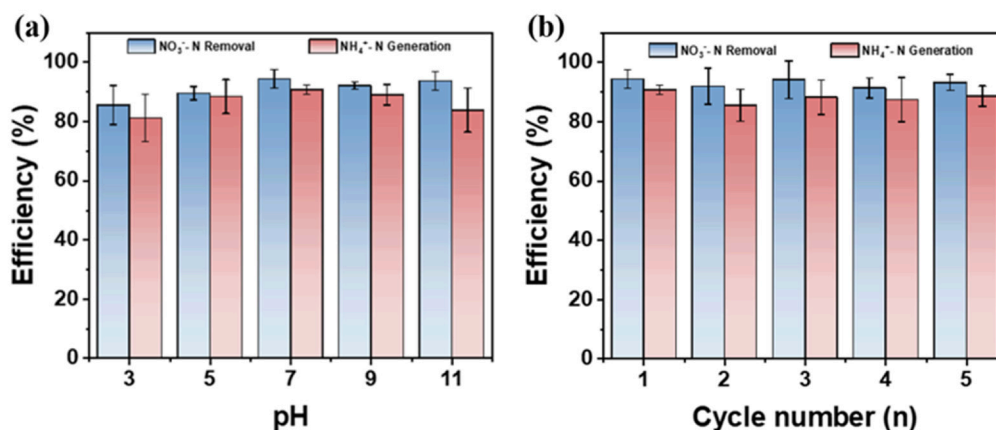


Figure 8. Effects of (a) the initial solution pH and (b) the reuse of the catalytic electrode on the performance of nitrate reduction to ammonia.

The CuCo-MOF-E catalytic electrode was subjected to cycling tests for NO_3^- reduction at the optimal current density of 20 mA cm^{-2} . Before each cycle, a sample was taken for testing; after 180 min of reaction, another sample was taken, and the electrolyte was replaced with fresh solution for the next cycle. The results are shown in Figure 8b. Within five consecutive cycles, the NO_3^- RE and NH_4^+ GE showed no significant decrease, demonstrating that the CuCo-MOF-E electrode has remarkable advantages in terms of both the stability and durability for ENRA.

3. Experimental Methods

3.1. CuCo-MOF-E Electrode Preparation

All chemical reagents used in this experiment were of analytical grade. The Cu mesh (100 mesh), serving as the substrate electrode material, was cut into $1 \times 1 \text{ cm}$ pieces and pretreated to remove surface oxides. It was ultrasonicated in acetone and $1 \text{ M H}_2\text{SO}_4$ for 10 min each, then ultrasonicated three times in deionized water and absolute ethanol to obtain clean Cu mesh.

The MOF-derived CuCo-MOF-E catalytic electrode was prepared via anodic oxidation and cathodic reduction methods [28]. First, in 25 mL of $20 \text{ mM Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}$ electrolyte, the pre-treated copper mesh was used as the cathode and Pt sheet as the anode. A constant current of 10 mA was applied for 5 min to obtain the $\text{Co(OH)}_2/\text{Cu}$ electrode. Then, the $\text{Co(OH)}_2/\text{Cu}$ electrode was used as the anode and copper mesh as the cathode. The electrolyte consisted of 12.5 mL ethanol, 12.5 mL water, 1 g hexadecyl trimethyl ammonium bromide (CTAB, the surfactant), 10 mg 1,4,8,11-tetraazacyclotetradecane (TCD, the ligand), and 5 mg tetramethyl ammonium bromide (TMAB, the template agent). At 70°C , a voltage difference of 10 V was applied between the anode and cathode for 5 min to form the CuCo-MOF electrode on the anode. The electrode was then removed and rinsed with deionized water. Before testing, the CuCo-MOF was used as the working electrode and Pt sheet as the counter electrode, with $100 \text{ mg L}^{-1} \text{ NO}_3^-$ -N and $0.05 \text{ M Na}_2\text{SO}_4$ as the electrolyte. The final CuCo-MOF-E electrode was obtained by reduction at a current density of 20 mA cm^{-2} for 600 s , followed by rinsing with deionized water.

The chemical structural information of the catalytic electrodes was analyzed by X-ray diffractometer (SmartLab 9, Rigaku, Tokyo, Japan) with the Cu target as the X-ray source, a scanning rate of 5° min^{-1} , and a range of $5\text{--}90^\circ$. The morphological characteristics of the electrodes were analyzed by field emission scanning electron microscope (JSM-7800F Prime, JEOL, Tokyo, Japan) at an operating voltage of 5 kV .

3.2. Electrocatalytic Procedures

The electrocatalytic reduction reaction was performed with an Autolab electrochemical workstation (PGSTAT302N, Metrohm, Herisau, The Netherlands). The CuCo-MOF-E electrode was used as the cathode and Pt sheet as the anode. The cathode and anode were spaced 1 cm apart and immersed in 25 mL of 100 mg L⁻¹ NO₃⁻-N electrolyte (containing 0.05 M Na₂SO₄). A constant current was applied for the reduction experiments. Each test was conducted three times at room temperature under identical conditions. The electrochemical performance tests, including linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), and constant current tests (I-t), were all performed on the Autolab electrochemical workstation.

The concentrations of NO₃⁻, NO₂⁻, and NH₄⁺ in the reactants and products were determined by UV-visible spectrophotometry (HJ/T 346-2007, GB 7493-87, HJ 536-2009), respectively (detailed information is provided in the Supplementary Materials). The conversion efficiency of N-containing species, and the product selectivity of ammonia were calculated to evaluate the catalytic electrode performance. The calculation methods for the main parameters are listed as follows:

$$RE(NO_3^- - N) = \frac{C(NO_3^- - N)_0 - C(NO_3^- - N)_t}{C(NO_3^- - N)_0} \times 100\% \quad (1)$$

$$GE(NO_2^- - N, NH_4^+ - N) = \frac{C(N)_t}{C(NO_3^- - N)_0} \times 100\% \quad (2)$$

$$S(NH_4^+ - N) = \frac{C(NH_4^+ - N)_t}{C(NO_3^- - N)_0 - C(NO_3^- - N)_t} \times 100\% \quad (3)$$

$$\eta = \frac{Q(N\text{-products})_t}{It/1000} \times 100\% \quad (4)$$

$$Q(N\text{-products})_t = \frac{n \times C(N)_t \times V \times F}{M_N} \times 100\% \quad (5)$$

where RE(NO₃⁻-N) is the nitrate removal efficiency; GE(NO₂⁻-N, NH₄⁺-N) is the generation efficiency of nitrite and ammonia, respectively; S(NH₄⁺-N) is the ammonia selectivity; η is the current utilization efficiency; C(NO₃⁻-N)₀ is the initial concentration of NO₃⁻-N, mg L⁻¹; C(N)_t is the concentration of N-containing species (NO₃⁻, NO₂⁻, and NH₄⁺) at time t, mg L⁻¹. Q(N-products)_t is the total amount of electricity required to convert NO₃⁻-N to N-containing products including NO₂⁻-N and NH₄⁺-N at time t, C; It/1000 is the total amount of electricity provided during time t, C; I is the current, mA; t is the time, s; n is the number of electron transfers; F is the Faraday constant, 96,487 C mol⁻¹; V is the volume of the solution, L; M_N is the molar mass, 14,000 mg mol⁻¹.

4. Conclusions

In this work, a CuCo-MOF-E catalytic electrode was constructed on a conductive Cu mesh substrate through anodic oxidation and cathodic electrodeposition strategies. The MOF structure in the precursor provided a high specific surface area and a three-dimensional hierarchical porous structure, with periodically arranged organic ligands uniformly dispersing Cu and Co active sites while maintaining close spatial proximity. Through ligand-bridged electronic coupling, the coupled tandem catalytic pairs formed by Cu sites and Co sites were strengthened. This dual-site synergistic mechanism resolved the selectivity issue arising from the mismatch between intermediate generation rates and hydrogenation rates on single Cu sites. Under reaction conditions of 20 mA cm⁻² for 150 min, CuCo-MOF-E achieved a NO₃⁻ removal efficiency of 94.26% and an NH₄⁺

generation efficiency of 90.58%, with NO_2^- accumulation effectively suppressed. This result not only reveals the unique advantages of MOF structure in bimetallic tandem catalysis, but also provides clear structure–function relationship insights for designing efficient electrocatalysts based on MOF platforms. The high activity and selectivity exhibited by this electrode at moderate current densities make it suitable for decentralized treatment of low-concentration nitrate wastewater and ammonia resource recovery. For this system, systematic investigation of the regulatory effects of MOF ligand types and defect engineering on the microenvironmental acidity/alkalinity and proton transfer rates remains to be addressed; overcoming these challenges will further advance this system toward better industrial applications.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal16070658/s1>, Figure S1: Standard curve of different nitrogen-containing compounds; Figure S2: Elemental mapping results of CuCo-MOF-E; Table S1: Performance of electrocatalytic nitrate reduction to ammonia with Cu-Co or MOF catalysts in recent related research. References [29–40] are cited in the Supplementary Materials.

Author Contributions: F.S.: Conceptualization, methodology, formal analysis, and writing. H.X.: Investigation, data curation, and formal analysis. D.G.: Validation, formal analysis, and writing. J.W.: Supervision, project administration, and funding acquisition. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the National Natural Science Foundation of China (No. 22306118, 22076117), and the Open Fund of Shanxi Key Laboratory of Water Pollution Prevention and Utilization (SWRFZYLY202515).

Data Availability Statement: Data will be made available on request.

Conflicts of Interest: The authors declare no conflicts of interest.

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