

Article

Kinetic Understanding of the Enhanced Electroreduction of Nitrate to Ammonia for Co_3O_4 -Modified Cu_{2+1}O Nanowire Electrocatalyst

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Abstract: Electrocatalytic nitrate reduction reaction (NO_3^- RR) to ammonia (NH_3) presents an alternative, sustainable approach to ammonia production. However, the existing catalysts suffer from poor NH_3 yield under lower concentrations of NO_3^- , and the kinetic understanding of bimetal catalysis is lacking. In this study, a Co_3O_4 -modified Cu_{2+1}O nanowire (CoCuNWs) catalyst with a high specific surface area was synthesized to effectively produce NH_3 from a 10 mM KNO_3 basic solution. CoCuNWs demonstrated a high NH_3 yield rate of $0.30 \text{ mmol h}^{-1} \text{ cm}^{-2}$ with an NH_3 Faradaic efficiency (FE) of 96.7% at -0.2 V vs. RHE, which is 1.5 times higher than the bare Cu_{2+1}O NWs. The synergistic effect between Co_3O_4 and Cu_{2+1}O significantly enhanced both the nitrate conversion and ammonia yield. Importantly, it is revealed that the surface of CoCuNWs is kinetically more easily saturated with NO_3^- (NO_2^-) ions than that of Cu_{2+1}O NWs, as evidenced by both the higher current density and the plateau occurring at higher NO_x^- concentrations. In addition, CoCuNWs exhibit a higher diffusion coefficient of NO_3^- , being 1.6 times higher than that of Cu_{2+1}O NWs, which also indicates that the presence of Co_3O_4 could promote the diffusion and adsorption of NO_3^- on CoCuNWs. Moreover, the ATR-SEIRAS analysis was applied to illustrate the reduction pathway of NO_3^- to NH_3 on CoCuNWs, which follows the formation of the key intermediate from $^*\text{NO}_2^-$, $^*\text{NO}$, $^*\text{NH}_2\text{OH}$ to $^*\text{NH}_3$. This work presents a strategy for constructing dual-metal catalysts for NO_3^- RR and provides an insight to understand the catalysis from the perspective of the kinetics.

Keywords: electrocatalytic nitrate reduction; electrocatalytic ammonia production; copper-cobalt catalysts; kinetic insights



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1. Introduction

Ammonia (NH_3) serves as a cornerstone chemical in the fertilizer, pharmaceutical, and fine chemical industries, with global annual production surpassing 180 million tons [1–3]. NH_3 is rapidly emerging in the energy sector as a key hydrogen energy carrier and carbon-neutral fuel. Furthermore, advances in ammonia cracking technology have further enhanced its potential as a clean energy carrier [4]. However, the current industrial ammonia synthesis process primarily depends on the energy-intensive Haber–Bosch method, which facilitates NH_3 production via the reaction of N_2 and H_2 under extreme high temperature and high pressure conditions [5,6]. Beyond the conventional Haber–Bosch process, various alternative approaches for ammonia synthesis have been investigated. Although

photocatalytic and plasma-assisted methods demonstrate theoretical potential, they face significant practical challenges: photocatalytic systems typically exhibit quantum efficiencies of less than 25% due to rapid charge recombination, while plasma-based methods require energy inputs exceeding 30 kW·h per kg of NH_3 [7–9]. Electrochemical nitrate reduction to ammonia (NO_3^- RR), which enables the efficient NH_3 synthesis under mild operational conditions utilizing clean energy, has emerged as a promising alternative to the Haber–Bosch process and has been demonstrated to be a highly effective process for both wastewater treatment and energy storage applications [10–14].

Copper is regarded as a promising candidate for NO_3^- RR due to its excellent conductivity and distinct catalytic properties [15–18]. However, the electronic structure of copper restricts its ability to regulate key reaction intermediates, thereby affecting product selectivity and formation rate [19]. The construction of bimetallic catalysts has emerged as an effective strategy to enhance the performance of copper-based catalysts, as it allows for electronic structure modulation, optimization of active site distribution, and improved adsorption properties of reaction intermediates ($^*\text{NO}_2^-$, $^*\text{NO}$, $^*\text{NH}_2\text{OH}$, etc.) [20]. Previous studies have demonstrated that forming bimetallic systems with transition metals such as Ni [21–23], Fe [24–26], and Co can significantly improve the selectivity and catalytic activity of copper-based catalysts. Among them, cobalt exhibits strong adsorption and activation capabilities of key intermediates, thus optimizing the reaction pathway and enhancing the NO_3^- RR selectivity of copper-based catalysts by synergistic effects and tandem mechanisms [27,28]. For example, Ren et al. [29] recently elucidated the dual-site synergistic mechanism in Cu/Co(OH)₂ tandem catalysts, where Cu sites selectively convert $\text{NO}_3^- \rightarrow \text{NO}_2^-$, while adjacent Co hydroxide moieties facilitate the subsequent $\text{NO}_2^- \rightarrow \text{NH}_3$ reduction. The development of bimetallic and nanostructured systems has been widely demonstrated to modulate the surface electronic structure and geometrical configuration, thereby enhancing reactant adsorption and the conversion efficiency of intermediates [30–32]. Furthermore, kinetic parameters are crucial to affect the catalytic performance [33,34]. Generally, the microscopic kinetics study is related to the diffusion and adsorption processes and the electron/proton transfer process. However, due to the complexity of the electrode/electrolyte interface, the unified kinetic models and the standardized method remain limited [35]. Consequently, the kinetic investigations—especially those concerning the adsorption–diffusion behavior in the NO_3^- RR process—remain limited and challenging.

In this work, a $\text{Co}_3\text{O}_4/\text{Cu}_{2+1}\text{O}$ nanowires (CoCuNWs) catalyst for efficient NO_3^- RR to NH_3 was synthesized through electrodepositing Co hydroxides on Cu hydroxides nanowires, followed by an annealing process. Comprehensive characterizations were conducted to identify the morphology, composition, and electrochemical properties. Additionally, the kinetic characteristics were explored to illustrate its catalytic improvement. Kinetic parameters, including saturated adsorption capacity and diffusion coefficient, were measured to elucidate the diffusion and adsorption behavior of NO_3^- and NO_2^- . As a result, CoCuNWs present a higher NH_3 yield rate of $0.30 \text{ mmol h}^{-1} \text{ cm}^{-2}$ with an NH_3 FE of 96.7% at -0.2 V vs. RHE in 10 mM KNO_3 basic solution, which is 1.5-fold that of bare Cu_{2+1}O NWs. Furthermore, ATR–SEIRAS analysis was performed to verify the hydrogenation pathway of NO_3^- RR to NH_3 for the CoCuNWs catalyst.

2. Results and Discussion

2.1. Material Characterizations

The synthesis of CoCuNWs is illustrated in Figure 1a, and the morphological evolution during the synthesis was confirmed by scanning electron microscopy (SEM). Under oxidation conditions, the copper foam was transformed into ordered nanowires (Figure 1b).

After electrodepositing for 300 s at -0.8 V vs. SCE, the sheet-like Co species grows along the primary nanowires (Figure 1c). The subsequent annealing process not only induces structural hybridization but also facilitates the dehydration of hydroxides, resulting in the formation of numerous porous sheets, as shown in Figure 1d. These structures exhibit a large specific surface area, which is in agreement with previous studies on similar hydroxide systems [36]. The transmission electron microscopy (TEM) images (Figure 1e–g) also reveal the morphology of nanowires wrapped with array sheets. Figure 1f displays the interplanar spacings of 0.151 nm and 0.244 nm, assigned to the (220) plane of Cu_{2+1}O and the (311) plane of Co_3O_4 [37,38]. Cu_{2+1}O is a non-stoichiometric copper oxide in which copper coexists in both +1 (Cu^+) and +2 (Cu^{2+}) valence states accompanied by an abundance of oxygen vacancies and defective structures [39]. The combination of valence states and defects could result in a distinctive electronic structure and catalytic activity [40]. Meanwhile, a boundary between Cu_{2+1}O and Co_3O_4 is clearly shown, meaning the existence of dual-metal $\text{Co}_3\text{O}_4/\text{Cu}_{2+1}\text{O}$ heterostructure. The elemental distribution spectrum (EDS) further presents the interface characteristics: Cu atoms are mainly concentrated in the core region of the nanowires, while Co atoms are distributed along the periphery area of Cu atoms (Figure 1g). The above results demonstrate that the CoCuNWs catalyst has been successfully prepared with the porous Co_3O_4 sheets grown on the surface of Cu_{2+1}O nanowires.

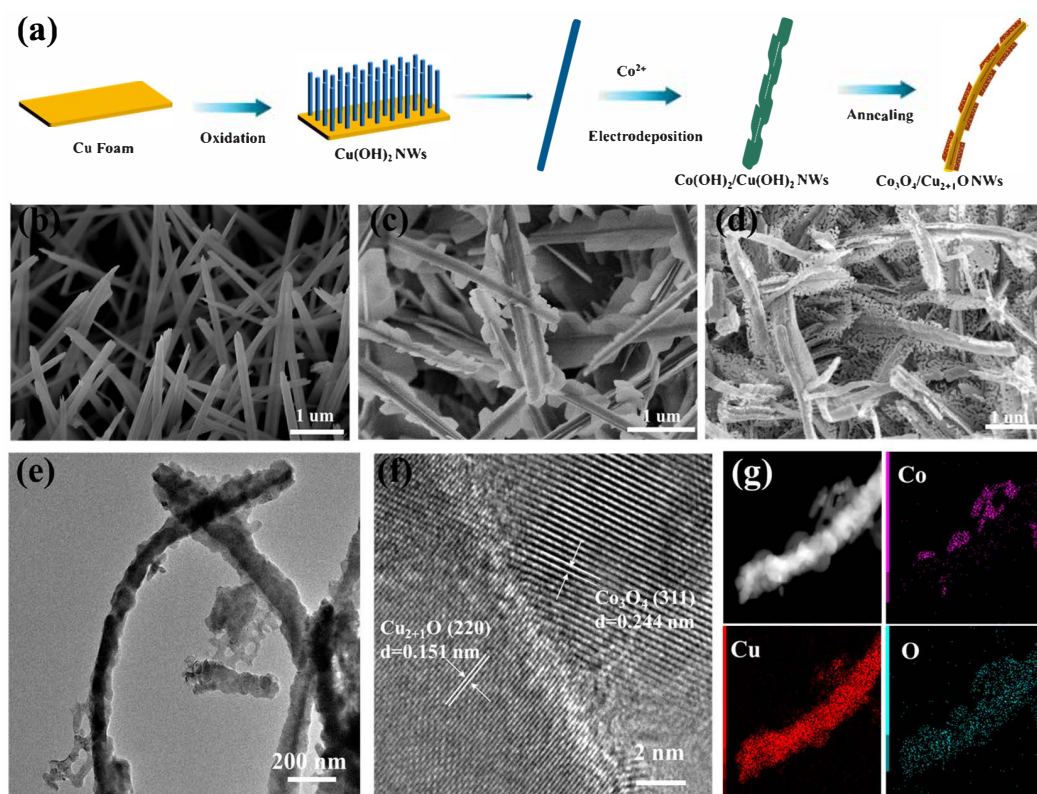


Figure 1. Illustration of the fabrication of CoCuNWs (a); SEM images of $\text{Cu}(\text{OH})_2$ NWs (b); $\text{Co}(\text{OH})_2/\text{Cu}(\text{OH})_2$ NWs (c); and $\text{Co}_3\text{O}_4/\text{Cu}_{2+1}\text{O}$ NWs (d); TEM image (e); and HRTEM image (f); of CoCuNWs (g); HAADF image and EDS elemental maps of CoCuNWs in which pink, red, and cyan refer to Co, Cu and O, respectively.

Moreover, the crystal phase and the surface composition of the catalyst CoCuNWs are characterized by X-ray Diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). Figure 2a presents the XRD patterns of CoCuNWs and the control sample Cu_{2+1}O NWs. Cu_{2+1}O NWs displays the diffraction peaks at 36.4° , 42.3° , and 61.3° attributed to the (111), (200), and (220) planes of Cu_{2+1}O (JCPDS No. 05–0667) [41], and the other strong

diffraction peaks due to the Cu foam substrate. In the case of the CoCuNWs samples examined, the relatively weak diffraction peaks of Co_3O_4 are not readily apparent (JCPDS No. 00-042-1467) [37]. The surface elemental composition and chemical states are shown in Figure 2b–d. The XPS spectrum of Cu 2p for Cu_{2+1}O NWs (Figure 2b) shows the double peaks at 932.3 eV, and 952.1 eV corresponding to the $2p_{3/2}$ and $2p_{1/2}$ peaks of Cu^0/Cu^+ , and the peaks at 934.7 eV and 954.4 eV attributed to the $2p_{3/2}$ and $2p_{1/2}$ peaks of Cu^{2+} . The typical satellite peaks at 942.4 eV and 962.5 eV further confirm the oxidized states of Cu species [42]. These binding energy (BE) values are in agreement with those of Cu_{2+1}O in previous reports [40,41]. As shown in Figure S1, the XPS full spectrum of CoCuNWs exhibits the presence of Cu, Co, and O elements, with the atomic ratio of Co to Cu being about 3:1 (Table S1). The spectrum of Co 2p for CoCuNWs is shown in Figure 2c. The binding energies at 779.6 eV and 794.4 eV are attributed to Co^{3+} species, and the peaks at 781.2 eV and 797.0 eV are assigned to Co^{2+} species, indicating the coexistence of multiple valence states of Co [43]. Meanwhile, the satellite peaks at 786.4 eV and 802.3 eV are also observed, which are consistent with previous reports [44]. While in the Cu2p spectrum for CoCuNWs (Figure 2d), the BEs of Cu 2p peaks are the same as Cu_{2+1}O NWs, indicating that the introduction of Co has no significant effect on the oxidation states of Cu. The above results again demonstrate the successful fabrication of the CoCuNWs catalyst.

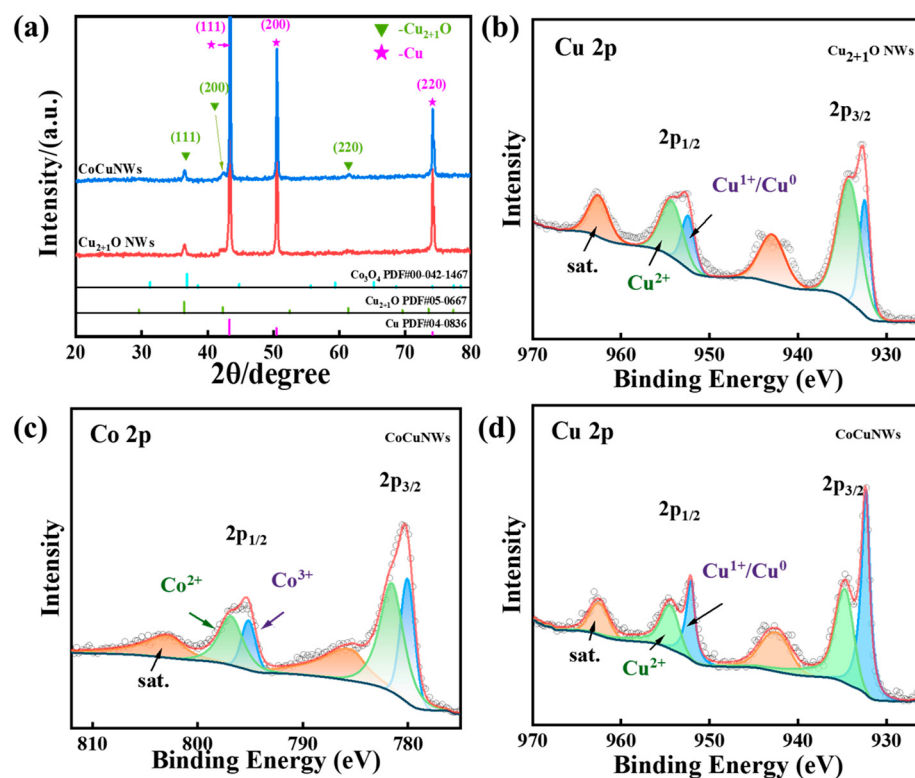


Figure 2. (a) XRD pattern of CoCuNWs and Cu_{2+1}O NWs; (b) Cu 2p XPS spectrum of Cu_{2+1}O NWs; (c) Co 2p XPS spectrum; and (d) Cu 2p XPS spectrum of CoCuNWs, where the circles represent the raw data and the red lines represent the fitted data.

To further investigate the electrochemical characteristics of CoCuNWs in comparison with the bare Cu_{2+1}O NWs, the electrochemical active surface area (ECSA) and electrochemical impedance spectroscopy (EIS) were evaluated. The ECSA of CoCuNWs, calculated from the double-layer capacitance (C_{dl}) (Figure S2a,b), is 6.12 mF cm^{-2} , which is 1.2 times greater than that of Cu_{2+1}O NWs (4.79 mF cm^{-2}) (Figure 3a). The higher ECSA suggests that CoCuNWs can provide more active sites for the NO_3^- -RR. As shown in Figure 3b and Table S2, the EIS data of Cu_{2+1}O NWs and CoCuNWs had been fitted using a circuit

model that includes charge transfer resistance (R_{ct}), C_{dl} (CPE1), and solution resistance (R_s). Notably, CoCuNWs exhibited a 57% smaller semicircle radius compared to Cu_{2+1}O NWs, corresponding to lower R_{ct} (10.57 vs. 25.00 $\text{ohm}\cdot\text{cm}^2$), which directly demonstrates enhanced electron transfer kinetics [45,46].

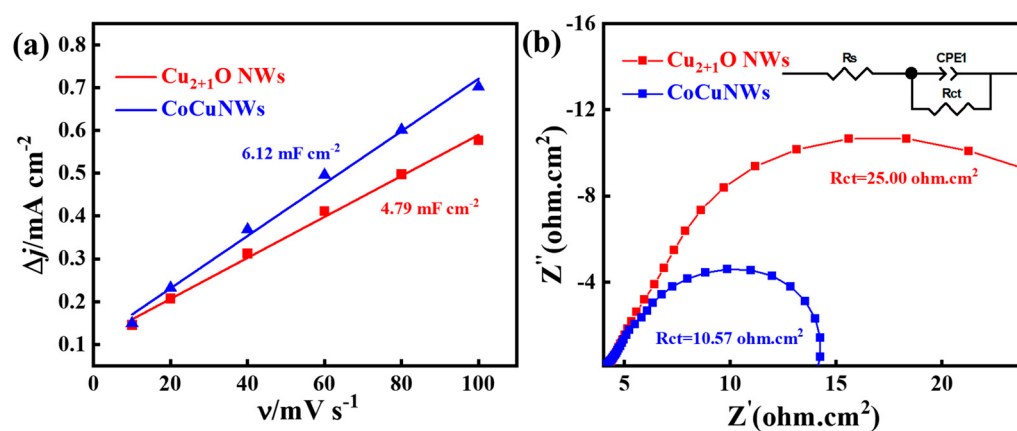


Figure 3. (a) Double-layer capacitance diagram and (b) electrochemical impedance spectra of Cu_{2+1}O NWs and CoCuNWs in 0.5 M KOH solution.

2.2. Electrocatalytic Performance in the Reduction of NO_3^- to NH_3

Firstly, the linear sweep voltammetry (LSV) tests were conducted to evaluate the NO_3^- RR activity of CoCuNWs and the control samples. Figure 4a shows the LSV curves obtained with and without NO_3^- . In the absence of NO_3^- , the observed current density with applied potential originates from the hydrogen evolution reaction (HER). Upon the addition of NO_3^- , the increased variations in the current density indicate the NO_3^- RR activity of the catalysts. Clearly, CoCuNWs exhibit the highest current rise, indicating that they have remarkably enhanced NO_3^- RR activity beyond that of Cu_{2+1}O NWs. In addition, $\text{Co}_3\text{O}_4/\text{NF}$ (nickel foam substrate) is also used to test the activity of bare Co_3O_4 [47]. It is indicated that the current increase due to NO_3^- RR on $\text{Co}_3\text{O}_4/\text{NF}$ is the lowest among the three samples. These results imply that neither Cu_{2+1}O nor Co_3O_4 alone can achieve satisfactory catalytic activity. Then, it is necessary to explore the NH_3 selectivity from NO_3^- RR on CoCuNWs.

The NO_3^- RR performances of CoCuNWs and the control samples were investigated using 0.5 M KOH solution containing 10 mM KNO_3 as the electrolyte in an H-type cell. The amounts of NO_3^- , NH_3 , and NO_2^- were quantified via ultraviolet–visible (UV–Vis) spectroscopy according to the calibration curves (Figures S3b, S4b, and S5b) [37]. Chronoamperometric electrolysis was conducted for 1 h at different potentials ranging from 0.0 to -0.4 V vs. RHE. As shown in Figure 4b, the FE for NH_3 (FE_{NH_3}) on CoCuNWs remains above 90% over the applied potential range from -0.1 V to -0.4 V vs. RHE, outperforming that of Cu_{2+1}O NWs. The HER is effectively suppressed at -0.2 V and -0.3 V, as evidenced by the high FE_{NH_3} . However, when the applied potential becomes more negative than -0.4 V, the HER becomes increasingly competitive, leading to a slight decrease in FE_{NH_3} . This observation aligns with the general trend reported in the literature for electrochemical nitrate reduction [42,43]. Correspondingly, Figure 4c shows the NH_3 yield rates at different potentials, where a more negative potential results in a higher NH_3 yield. At an optimal potential of -0.2 V vs. RHE, the NH_3 yield rate reaches $0.3 \text{ mmol h}^{-1} \text{ cm}^{-2}$. The remarkable NH_3 yield on CoCuNWs should be attributed to the cooperation of Cu_{2+1}O with Co_3O_4 , according to the tandem catalysis mechanism [37]. As illustrated in Figure S6, the CoCuNWs catalyst achieves above 90% conversion of NO_3^- at -0.2 V vs. RHE across the tested concentration range. These results demonstrate the broad applicability of the

catalyst in various NO_3^- concentrations and support its potential for real-world water treatment applications.

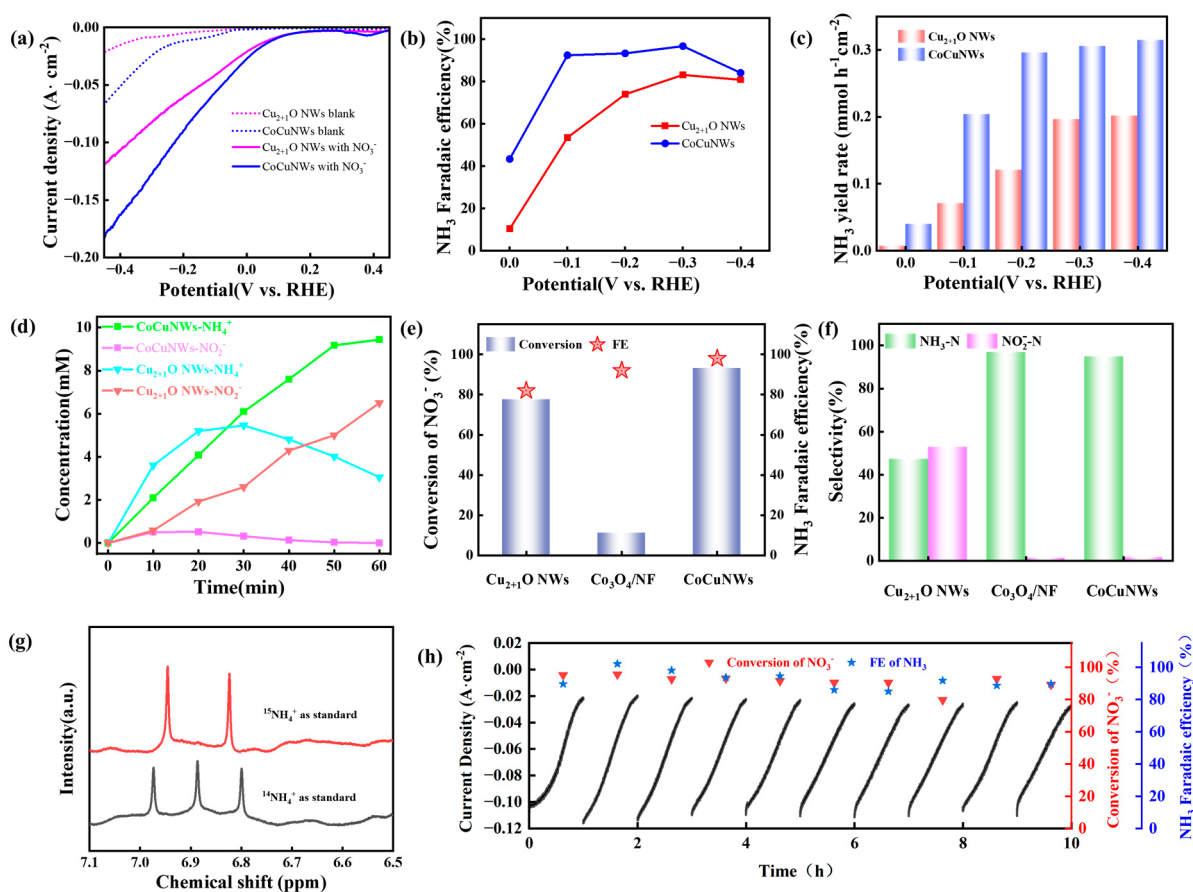


Figure 4. (a) LSV curves of the samples in 0.5 M KOH solutions with and without 10 mM KNO_3 at a scan rate of 5 mV s^{-1} ; (b) Faraday efficiency of NH_3 (FE_{NH_3}); and (c) NH_3 yield of the samples in 0.5 M KOH + 10 mM KNO_3 solution at different potentials; (d) Concentration changes of NO_3^- and NH_4^+ on CoCuNWs at -0.2 V vs. RHE in 0.5 M KOH + 10 mM KNO_3 ; (e) Conversion rate of NO_3^- and FE ; (f) selectivity of $\text{NH}_3\text{-N}$ and $\text{NO}_2^-\text{-N}$ over different samples at -0.2 V vs. RHE in 10 mM KNO_3 and 0.5 M KOH; (g) ^1H NMR spectra of electrolyte after the NO_3^- reduction at -0.2 V vs. RHE for 1 h using K^{14}NO_3 and K^{15}NO_3 as N-source; (h) Conversion rate and FE_{NH_3} of CoCuNWs during 10 consecutive tests at -0.2 V vs. RHE in 0.5 M KOH + 10 mM KNO_3 , with electrolyte replacement after each test.

To further verify the role of Cu_{2+1}O and Co_3O_4 , the time-dependent concentrations of NO_2^- ions and the product NH_3 were obtained. As shown in Figure 4d, it can be observed that both CoCuNWs and Cu_{2+1}O NWs present an increasing concentration of the product NH_4^+ ions with reaction time. In contrast, CoCuNWs exhibits only a small accumulation of NO_2^- ions, over against the much higher amount of NO_2^- ions remaining during the entire reaction by Cu_{2+1}O NWs catalysis. It is obviously indicated that the consumption rate of NO_2^- to NH_3 is much faster due to the role of Co_3O_4 in CoCuNWs . In other words, the low yield rate on bare Cu_{2+1}O is due to its inferior ability to convert NO_2^- ions. This result highlights the crucial role of Co_3O_4 in promoting NO_2^- reduction to NH_3 , thereby improving the selectivity of NH_3 . More control experiments were conducted to gain a clear understanding of the role of Co_3O_4 . Clearly, the Cu_{2+1}O NWs exhibited a high NO_3^- ions conversion rate (Figure 4e) but poor selectivity toward NH_3 (Figure 4f), suggesting the efficient reduction of NO_3^- to NO_2^- while displaying limited capability for further hydrogenation to NH_3 . In contrast, the $\text{Co}_3\text{O}_4/\text{NF}$ catalyst showed a lower

overall conversion yet significantly high NH_3 selectivity, implying that Co_3O_4 is more effective in promoting the formation of NH_3 . Notably, CoCuNWs catalyst outperformed both counterparts in terms of conversion efficiency of NO_3^- and FE_{NH_3} , indicating the successful cooperative catalysis between Cu_{2+1}O and Co_3O_4 . This synergistic behavior not only mitigates the bottleneck in NO_3^- to NO_2^- conversion but also facilitates the subsequent hydrogenation to NH_3 [28]. Furthermore, the yield rate based on ECSA for CoCuNWs was found to be higher, indicating that CoCuNWs exhibit higher intrinsic activity toward NO_3^- electroreduction, as shown in Figure S7. Moreover, isotope-labeling experiments were conducted using K^{15}NO_3 and K^{14}NO_3 as nitrogen sources to determine the source of NH_3 . The electroreduction products $^{15}\text{NH}_4^+$ and $^{14}\text{NH}_4^+$ were analyzed using proton nuclear magnetic resonance (^1H NMR) spectroscopy. The results indicate that when K^{15}NO_3 was used as the reactant, the produced $^{15}\text{NH}_4^+$ exhibited a characteristic doublet peak, whereas K^{14}NO_3 generated a triplet peak, closely associated with $^{14}\text{NH}_4^+$ (Figure 4g) [48]. This confirms that NH_3 originates from NO_3^- without interference from other impurities, which undergoes electrochemical reduction in the electrolyte.

The stability of CoCuNWs was tested through 10 electrolysis cycles at -0.2 V, with each cycle time of 1 h. As shown in Figure 4h, FE_{NH_3} remained above 88% throughout the entire cycling process, while the conversion rate remained nearly 90%. The used CoCuNWs were characterized by SEM and XPS. It is observed, as shown in Figures S8 and S9. There is no significant difference in structure and compositions from the fresh one, which indicates good stability of CoCuNWs. Moreover, in comparison with the reported catalysts (Table S3), CoCuNWs exhibited excellent performance in terms of the selectivity of NH_3 under low concentrations of NO_3^- .

2.3. Mechanism Study of CoCuNWs in NO_3^- RR

NO_3^- RR is a multi-electron transfer process, and the kinetics may be controlled by multiple steps [49–51]. Both adsorption and diffusion are crucial factors influencing the reaction rate [52,53]. This section explores the synergistic effect of Co_3O_4 and Cu_{2+1}O in multi-step catalysis from two perspectives: adsorption and diffusion behavior, as well as the reaction pathway.

2.3.1. Kinetics Study: Diffusion and Adsorption Behavior on CoCuNWs and Cu_{2+1}O NWs Catalysts

In multiphase electrocatalytic reactions, the diffusion process exerts a significant influence on the reaction rate [53]. In order to investigate the extent of the diffusion limitation of NO_3^- and NO_2^- under the influence of CoCuNWs and Cu_{2+1}O NWs, i - t tests were conducted under unstirred conditions at -0.2 V vs. RHE for a duration of 2 h in a 0.5 M KOH solution containing 0.1 M KNO_3 or 0.1 M KNO_2 (Figure S10). The obtained i - t curves indicate that CoCuNWs have higher current densities in comparison to Cu_{2+1}O NW, either in the presence of the reactant NO_3^- or the intermediate NO_2^- , which indicates higher catalytic properties and reduced diffusion limitations [54]. According to the Cottrell equation [55–57], the diffusion coefficients (D) can then be calculated from the dependence of the current on $t^{-1/2}$ (Figure 5a,b). The D values of NO_3^- and NO_2^- for CoCuNWs were 1.807×10^{-2} and $1.176 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$, which are higher than those for Cu_{2+1}O NWs (1.147×10^{-2} and $1.030 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$). The enhanced mass transport should be attributed to the nanowire/nanosheet hierarchical structure effect and, in turn, the surface adsorption ability [52,58]. A higher D means faster reactant delivery to active sites, thereby improving the overall reaction rate and helping eliminate diffusion limitations, making surface kinetics the determining factor. In low-concentration solutions, the more reactant adsorbed on the catalyst surface typically results in faster reaction rates [34,59]. From this perspective, CoCuNWs and Cu_{2+1}O NWs were subjected to LSV tests in 0.5 M KOH with

varying $\text{KNO}_3/\text{KNO}_2$ concentrations to observe the adsorption property on the catalyst surface (Figures 5c,d, S11a,b, and S12a,b). For CoCuNWs, as the NO_3^- concentration increased from 0.1 M to 1.6 M, the current density gradually increased, reaching a plateau at 1.8 M with a current density of approximately 330 mA cm^{-2} (Figure 5c). According to the Langmuir adsorption model [60], this plateau indicates that the reaction had reached a zero-order kinetic state, suggesting that NO_3^- adsorption on CoCuNWs was saturated. In contrast, Cu_{2+1}O NWs reached a current density plateau at 1.4 M NO_3^- (Figure 5c), with a current density of approximately 250 mA cm^{-2} , which was lower than that of CoCuNWs. A similar trend was observed for different concentrations of NO_2^- solutions (Figure S12a,b), with Cu_{2+1}O NWs reaching the plateau at 1.0 M (180 mA cm^{-2}) (Figure 5d), and CoCuNWs showing a consistent increase in current with increasing NO_2^- concentration. These findings suggest that the surface of CoCuNWs is kinetically more easily saturated with NO_3^- (NO_2^-) ions than that of Cu_{2+1}O NWs. In other words, it is demonstrated that the surface of CoCuNWs possesses the high capacity to accommodate a higher amount of NO_3^- and exhibits a larger saturable adsorption amount for NO_3^- . The enhanced saturated adsorption can be attributed to the presence of more effective adsorption sites on the surface of CoCuNWs [61,62]. The above results demonstrated that the integration of Co_3O_4 sheets with Cu_{2+1}O nanowires facilitates the kinetic process of CoCuNWs by improving the diffusion and adsorption of NO_3^- and NO_2^- to the catalyst surface. Thereafter, with the help of Co_3O_4 promoting the successive hydrogenation of NO_2^- to NH_3 , the remarkable enhancement of NH_3 yield is achieved on CoCuNWs.

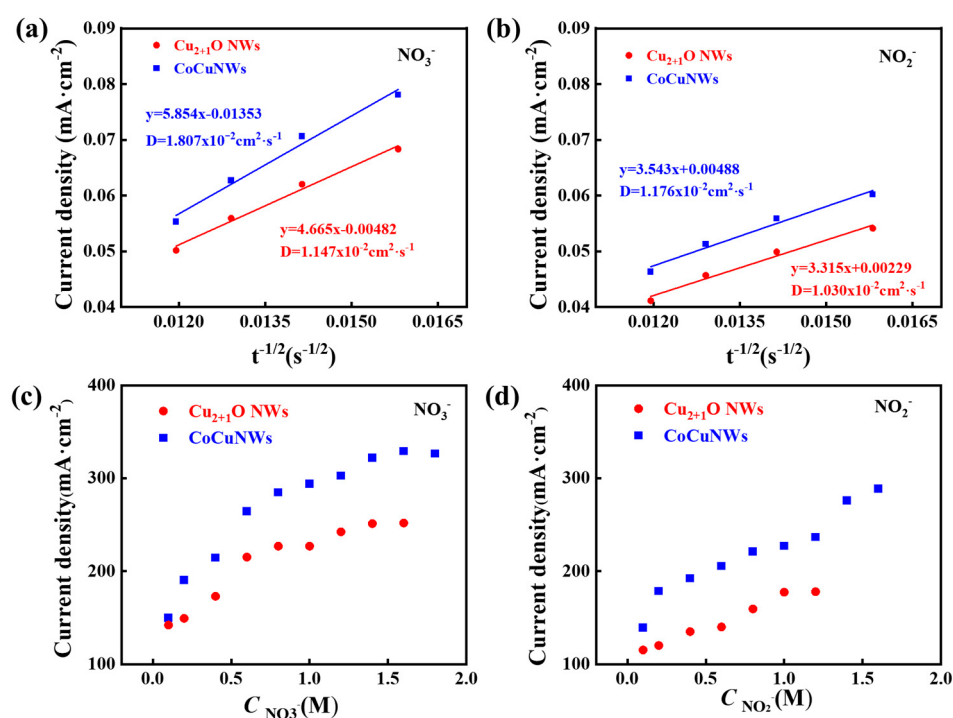


Figure 5. (a) The dependence of current density on $t^{-1/2}$ for 0.1 M NO_3^- over CoCuNWs and Cu_{2+1}O NWs. (b) The dependence of current density on $t^{-1/2}$ for 0.1 M NO_3^- and 0.1 M NO_2^- over CoCuNWs and Cu_{2+1}O NWs. (c) Current density of CoCuNWs and Cu_{2+1}O in the electrolyte with different concentrations of NO_3^- at -0.4 V vs. RHE. (d) Current density of CoCuNWs and Cu_{2+1}O in the electrolyte with different concentrations of NO_2^- at -0.4 V vs. RHE.

2.3.2. Reaction Pathway on CoCuNWs

It is important to note that NO_3^- RR occurs in an aqueous medium, where the hydrogen evolution reaction (HER) is an inevitable competing reaction that may suppress ammonia formation and negatively impact the Faradaic efficiency [11,63]. HER proceeds

via the Volmer step to form surface-active hydrogen (*H), followed by hydrogen gas (H₂) formation through the Heyrovsky or Tafel steps [64,65]. The impact of *H on the catalytic process was studied by using tert-butyl alcohol (TBA) to scavenge *H. As shown in Figure 6a, the introduction of TBA markedly slowed down NO₃[−] reduction, suggesting a complex interplay between *H formation/consumption and the NO₃[−] reduction pathway. The removal of *H directly inhibited NO₃[−] reduction. These results indicate that the NO₃[−]RR process mediated by CoCuNWs follows a Langmuir–Hinshelwood (LH) mechanism, which involves interactions between *H and nitrogen-containing intermediates (*M), represented as *M + *H = *MH [66]. This mechanism highlights the crucial role of *H in promoting NO₃[−]RR.

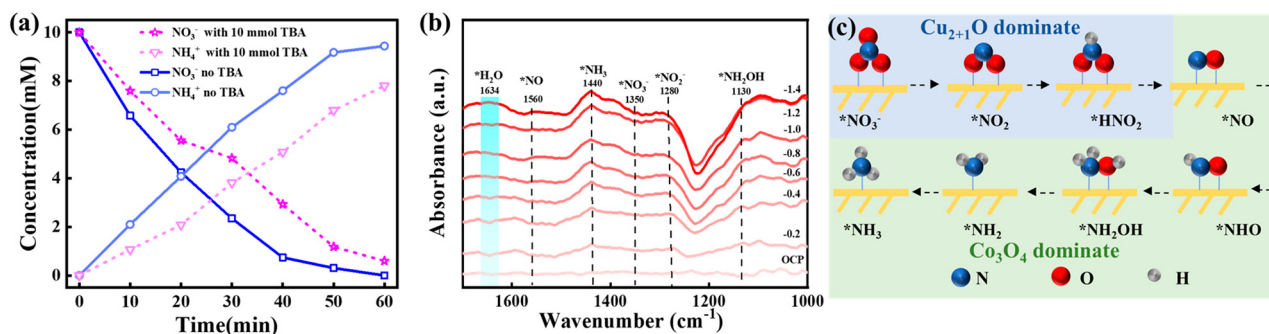


Figure 6. (a) Effect of TBA on the concentration changes of NO₃[−] and NH₄⁺ for CoCuNWs after 1 h reaction at −0.2 V vs. RHE in 0.5 M KOH + 10 mM KNO₃; (b) ATR–SEIRAS spectra of the CoCuNWs catalyst in 0.5 M KOH and 10 mM KNO₃ (* denotes adsorbed species). The background spectrum is obtained at open circuit potential; (c) a Schematic diagram of the NO₃[−]RR pathway on CoCuNWs.

The NH₃ formation pathway on CoCuNWs was explored by the ATR–SEIRAS test [67]. As shown in Figure 6b, a slight downward peak at 1350 cm^{−1} corresponds to the asymmetric stretching vibration of NO₃[−], while the peak at 1280 cm^{−1} is attributed to the asymmetric stretching vibration of NO₂[−], indicating the reduction of NO₃[−] to NO₂[−]. The peaks observed at approximately 1140 cm^{−1} and 1560 cm^{−1} are attributed to the vibrational modes of the *NH₂OH intermediate and the *NO species, respectively. These observations provide evidence for the formation of NH₂OH and *NO intermediates during the NO₃[−]RR [23,68,69].

As shown in Figure 6c, combined with the above comprehensive results, it is proposed that Cu₂₊₁O can facilitate the reduction of NO₃[−] to NO₂[−], while Co₃O₄ can promote the subsequent conversion of NO₂[−] to NH₃, where the synergetic catalytic effect leads to the remarkable enhancement of FE_{NH3} and NH₃ yield rate on CoCuNWs. Moreover, NO₃[−]RR catalyzed by CoCuNWs should proceed through the following pathway: *NO₃[−] → *NO₂[−] → *HNO₂ → *NO → *NHO → *NH₂OH → *NH₂ → *NH₃.

3. Materials and Methods

3.1. Reagent and Chemicals

Cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O), potassium sulfate (K₂SO₄), potassium nitrate (KNO₃), potassium nitrite (KNO₂), tert-butanol (TBA), sulfanilamide, dimethyl sulfoxide (DMSO–d₆), sodium salicylate, and potassium sodium tartrate were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd, (Shanghai, China). Copper foam and nickel foam were obtained from Tianjin Leviathan Technology Co., Ltd, (Tianjin, China). Potassium hydroxide (KOH), ammonium chloride (NH₄Cl), maleic acid, sodium hypochlorite solution (NaClO), sodium hydroxide (NaOH), and ethanol (C₂H₅OH) were purchased from Macklin Reagent Co., Ltd, (Shanghai, China). N–(1-Naphthyl) ethylenediamine was obtained from Beijing Inoke Technology Co., Ltd., (Beijing, China),

while hydrochloric acid (HCl) and sulfuric acid (H₂SO₄) were supplied by Jiangtian Chemical Co., Ltd. (Tianjin, China). Nafion 212 membranes were purchased from DuPont de Nemours, Inc., (Wilmington, DE, USA). All chemicals and materials were used as received without further purification. Deionized water was used in all experiments.

3.2. Material Synthesis

3.2.1. Synthesis of Cu(OH)₂ NWs

Cut copper foam sheets (15 mm × 30 mm) and first ultrasonically clean them in ethanol for 5 min to remove impurities. Then, ultrasonically clean the copper foam in 3 M HCl solution for 5 min to remove the oxide layer. Finally, ultrasonically clean the foam copper in deionized water for 5 min and dry it for later use. Mix 10.0 mL of 2.5 M NaOH solution with 10.0 mL of 0.125 M (NH₄)₂S₂O₈ solution until the solution becomes transparent. Then, immerse the pretreated foam copper sheet into the above-mixed solution and react at room temperature for 10 min. The reacted copper foam, which functioned as the Cu(OH)₂ NWs precursor, was rinsed three times alternately with deionized water and ethanol, then vacuum-dried at 60 °C for 2 h.

3.2.2. Synthesis of Co(OH)₂/Cu(OH)₂ NWs

Constant current electrodeposition was performed at a constant potential of −0.8 V vs. SCE for 300 s. The electrochemical cell was a single-compartment three-electrode system, with a platinum electrode (1 cm × 1 cm) as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode, and a platinum wire electrode containing the Cu(OH)₂ NWs precursor as the working electrode. The electrode sheet was cut to a size of 15 mm × 10 mm and immersed in the electrolysis solution, with an immersion area of 10 mm × 10 mm. The electrolyte was composed of 0.1 M Co(NO₃)₂·6H₂O and 0.1 M KCl. Through electrodeposition, a Co(OH)₂/Cu(OH)₂ NWs precursor was formed on the copper foam substrate. The obtained precursor was rinsed three times alternately with deionized water and ethanol, then vacuum-dried at 60 °C for 2 h.

3.2.3. Synthesis of CoCuNWs, Cu₂₊₁O NWs and Co₃O₄/NF

Co(OH)₂/Cu(OH)₂ NWs were annealed in a tubular furnace under a nitrogen atmosphere at a heating rate of 2.5 °C min^{−1} at 350 °C for 2 h. After natural cooling, the final Co₃O₄/Cu₂₊₁O NWs (CoCuNWs) were collected. The flowchart of the entire catalyst preparation process is shown in Figure 1. As a control, Cu₂₊₁O nanowires (Cu₂₊₁O NWs) were directly obtained by calcining the Cu(OH)₂ NWs precursor under the same conditions as those used for Co₃O₄/Cu₂₊₁O NWs. For Co₃O₄/NF, Cu(OH)₂ NWs were replaced by nickel foam, while all other conditions remained the same as those for preparing Co₃O₄/Cu₂₊₁O NWs.

3.3. Materials Characterization

Scanning electron microscopy (SEM, Tokyo, Japan, Hitachi Limited, Regulus 8600 and 4800); transmission electron microscopy (TEM, Tokyo, Japan, JEOL, JEM-F200); X-ray diffraction (XRD, Karlsruhe, Germany, Bruker D8, Cu Kα, λ = 0.154178 nm); X-ray photoelectron spectroscopy (XPS, Waltham, MA, USA, Thermo Fisher Scientific, K-Alpha+); ultraviolet–visible spectrophotometry (UV-vis, Shanghai, China, YOKE INSTRUMENT, T2602); nuclear magnetic resonancespectroscopy (NMR, Palo Alto, CA, USA, Varian Mercury Plus 600 MHz, 1H NMR).

3.4. Electrochemical Measurements

Electrochemical measurements were performed using an H-type electrolytic cell (separated by Nafion 212 membrane; magnetic stirring rate of 300 rpm) and a CHI 660D

workstation (Shanghai Chenhua, Shanghai, China) in a three-electrode system. All samples (10 mm × 10 mm) were used as the working electrode, with a platinum foil (2 cm × 1 cm) and a saturated calomel electrode (filled with saturated KCl solution) used as the counter and reference electrodes, respectively. Prior to testing, all catalysts were activated in the electrolyte via cyclic voltammetry, with a scan rate of 50 mV s^{−1}, a scan range of −0.6 to −1.6 V vs. SCE, and 20 cycles. A 0.5 M KOH aqueous solution containing 10 mM KNO₃ (30 mL) was used as the electrolyte. Linear sweep voltammetry (LSV) curves were obtained in the H-type cell with a scan rate of 5 mV s^{−1}. Unless otherwise stated, the current density was normalized to the geometric electrode area (1 cm²). Constant potential tests were conducted at a stirring rate of 300 rpm for 1 h. After the reaction, 1 mL of cathodic electrolyte was diluted 100 times in a 100 mL volumetric flask for further analysis.

3.5. ATR–SEIRAS Test

Attenuated Total Reflectance Surface–Enhanced Infrared Absorption Spectroscopy (ATR–SEIRAS) tests were conducted on the WQF–530A Fourier transform infrared spectrometer (Beijing Beifen Ruili Analytical Instrument (Group) Co., Ltd., Beijing, China) equipped with a Mercury Cadmium Telluride (MCT) detector in a homemade three-electrode electrochemical cell. A platinum electrode and a solid-state Ag/AgCl electrode were used as the counter and reference electrodes, respectively. The cathode ink was dropped onto a gold-sputtered silicon prism as the working electrode. A 10 mM KNO₃ and 0.5 M KOH solution was used as the electrolyte. Before spectral acquisition, electrolysis was performed for 1 min at different cathode potentials using the chronoamperometry method. All spectra were subtracted from the background.

4. Conclusions

In summary, a novel dual-metal CoCuNWs catalyst was successfully developed for NO₃[−] reduction reaction to ammonia, achieving a Faradaic efficiency of NH₃ exceeding 96.7% and a production rate of 0.30 mmol h^{−1} cm^{−2} at −0.2 V vs. RHE in 10 mM KNO₃. Comparative experiments demonstrate that Cu₂₊₁O primarily facilitates the initial reduction of NO₃[−] to nitrite NO₂[−], while Co₃O₄ is more effective in driving the subsequent conversion of NO₂[−] to NH₃. The synergistic interaction significantly increases both the NO₃[−] conversion rate and the selectivity toward NH₃. Moreover, the kinetic analyses demonstrated that CoCuNWs possess the significantly enhanced diffusion and adsorption ability of NO₃[−] and NO₂[−], as evidenced by higher saturated adsorption capacity and diffusion coefficients compared to bare Cu₂₊₁O NWs, thereby accelerating the reaction kinetics. Furthermore, ATR–SEIRAS confirmed a stepwise hydrogenation pathway involving *NO₂[−], *NO, *NH₂OH, and *NH₃ intermediates. This work highlights the crucial role of the synergistic effect in bimetallic catalysts for improving electrocatalytic efficiency and provides a new insight from the kinetic perspectives to investigate the NO₃[−] reduction reaction.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal15050491/s1>. Figure S1: (a) The full spectra XPS of CoCuNWs and (b) Cu LMM spectra for CoCuNWs; Figure S2: (a) The CV curves at various scan rates of the Cu₂₊₁O NWs and (b) the CV curves at various scan rates of the CoCuNWs; Figure S3: (a) UV–vis absorption spectroscopies for various concentrations of NH₄⁺ and (b) calibration curve used to estimate the concentration of NH₄⁺; Figure S4: (a) UV–vis absorption spectroscopies for various concentrations of NO₂[−] and (b) calibration curve used to estimate the concentration of NO₂[−]; Figure S5: (a) UV–vis absorption spectroscopies for various concentrations of NO₃[−] and (b) calibration curve used to estimate the concentration of NO₃[−]; Figure S6: Conversion of NO₃[−] and NH₃ yield rate in different concentration nitrate sources and 0.5 M KOH at −0.2 V vs. RHE; Figure S7:

Yield rate base on ECSA for NH_3 of Cu_{2+1}O NWs and CoCuNWs at different applied potentials with 10 mM NO_3^- ; Figure S8: SEM of CoCuNWs after 10-cycle tests; Figure S9: High-resolution XPS spectra of (a) Co 2p, (b) Cu 2p of CoCuNWs after electrolysis, where the circles represent the raw data and the red lines represent the fitted data; Figure S10: I-t curves of NO_3^- reduction over CoCuNWs and Cu_{2+1}O NWs in 0.1 M NO_3^- and 0.1 M NO_2^- at -0.2 V vs. RHE without stirring; Figure S11: The LSV curves of (a) CoCuNWs and (b) Cu_{2+1}O NWs in 0.5 M KOH and different concentrations of KNO_3 at the scan rate of 20 mV s^{-1} ; Figure S12: The LSV curves of (a) CoCuNWs and (b) Cu_{2+1}O NWs in 0.5 M KOH and different concentrations of KNO_2 at the scan rate of 20 mV s^{-1} . Table S1: The proportion of different elements in XPS analysis for CoCuNWs; Table S2: Electrochemical impedance parameters as estimated from the fitted data of the impedance spectra shown in Figure 3b using the frequency range of 0.1 to 100 K Hz; Table S3: The comparison of electrochemical NO_3^- RR performance between CoCuNWs and other reported electrocatalysts. References [37,55,56,70–75] are cited in the Supplementary Materials.

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