

# Phase-dependent Electrocatalytic Nitrate Reduction to Ammonia on Janus Cu@Ni Tandem Catalyst

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**ABSTRACT:** Electrosynthesis of  $\text{NH}_3$  from nitrate anion ( $\text{NO}_3^-$ ) reduction ( $\text{NO}_3^-$ RR) is a cascade reaction, which is considered a great potential alternative to the Haber–Bosch route to reduce  $\text{CO}_2$  emissions and alleviate the adverse effects of excessive  $\text{NO}_3^-$  contamination in the environment. Frequently, solid solution alloys (SSAs) with a single-phase active site may struggle to fully utilize their benefits during the entire process of nitrate ( $\text{NO}_3^-$ ) reduction, which involves multiple intermediate reactions. In this study, we showed that by separating Cu and Ni in a Janus Cu@Ni catalyst structure, we can achieve high performance in  $\text{NO}_3^-$ RR, yielding a high Faradaic efficiency (92.5%) and a production rate of  $\text{NH}_3$  ( $1127 \text{ mmol h}^{-1} \text{ g}^{-1}$ ) at  $-0.2 \text{ V}$  versus RHE, compared to CuNi SSA ( $82.6\%$ ,  $264 \text{ mmol h}^{-1} \text{ g}^{-1}$ ). Here, we demonstrate that a Janus Cu@Ni catalyst with short-range ordered catalytic sites favors the adsorption of NO through a bridge-bond mode. Simultaneously, a hydrogen spillover process was observed, in which Ni dissociates  $\text{H}_2\text{O}$  to generate  $^*\text{H}$  which spontaneously migrates to adjacent catalytic sites to hydrogenate the  $^*\text{NO}_x$  intermediates. This facilitates N–O bond cleavage, resulting in the  $\text{NH}_3$  production rate nearly 5 times higher than that of CuNi SSA, where NO was linearly bonded on its surface. The study of this catalytic effect, a cooperative tandem enhancement, provides insights into the design of multifunctional heterogeneous catalysts for electrochemical  $\text{NH}_3$  synthesis.

**KEYWORDS:** electrochemical ammonia synthesis, Cu@Ni, phase separation, tandem catalyst, short-range ordered catalytic sites



## INTRODUCTION

Catalysts based on bimetallic nanoparticles have received tremendous scientific and industrial investigation and have established themselves as an essential class of active catalysts. Indeed, alloying two metals can dramatically enhance catalytic activity and products selectivity compared to analogous monometallic counterparts.<sup>1</sup> The improved catalytic performances of alloy catalysts are mainly due to the synergistic cooperation between the two metals within the bimetallic catalyst through structural and electronic effects.<sup>2,3</sup> Thanks to these two effects, the interactions of reaction intermediates with the catalyst surface can be effectively modulated, significantly influencing the overall reaction activity and selectivity during catalysis. To date, most bimetallic catalysts reported in the literature are solid-solution alloys that contain a single phase. Their properties are usually the weighted average of the different local atomic arrangements. Another kind of bimetallic catalyst is a Janus bimetallic alloy that has a separation of the two metals and is commonly applied for tandem catalysis. Janus alloys with multifunctional active sites with different catalytic properties produce the nanoparticle of a great activity in cascade catalytic reactions,<sup>4</sup> which has always been challenging with the solid-solution alloys (SSAs). However, there has not been an adequate understanding of the unique potential of Janus alloys in catalysis,

although recent studies have revealed that some Janus bimetallic catalysts have better catalytic performances than SSA of the same composition.<sup>5–7</sup>

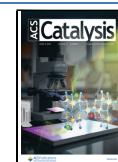
For the target of attaining net zero carbon by 2050, researchers have been seeking new sustainable technologies to facilitate “greener” and more efficient chemical synthesis routes. The industrial synthesis of  $\text{NH}_3$  relies heavily on the Haber–Bosch route,<sup>8</sup> which accounts for roughly 1.2% of global annual  $\text{CO}_2$  emissions that surpasses any other industrial chemical-making reactions.<sup>9,10</sup> Electrosynthesis of  $\text{NH}_3$  from nitrate anion ( $\text{NO}_3^-$ ) reduction ( $\text{NO}_3^-$ RR), which could be powered by renewable energy, has been considered as a potential alternative to the Haber–Bosch route.<sup>11</sup>  $\text{NO}_3^-$  is found extensively throughout both industrial and agricultural wastewater.<sup>12</sup> Not only could electroreduction of  $\text{NO}_3^-$  from sewage alleviate the adverse effects of excessive  $\text{NO}_3^-$  contamination in the environment,<sup>13</sup> electrocatalytic production of  $\text{NH}_3$  also reduces

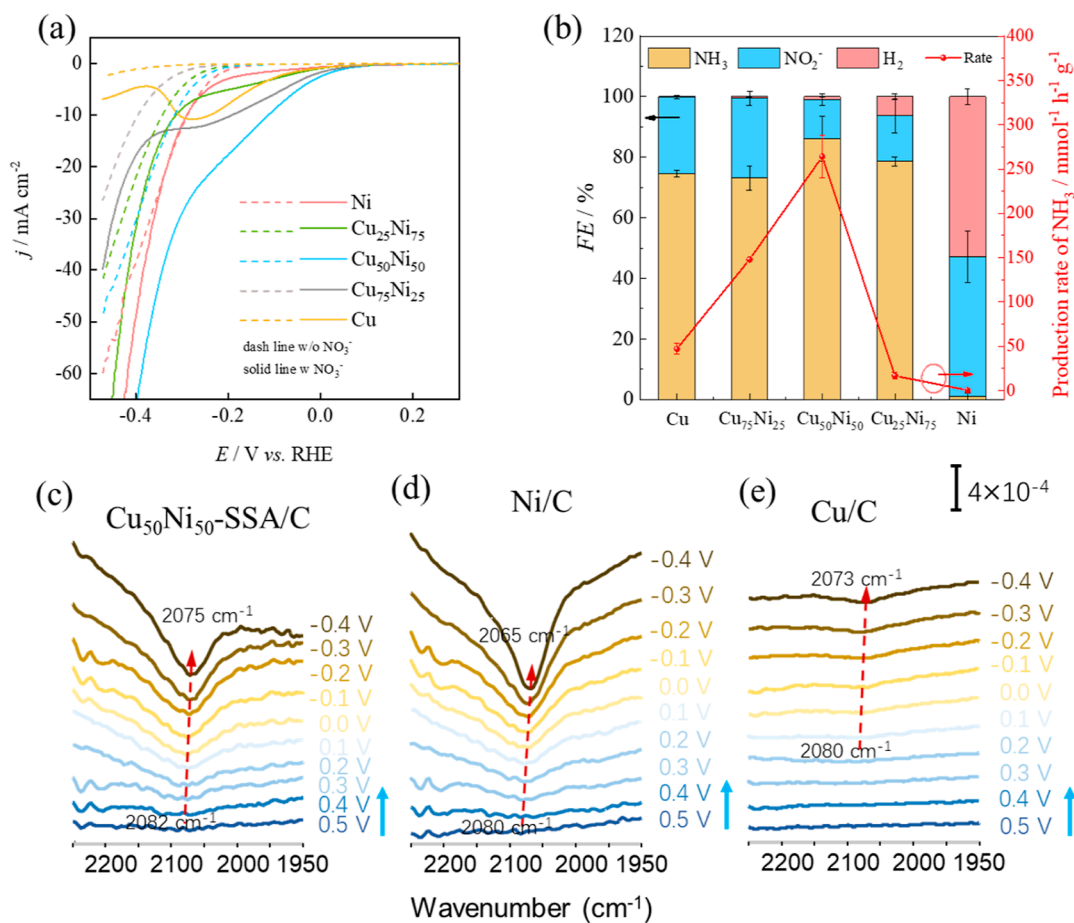
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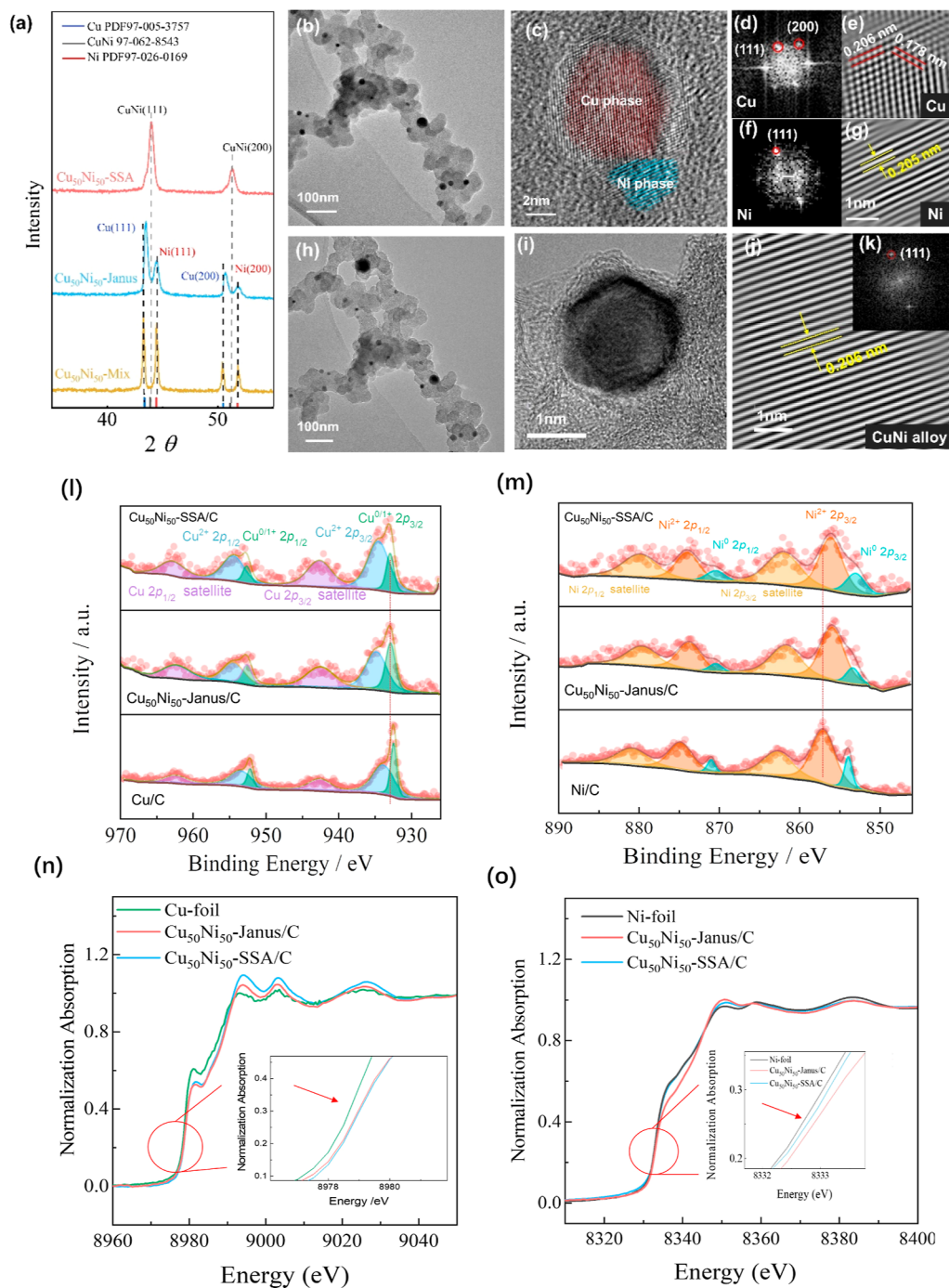




**Figure 1.** (a) Linear sweep voltammetry of Cu/C, Cu<sub>75</sub>Ni<sub>25</sub>-SSA/C, Cu<sub>50</sub>Ni<sub>50</sub>-SSA/C, Cu<sub>25</sub>Ni<sub>75</sub>-SSA/C, and Ni/C in 1 M KOH with (solid line) and without (dashed line) 0.1 M KNO<sub>3</sub>. Scan rate: 10 mV s<sup>-1</sup>. (b) Faradaic efficiency of NH<sub>3</sub>, NO<sub>2</sub><sup>-</sup>, and H<sub>2</sub> (histogram) and production rate of NH<sub>3</sub> (line) over Cu/C, Cu<sub>75</sub>Ni<sub>25</sub>-SSA/C, Cu<sub>50</sub>Ni<sub>50</sub>-SSA/C, Cu<sub>25</sub>Ni<sub>75</sub>-SSA/C, and Ni/C at -0.2 V vs RHE. Electrochemical FTIR spectra of Cu<sub>50</sub>Ni<sub>50</sub>-SSA/C (c), Ni/C (d), and Cu/C (e) in 1 M KOH without KNO<sub>3</sub>. The associated error bars correspond to the mean ± s.d. (*n* = 3).

the CO<sub>2</sub> emissions, that helps achieve the goal of carbon neutrality. According to some studies,<sup>14,15</sup> NO<sub>3</sub><sup>-</sup>RR to NH<sub>3</sub> is considered as a cascade reaction, involving the transfer of eight electrons and nine protons, where NO<sub>3</sub><sup>-</sup> is first reduced into NO<sub>2</sub><sup>-</sup>, and subsequently further reduced to NH<sub>3</sub>. Catalyst with a single type of catalytic site (such as SSA) can hardly benefit from their homogeneous alloying structure in the whole NO<sub>3</sub><sup>-</sup>RR process. In comparison, the Janus catalyst with tandem sites has the capability to modify the adsorption energies of NO<sub>3</sub><sup>-</sup>RR intermediates by adjusting the electronic structure but also could optimize the reaction pathway. For example, between the Pd(111) and Pd(100) facets over the surface structure of Pd nanoparticles;<sup>16</sup> particles with a core-shell structure containing Cu/CuO<sub>x</sub> and Co/CoO phases, respectively.<sup>4</sup> This in turn accelerates the reaction kinetics by leveraging its multifunctional catalytic sites for the relay reactions. Herein, it is with utmost importance to provide an alternative explanation on the mechanism of this reaction over Janus alloy where the catalytic activity may be enhanced. Typically, Cu is considered as one of the best electrocatalysts for NO<sub>3</sub><sup>-</sup>RR to NH<sub>3</sub>,<sup>17,18</sup> owing to the similar energy level between d-orbital on it and LUMO π\* orbital of NO<sub>3</sub><sup>-</sup> resulting in a good affinity for the reduction of NO<sub>3</sub><sup>-</sup> as well as its hydrogenated intermediates.<sup>19</sup> However, Cu has a low \*H (adsorbed hydrogen) formation ability,<sup>20</sup> which causes the accumulation of NO<sub>2</sub><sup>-</sup> intermediates on the surface (i.e., high coverage of nitrogenous species and low coverage of

\*H). This effect poisons the active sites and leads to unsatisfactory catalytic activity and low product selectivity over pure Cu. The imbalance between \*NO<sub>x</sub> and \*H adsorption can be a limiting factor.<sup>21,22</sup> To address this issue, researchers have explored Cu-based alloyed catalysts, e.g., Pd-Cu, Co-Cu, Ni-Cu, and Ru-Cu, which have demonstrated enhanced catalytic activities by fine-tuning the adsorption energy of \*H and \*NO<sub>x</sub>.<sup>21,23–26</sup> Despite these encouraging progresses, their achievable performances still fall short of expectations due to the cascade reaction system of the NO<sub>3</sub><sup>-</sup>RR to NH<sub>3</sub>. Indeed, Cu-based alloyed catalysts can rarely display activity for certain reaction steps of the cascade process. In the present work, we have compared the activity of a classical CuNi SSA/C with a Janus Cu@Ni catalyst supported on XC-72 and a physical mixture of Cu/C and Ni/C. Due to its intrinsic structure, the Janus Cu@Ni catalyst exhibits a high activity (almost 5 times to the current density over alloyed catalyst) across all the reaction steps of the NO<sub>3</sub><sup>-</sup>RR process. The underlying mechanism over the Janus Cu@Ni catalyst during NO<sub>3</sub><sup>-</sup>RR is attributed to the cooperative effect observed within its multiphased structure, where the short-range ordered catalytic sites favor the adsorption of NO through a bridge-bond mode. In contrast, the NO intermediate was linearly bonded over the CuNi SSA/C catalyst. All of the investigations in this study were well supported by in situ electrochemical ATR-FTIR and DFT calculations. Our emphasis lies in the investigation of the



**Figure 2.** XRD patterns of Cu<sub>50</sub>Ni<sub>50</sub>-Mix/C, Cu<sub>50</sub>Ni<sub>50</sub>-Janus/C, and Cu<sub>50</sub>Ni<sub>50</sub>-SSA (a). TEM image of Cu<sub>50</sub>Ni<sub>50</sub>-Janus/C (b), HR-TEM image of a single nanoparticle of Cu<sub>50</sub>Ni<sub>50</sub>-Janus/C (c), and the corresponding FFT diffraction pattern (d,f) and IFFT image (e,g) of the Cu-rich and Ni-rich phase, respectively. TEM image of Cu<sub>50</sub>Ni<sub>50</sub>-SSA/C (h). HRTEM image of a single nanoparticle of Cu<sub>50</sub>Ni<sub>50</sub>-SSA/C (i) and the corresponding IFFT image (j) and FFT diffraction pattern (k). XPS spectra of Cu 2p (l) and Ni 2p (m) of Cu<sub>50</sub>Ni<sub>50</sub>-Janus/C and Cu<sub>50</sub>Ni<sub>50</sub>-SSA/C, compared to Cu/C and Ni/C. X-ray absorption near edge structure (XANES) spectra of Cu (n) and Ni (o) K-edge of the Cu<sub>50</sub>Ni<sub>50</sub>-Janus/C, Cu<sub>50</sub>Ni<sub>50</sub>-SSA/C, and standard samples.

mechanism, highlighting the novelty of metal separation that actively catalyzes the electrochemical reaction. This is an alternative to the widely reported homogeneously alloyed catalysts.

## RESULTS AND DISCUSSION

CuNi SSAs supported on XC-72 with Cu/Ni ratios of 25:75, 50:50, and 75:25, along with their monometallic counterparts

were prepared via a simple impregnation method (Supporting Information, Text S1, Table S1 and Figure S1), and their activity was subsequently assessed (Figure 1a). In the absence of nitrate, the highest hydrogen evolution reaction (HER) activity was observed over the monometallic Ni/C displaying the smallest HER Tafel slope, i.e., 87.5 mV dec<sup>-1</sup> (Supporting Information, Figure S2). This value close to 118 mV dec<sup>-1</sup> revealed that the Volmer step was the rate-determining step (RDS).<sup>27</sup> In the

presence of 100 mM  $\text{NO}_3^-$ , the current density ( $j$ ) increased greatly over all the Cu-based catalysts, notably, the  $\text{Cu}_{50}\text{Ni}_{50}$ -SSA/C catalyst showed the highest  $\text{NO}_3^-$ RR current density than any other catalysts with different metal ratios (Figure 1a). In comparison, a negligible increase of the current density was observed over Ni/C. The  $\text{NH}_3$  yield rate ( $Y_{\text{NH}_3}$ ) on Cu/C (47.2  $\text{mmol}^{-1} \text{h}^{-1} \text{g}^{-1}$ ) was about 118 times higher than that on Ni/C (0.4  $\text{mmol}^{-1} \text{h}^{-1} \text{g}^{-1}$ ), see Figure 1b. The addition of Ni to Cu dramatically increased the  $Y_{\text{NH}_3}$  from 47.2  $\text{mmol}^{-1} \text{h}^{-1} \text{g}^{-1}$  on Cu/C to 264.1  $\text{mmol}^{-1} \text{h}^{-1} \text{g}^{-1}$  on  $\text{Cu}_{50}\text{Ni}_{50}$ -SSA/C. Based on these results, it can be inferred that Cu sites serve as the main active site for  $\text{NO}_3^-$  adsorption during  $\text{NO}_3^-$ RR while Ni sites play an important role in providing  $^*\text{H}$  via the Volmer step ( $\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}^* + \text{OH}^-$ ). When the Ni proportion in the alloy exceeded 50%, a sharp decrease in  $Y_{\text{NH}_3}$  was observed. For example, only about 17  $\text{mmol}^{-1} \text{h}^{-1} \text{g}^{-1}$  of  $Y_{\text{NH}_3}$  was generated on  $\text{Cu}_{25}\text{Ni}_{75}$ -SSA/C, and this was ascribed to the ensemble effect caused by the dilution of the Cu sites by Ni atoms' incorporation.<sup>28</sup> In that case, the  $^*\text{H}$  coverage was sufficiently high to prevent the adsorption of  $\text{NO}_3^-$  over  $\text{Cu}_{25}\text{Ni}_{75}$ -SSA/C. The volcano shape of  $Y_{\text{NH}_3}$  substantiated that Cu was the main active sites for  $\text{NO}_3^-$  adsorption during  $\text{NO}_3^-$ RR to  $\text{NH}_3$ . It is evident from this data that an appropriate Cu/Ni ratio plays a crucial role in achieving a balanced coverage of  $^*\text{NO}_3^-$  and  $^*\text{H}$  on the catalytic surface, which is critical to maintaining high catalytic performances in  $\text{NH}_3$  production.<sup>21</sup> It is also interesting to note that the Faradaic efficiency of  $\text{NH}_3$  ( $FE_{\text{NH}_3}$ ) was comparable and between 74 and 86% among Cu-based catalysts, indicating that the introduction of Ni could tune  $^*\text{H}$  coverage but not affect  $FE_{\text{NH}_3}$ .

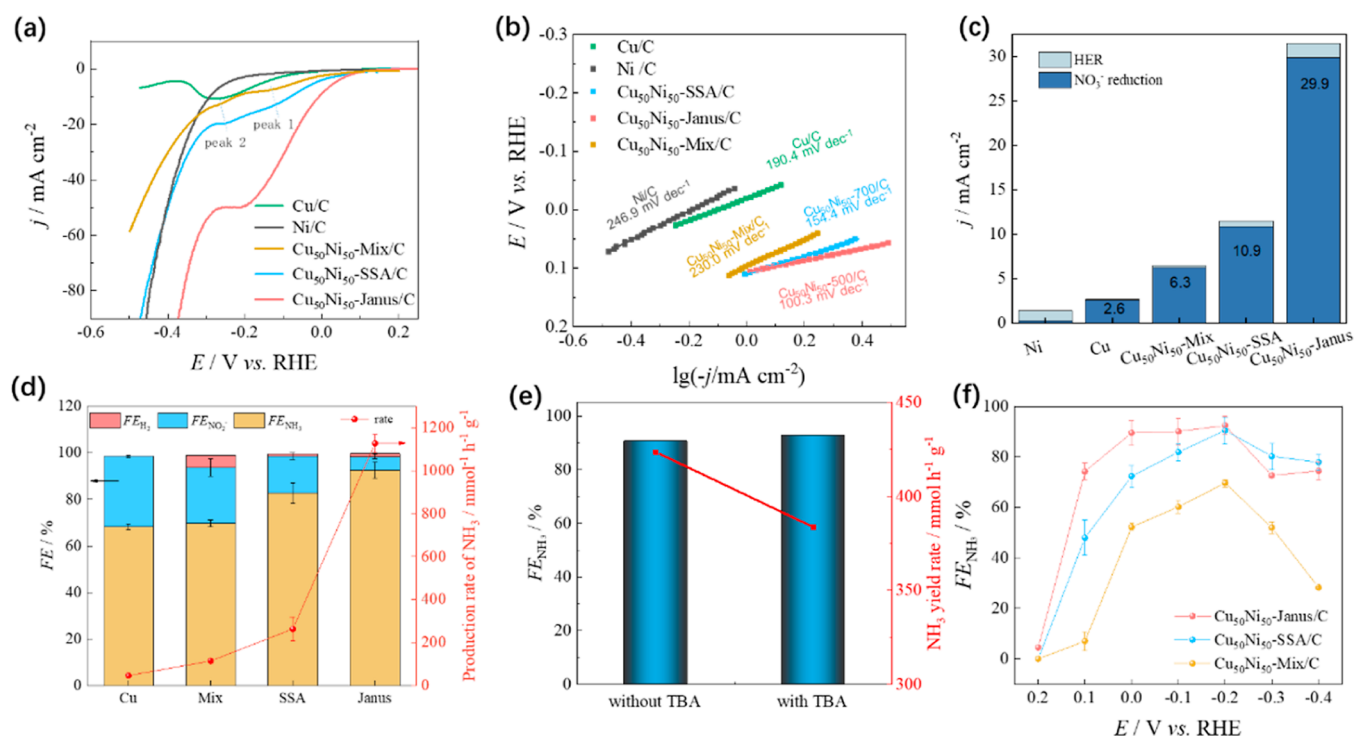
In situ electrochemical attenuated total reflection FTIR (ATR-FTIR) spectroscopy was used to monitor the signals of  $^*\text{H}$  on the catalysts. A downward peak at 2082  $\text{cm}^{-1}$  assigned to the vibration of the bond of  $^*\text{H}$  and a metal surface was observed at 0.3 V versus RHE in 1 M KOH electrolyte free of  $\text{NO}_3^-$  on  $\text{Cu}_{50}\text{Ni}_{50}$ -SSA/C (Figure 1c). The band center was red-shifted to 2075  $\text{cm}^{-1}$  at -0.4 V, yielding a Stark turn rate of 10  $\text{cm}^{-1} \text{V}^{-1}$ . The Stark effect in the vibration frequency indicated the enhanced adsorption of hydrogen atoms on the  $\text{Cu}_{50}\text{Ni}_{50}$ -SSA/C surface at higher overpotentials ( $\eta$ ) according to eq 1. When the potential negatively shifted, the intensity of  $^*\text{H}$  gradually raised. In that case, the Volmer step was highly promoted, and therefore, more  $^*\text{H}$  were generated, which in turn enhanced the hydrodeoxidation reaction and gave a higher  $\frac{\text{NH}_3}{\text{NO}_2^- + \text{NH}_3}$  ratio (Supporting Information, Figure S3). The fact that  $^*\text{H}$  signals on  $\text{Cu}_{50}\text{Ni}_{50}$ -SSA/C and Ni/C were much stronger than that over Cu (appearing potential was positively shifted by 200 mV), Figure 1d,e, gave strong evidence that  $^*\text{H}$  on CuNi bimetallic catalysts was mainly attributed to water dissociation on Ni sites. With the addition of  $\text{NO}_3^-$ , the peak intensity from  $^*\text{H}$  decreased on  $\text{Cu}_{50}\text{Ni}_{50}$ -SSA/C (Supporting Information, Figure S4a) due to the competitive adsorption of  $^*\text{NO}_3^-$  with  $^*\text{H}$  on the catalytic surface. In the Cu/C spectra,  $^*\text{H}$  vanished (Supporting Information, Figure S4b), while the Ni/C surface maintained the  $^*\text{H}$  signal (Figure S4c), reaffirming that Cu and Ni sites were responsible for  $\text{NO}_3^-$  and H adsorption, respectively. Electron paramagnetic resonance (EPR) spectroscopy was conducted to detect the presence of  $^*\text{H}$  (Supporting Information Figure S5) using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as a spin trap.<sup>29</sup> In the presence of nitrate, the intensity of the EPR signal of the DMPO- $^*\text{H}$  adduct on  $\text{Cu}_{50}\text{Ni}_{50}$ -SSA/C

decreased. These results align consistently with the ATR-FTIR analysis.

$$\eta = E - E_{\text{eq}} = \frac{RT}{F} \ln \frac{\theta_{\text{H}}}{\theta_{\text{H}}^0} \quad (1)$$

Where  $\theta_{\text{H}}$  and  $\theta_{\text{H}}^0$  are the  $^*\text{H}$  coverage at E and  $E^0$ , respectively; F is the Faraday constant, 96485 C mol<sup>-1</sup>; R is the gas constant, 8.314 J mol<sup>-1</sup> K<sup>-1</sup>; and T is the kelvin temperature, K.

While CuNi catalysts with other ratios and their physical structures remain of importance, we opted to primarily focus on the Cu/Ni ratio of 50:50 which showed the highest activity in the  $\text{NO}_3^-$ RR (Figure 1a). To gain insights into this behavior, we prepared two other samples with the same 50:50 ratio. These samples include the XC-72 supported Cu@Ni Janus alloy (referred to as  $\text{Cu}_{50}\text{Ni}_{50}$ -Janus/C, Figure 2) and a physical mixture of Cu/C and Ni/C catalysts (denoted as  $\text{Cu}_{50}\text{Ni}_{50}$ -Mix/C). The preparation for  $\text{Cu}_{50}\text{Ni}_{50}$ -Janus/C followed the same step as that of the  $\text{Cu}_{50}\text{Ni}_{50}$ -SSA/C synthesis (700 °C), with the exception that the annealing temperature was set at 500 °C. TEM-EDS mapping of  $\text{Cu}_{50}\text{Ni}_{50}$ -Janus/C and  $\text{Cu}_{50}\text{Ni}_{50}$ -SSA/C revealed a uniform distribution of Cu and Ni on the carbon substrate (Supporting Information, Figure S6). The average particle size was similar for both catalysts, measuring  $22.2 \pm 11.1$  and  $23.6 \pm 10.8$  nm, respectively (Supporting Information, Figure S7a,b). The XRD pattern of  $\text{Cu}_{50}\text{Ni}_{50}$ -SSA/C (PDF #062-8543) displayed two peaks assigned to a pure alloy. The peak fitting and refinement of the main peak of  $\text{Cu}_{50}\text{Ni}_{50}$ -SSA/C were performed (Supporting Information, Figure S7c). There were two subpeaks obtained at 43.4 and 44.0°, which were accounted for 9.9 and 91% of the peak area. The main subpeak at 44.0° was assigned to CuNi(111) and the minor subpeak at 43.4° was should ascribed to Cu(111) at 42.3° that was incorporated by Ni atoms. The XRD pattern of  $\text{Cu}_{50}\text{Ni}_{50}$ -Janus/C confirmed the separation of Cu and Ni, by exhibiting two sets of diffraction peaks assigned to a typical face-centered cubic (fcc) structure for Cu (PDF #005-3757) and Ni (PDF #026-0169) (Figure 2a), respectively, and was similar to the pattern of  $\text{Cu}_{50}\text{Ni}_{50}$ -Mix/C. The two sets of diffraction peaks of  $\text{Cu}_{50}\text{Ni}_{50}$ -Janus/C showed a convergence toward each other, indicating that  $\text{Cu}_{50}\text{Ni}_{50}$ -Janus/C had a Janus structure with coexisting Cu-rich and Ni-rich solid solutions. The Janus structure was also confirmed by the HR-TEM image of a single nanoparticle (Figure 2b,c) with the assistance of Fourier transform (FFT)/inverse Fourier transform (IFFT) images (Figure 2d-g). The lattice spacing constriction observed on the Cu phase, as compared to the PDF standard card for fcc Cu (PDF #005-3757), further indicates the incorporation of some Ni atoms within the Cu lattice. In parallel, the same phenomenon was observed with Ni, indicating the incorporation of some Cu atoms in its lattice. In the case of  $\text{Cu}_{50}\text{Ni}_{50}$ -SSA/C, the HR-TEM and corresponding FFT/IFFT images displayed a homogeneous distribution of Cu and Ni within the nanoparticle with a one-phase structure, supporting the existence of a CuNi alloy phase (Figure 2h-k). The extended X-ray absorption fine structure (EXAFS) analysis further confirmed the coordination structures of those two CuNi bimetallic alloys (Supporting Information, Figure S8). The Fourier transform (FT)  $K_3$ -weighted EXAFS spectra exhibited a metal interaction peak around 2.2 Å, indicating the main formation of metallic bonds. The structural parameters of Cu and Ni atoms were also obtained and are summarized in Supporting Information, Table S2. In  $\text{Cu}_{50}\text{Ni}_{50}$ -



**Figure 3.**  $j$ - $E$  curve (80%  $iR$  corrected) over Cu<sub>50</sub>Ni<sub>50</sub>-Janus/C, Cu<sub>50</sub>Ni<sub>50</sub>-SSA/C, Cu<sub>50</sub>Ni<sub>50</sub>-Mix/C, and Cu/C and Ni/C modified rotate disk electrode (catalysts loading was  $0.2 \text{ mg cm}^{-2}$ ) in 1 M KOH solution containing 100 mM KNO<sub>3</sub> at a scan rate of  $10 \text{ mV s}^{-1}$  with the rotate rate as 900 rpm (a). Tafel slopes (b). According to the results from (a) Bias current density of NO<sub>3</sub><sup>-</sup>RR and HER according to (c). FE and Y<sub>NH<sub>3</sub></sub> over Cu<sub>50</sub>Ni<sub>50</sub>-Janus/C, Cu<sub>50</sub>Ni<sub>50</sub>-SSA/C, Cu<sub>50</sub>Ni<sub>50</sub>-Mix/C, Cu/C, and Ni/C-coated carbon cloth ( $5 \text{ mg cm}^{-2}$ ) at  $-0.2 \text{ V}$  vs RHE in 1 M KOH solution containing 100 mM KNO<sub>3</sub> (d). FE<sub>NH<sub>3</sub></sub> and Y<sub>NH<sub>3</sub></sub> over Cu<sub>50</sub>Ni<sub>50</sub>-SSA/C-coated carbon cloth ( $5 \text{ mg cm}^{-2}$ ) at  $-0.2 \text{ V}$  vs RHE in 1 M KOH solution containing 100 mM KNO<sub>3</sub> with and without TBA addition (50 mM) (e). FE<sub>NH<sub>3</sub></sub> over Cu<sub>50</sub>Ni<sub>50</sub>-Janus/C, Cu<sub>50</sub>Ni<sub>50</sub>-SSA/C, Cu<sub>50</sub>Ni<sub>50</sub>-Mix/C, Cu/C, and Ni/C coated on carbon cloth ( $5 \text{ mg cm}^{-2}$ ) in the potential window from 0.2 to  $-0.4 \text{ V}$  vs RHE (f). The associated error bars correspond to mean  $\pm$  s.d. ( $n = 3$ ).

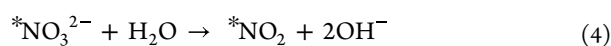
Janus/C, each Cu atom is coordinated by an average of approximately 10.8 Cu and 1.2 Ni atoms, while each Ni atom is coordinated by an average of 10.8 Ni and 1.2 Cu atoms. This observation supports the preservation of a short-range ordered structure in both the Cu-rich and Ni-rich phases. On the other hand, in Cu<sub>50</sub>Ni<sub>50</sub>-SSA/C, Cu and Ni atoms were each coordinated by six Cu and six Ni atoms, respectively, confirming its solid solution alloy structure with a uniform 1:1 mixture of Cu and Ni.

The electronic structure of Cu<sub>50</sub>Ni<sub>50</sub>-SSA/C and Cu<sub>50</sub>Ni<sub>50</sub>-Janus/C was further studied, given that the alloying degree of Ni with Cu can tune the electronic structure of the catalysts.<sup>30</sup> The XPS results revealed high-intensity signals for Cu<sup>2+</sup>  $2p$  and Ni<sup>2+</sup>  $2p$  on Cu/C, Ni/C, and bimetallic catalysts due to the oxidation of metallic sites resulting from the exposition of the catalyst to air (Figure 2l,m). In addition, compared with the Cu/C catalyst, the Cu<sup>0/1+</sup>  $2p_{3/2}$  peak of the alloy catalyst shifted toward a lower binding energy. Similarly, compared with the Ni/C catalyst, the Ni<sup>2+</sup>  $2p_{3/2}$  peak of the alloy catalyst shifted toward a higher binding energy, indicating a redistribution of electrons among Cu and Ni atoms within their alloyed structure. These results aligned consistently with XANES characterization (Figure 2n,o). The Ni K-edge of CuNi bimetals showed a slight positive shift as compared with the Ni reference, which demonstrated an increase in the Ni valence state of Cu<sub>50</sub>Ni<sub>50</sub>-Janus/C and Cu<sub>50</sub>Ni<sub>50</sub>-SSA/C. The Cu K-edge of the CuNi bimetals also showed a positive shift toward a higher energy than that of the Cu reference, which could be ascribed to the oxidation of Cu when being exposed to air. In addition, according to the Bader charge analysis, a charge redistribution on CuNi(111) was

observed in comparison to monometallic Cu and Ni; within this redistribution, the Ni center displayed an increased Bader charge, while the Cu center showed a decreased Bader charge (Supporting Information, Figure S9). Furthermore, the impedance of Cu<sub>50</sub>Ni<sub>50</sub>-Mix/C ( $74.1 \Omega$ ) was significantly higher than that of the CuNi alloy catalyst ( $46.3 \Omega$  for Cu<sub>50</sub>Ni<sub>50</sub>-SSA/C and  $48.2 \Omega$  for Cu<sub>50</sub>Ni<sub>50</sub>-Janus/C), Supporting Information, Figure S10. The electrons redistribution between Cu and Ni atoms plays an important role in modulating the adsorption energy of the \*NO<sub>3</sub><sup>-</sup>, and reducing intermediate species and \*H.<sup>30</sup> The electrocatalytic activities of Cu<sub>50</sub>Ni<sub>50</sub>-Janus/C, Cu<sub>50</sub>Ni<sub>50</sub>-SSA/C, and Cu<sub>50</sub>Ni<sub>50</sub>-Mix/C toward NO<sub>3</sub><sup>-</sup>RR, in comparison to Cu/C and Ni/C were then evaluated.

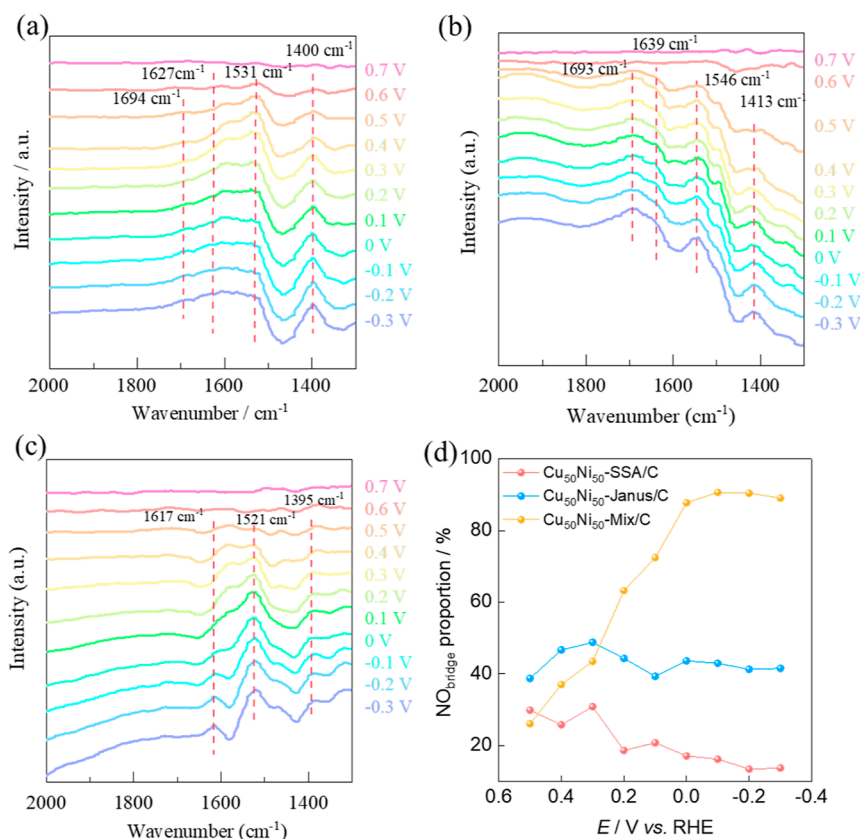
First, the linear sweep voltammograms (LSVs) were performed in Ar-saturated solutions of 1 M KOH +100 mM KNO<sub>3</sub> (Figure 3a). Two reduction current peaks (Peaks 1 and 2) appeared in the Cu-based catalysts' curves. According to previous studies,<sup>31,32</sup> the Peak 1 near  $-0.1 \text{ V}$  versus RHE was assigned to the reduction of \*NO<sub>3</sub><sup>-</sup> (adsorbed NO<sub>3</sub><sup>-</sup>) into \*NO<sub>2</sub><sup>-</sup> following a two-electron transfer process (\*NO<sub>3</sub><sup>-</sup> + 2e<sup>-</sup> + H<sub>2</sub>O → \*NO<sub>2</sub><sup>-</sup> + 2OH<sup>-</sup>), while the Peak 2 was mainly attributed to the \*NO<sub>2</sub><sup>-</sup> reduction into \*NH<sub>3</sub> following a six-electron transfer process (\*NO<sub>2</sub><sup>-</sup> + 6e<sup>-</sup> + 5H<sub>2</sub>O → \*NH<sub>3</sub> + 7OH<sup>-</sup>). The Tafel curves were fitted and the obtained Tafel slopes were close to or greater than  $118 \text{ mV dec}^{-1}$  on all the catalysts (Figure 3b), indicating that the rate-determining step (RDS) was the electron transfer during \*NO<sub>3</sub><sup>-</sup> to \*NO<sub>2</sub><sup>-</sup> step, (eqs 2–5).<sup>33</sup> According to the Tafel slopes and bias current density of NO<sub>3</sub><sup>-</sup> reduction ( $j_{\text{NO}_3^-}$ ), Cu<sub>50</sub>Ni<sub>50</sub>-Janus/C ( $100 \text{ mV dec}^{-1}$ ,  $30 \text{ mA cm}^{-2}$  at  $-0.1 \text{ V}$ ), and Cu<sub>50</sub>Ni<sub>50</sub>-SSA/C ( $154.4 \text{ mV dec}^{-1}$ ,  $11 \text{ mA cm}^{-2}$  at  $-0.1$

V) had an obviously higher kinetic activity for  $^*\text{NO}_3^-$  to  $^*\text{NO}_2^-$  step the  $\text{Cu}_{50}\text{Ni}_{50}$ -Mix/C (230  $\text{mV dec}^{-1}$ , 6  $\text{mA cm}^{-2}$  at  $-0.1$  V). This is due to the redistribution of electrons within the alloy, as evidenced by XPS results and Bader charge analysis, which facilitates the transfer of electrons from the catalyst to  $^*\text{NO}_3^-$  and promotes the RDS. Although the number of Cu sites on  $\text{Cu}_{50}\text{Ni}_{50}$ -Mix/C was half of the Cu/C, the  $j_{\text{NO}_3^-}$  over  $\text{Cu}_{50}\text{Ni}_{50}$ -Mix/C was nearly 3 times higher than that of Cu/C (Figure 3c). Furthermore, the current density of  $\text{NO}_3^-$ RR using  $\text{Cu}_{50}\text{Ni}_{50}$ -Mix (6.3  $\text{mA cm}^{-2}$ ) was approximately 2.3 times higher than the additive contribution from Ni and Cu ( $2.6 + 0.1 = 2.7$   $\text{mA cm}^{-2}$ ), where it demonstrates an effect of  $1 + 1 > 2$  in electrochemical ammonia synthesis. The higher  $j_{\text{NO}_3^-}$  of  $\text{Cu}_{50}\text{Ni}_{50}$ -Mix/C can be attributed to a strong synergy between Cu and Ni in both Janus type and physical mixture configurations, the efficient generation of  $^*\text{H}$  on the Ni/C, which subsequently spills over to the Cu/C surface, thereby promoting the hydrodeoxidation of  $^*\text{NO}_3^-$  species. The gaseous and liquid products after 1 h electrolysis at  $-0.2$  V were collected, and the results are displayed in Figure 3d.  $\text{NH}_3$  species were the primary products observed on the Cu-based catalysts. The  $Y_{\text{NH}_3}$  over  $\text{Cu}_{50}\text{Ni}_{50}$ -Mix/C was almost 2.5 times higher than that of Cu/C at  $-0.2$  V, demonstrating the effect of hydrogen spillover from Ni sites to Cu sites. Comparable  $\text{NH}_3$  selectivity was observed on both  $\text{Cu}_{50}\text{Ni}_{50}$ -Mix/C and Cu/C, revealing that the presence of  $^*\text{H}$  mainly contributed to the increased  $Y_{\text{NH}_3}$ . This could be further substantiated using a  $^*\text{H}$  scavenger such as tert-butanol (TBA) which resulted in a decrease in  $Y_{\text{NH}_3}$  from 424 to 380  $\text{mmol h}^{-1} \text{g}^{-1}$ . However, the  $FE_{\text{NH}_3}$  remained stable at approximately 91% on  $\text{Cu}_{50}\text{Ni}_{50}$ -SSA/C (Figure 3e).  $\text{Cu}_{50}\text{Ni}_{50}$ -Janus/C demonstrated the utmost efficiency in  $\text{NH}_3$  production, as evidenced by the highest  $FE_{\text{NH}_3}$  and the highest  $Y_{\text{NH}_3}$ , reaching, respectively, 92.5% and 1127  $\text{mmol h}^{-1} \text{g}^{-1}$  at  $-0.2$  V (Figure 3f). The current density for  $\text{NH}_3$  formation in the solution in the presence of  $\text{NO}_3^-$  ions is over 145-fold higher than in its absence, where the trace amount of  $\text{NH}_3$  might come from the  $\text{N}_2$  reduction. Hence, the  $\text{N}_2$  reduction reaction has little effect on the quantification of  $\text{NH}_3$  produced by  $\text{NO}_3^-$ RR. The  $\text{NH}_3$  production rate was also higher than that of the state-of-the-art catalysts reported in the literature (Supporting Information, Figure S11 and Table S3). In comparison,  $\text{Cu}_{50}\text{Ni}_{50}$ -SSA/C achieved a  $FE_{\text{NH}_3}$  of 82.6% and a  $Y_{\text{NH}_3}$  of 264  $\text{mmol h}^{-1} \text{g}^{-1}$ ;  $\text{Cu}_{50}\text{Ni}_{50}$ -Mix/C achieved a  $FE_{\text{NH}_3}$  of 69.7% and a  $Y_{\text{NH}_3}$  of 115  $\text{mmol h}^{-1} \text{g}^{-1}$ . Most importantly,  $\text{Cu}_{50}\text{Ni}_{50}$ -Janus/C maintained a  $FE_{\text{NH}_3}$  over 90% from 0 V to  $-0.2$  V. The concentrations of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions in the electrolyte after 2 h electrolysis at  $-0.2$  V versus RHE values were also determined by ICP-MS. There were about 0.015  $\text{mg L}^{-1}$   $\text{Cu}^{2+}$  ions and 0.01  $\text{mg L}^{-1}$   $\text{Ni}^{2+}$  ions detected in the final solutions, which was much lower than the limitations for discharge of heavy metals (GB5759-5005). The concentration of  $\text{NO}_3^-$  in real wastewater can vary from 1  $\text{mmol L}^{-1}$  to 2  $\text{mol L}^{-1}$ .<sup>33</sup> Therefore,  $\text{NO}_3^-$ RR on the Janus catalyst was performed at a wide range of  $\text{NO}_3^-$  concentrations (1–100  $\text{mmol L}^{-1}$ ) in neutral media. The  $FE_{\text{NH}_3}$  was maintained above 85% in the whole range of  $\text{NO}_3^-$  concentrations at  $-0.2$  V. These results demonstrated the excellent property of Janus catalysts toward  $\text{NO}_3^-$  recovery in various environmental wastewater systems.

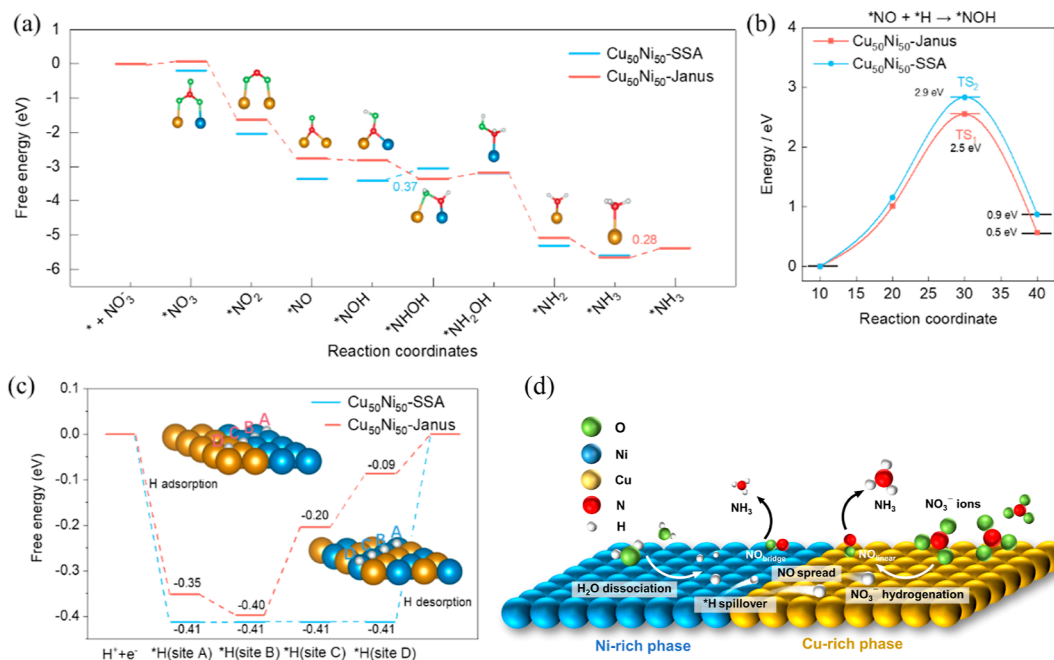


To gain a better understanding of the role of  $^*\text{H}$  in the steps of  $\text{NO}_3^-$  reduction to  $\text{NH}_3$ , we investigated the catalytic activities of  $\text{NO}_2^-$ RR and NORR. This is significant because  $\text{NO}_2^-$  and  $\text{NO}$  are key intermediates in the  $\text{NO}_3^-$  reduction to  $\text{NH}_3$  process.<sup>14,34</sup> At the onset potential of the  $\text{NO}_2^-$ RR around 0 V, the  $^*\text{H}$  coverage was low since the HER did not occur over any of the studied catalysts (Supporting Information, Figure S12a). Ni/C had the largest Tafel slope of 168.5  $\text{mV dec}^{-1}$  for the  $\text{NO}_2^-$ RR at 0 V (Supporting Information, Figure S12b), indicating a very low catalytic activity of the  $\text{NO}_2^-$ RR over Ni when the  $^*\text{H}$  coverage was small. When the potential went to  $-0.2$  V, where the HER was enhanced, it leads to a higher  $^*\text{H}$  coverage, and an enhanced  $j_{\text{NO}_2^-}$  (4.6  $\text{mA cm}^{-2}$ ) over Ni/C surpassing even the performance of Cu (2.9  $\text{mA cm}^{-2}$ ), Supporting Information, Figure S12c. Indeed, according to the product analysis, Ni/C has a higher  $Y_{\text{NH}_3}$  (235  $\text{mmol h}^{-1} \text{g}^{-1}$ ) and  $FE_{\text{NH}_3}$  (100%) than Cu (154  $\text{mmol h}^{-1} \text{g}^{-1}$ , 89%), Supporting Information, Figure S12d. This phenomenon contrasts with the case of the  $\text{NO}_3^-$  reduction. A scavenger test was also performed on Ni/C during the  $\text{NO}_2^-$  reduction. After adding TBA,  $Y_{\text{NH}_3}$  on Ni/C decreased from 235 to 123  $\text{mmol h}^{-1} \text{g}^{-1}$  but  $FE_{\text{NH}_3}$  remained around 100%, Supporting Information, Figure S12e. This demonstrates that the  $^*\text{H}$  on the surface primarily enhances the  $Y_{\text{NH}_3}$  rather than  $FE_{\text{NH}_3}$  during the  $\text{NO}_2^-$ RR. Similar behaviors were observed for the NORR on all of the catalysts (Supporting Information, Figure S13). According to the above discussion, it could be rationally inferred that the reduction of  $\text{NO}_3^-$  to  $\text{NO}_2^-$  is limited by electronic transfer within the bimetallic catalyst which could impact the  $FE_{\text{NH}_3}$ . In contrast,  $^*\text{H}$  plays a significant role in the reduction of  $\text{NO}_2^-$  to  $\text{NH}_3$  and mainly affects the  $Y_{\text{NH}_3}$ . The electrochemically active surface area (ECSA) was obtained according to the electrochemical double-layer capacitance determination (Figure S14a–c). The normalized LSV of  $\text{Cu}_{50}\text{Ni}_{50}$ -SSA and  $\text{Cu}_{50}\text{Ni}_{50}$ -Janus was then presented and a higher  $j_{(\text{ECSA})}$  was observed on  $\text{Cu}_{50}\text{Ni}_{50}$ -Janus than  $\text{Cu}_{50}\text{Ni}_{50}$ -SSA (Figure S14d). The above results demonstrated that  $\text{Cu}_{50}\text{Ni}_{50}$ -Janus had a higher intrinsic activity than the  $\text{Cu}_{50}\text{Ni}_{50}$ -SSA. The electronic and composition properties of the  $\text{Cu}_{50}\text{Ni}_{50}$ -Janus/C post reaction were analyzed by XPS and XRD (Supporting Information, Figures S15 and S16). After electrolysis, the electronic structure and composition were well preserved.

So far, our results indicate that the catalytic activities of  $\text{NO}_3^-$ RR,  $\text{NO}_2^-$ RR, and NORR over  $\text{Cu}_{50}\text{Ni}_{50}$ -Janus/C were significantly higher than that on  $\text{Cu}_{50}\text{Ni}_{50}$ -SSA/C, revealing that the  $\text{NO}_3^-$ RR,  $\text{NO}_2^-$ RR, and NORR were phase-dependent reactions on CuNi bimetallic catalysts. This effect is associated with the surface coordination number between active-metal atoms.<sup>28</sup> Compared to  $\text{Cu}_{50}\text{Ni}_{50}$ -SSA/C which features a homogeneous mixture of Cu and Ni atoms,  $\text{Cu}_{50}\text{Ni}_{50}$ -Janus/C exhibited the formation of a greater number of short-range ordered active sites. In particular, nitrogenous species can form various associations with metallic catalytic surfaces. For instance, the adsorption of  $\text{NO}_x$  on a catalyst surface may involve conformational variations, encompassing the N-bound nitro, O-bound nitrito, doubly O-bound chelating nitrito, as well as N- and O-bound bridging nitro modes of association. Therefore, it is anticipated that  $\text{Cu}_{50}\text{Ni}_{50}$ -Janus/C with a short-range



**Figure 4.** In situ electrochemical ATR-FTIR spectra of NO reduction on  $\text{Cu}_{50}\text{Ni}_{50}\text{-SSA/C}$  (a),  $\text{Cu}_{50}\text{Ni}_{50}\text{-Janus/C}$  (b), and  $\text{Cu}_{50}\text{Ni}_{50}\text{-Mix/C}$  (c) in 1 M KOH. (d)  $\text{NO}_{\text{bridge}}$  proportion on  $\text{Cu}_{50}\text{Ni}_{50}\text{-SSA/C}$ ,  $\text{Cu}_{50}\text{Ni}_{50}\text{-Janus/C}$ , and  $\text{Cu}_{50}\text{Ni}_{50}\text{-Mix/C}$ .



**Figure 5.** Gibbs free energy diagram of the intermediates generated during electrocatalytic  $\text{NO}_3^-$ RR over pure  $\text{CuNi-SSA}$  and  $\text{CuNi-Janus}$  (a). The structural models represent the adsorption form of various intermediates on  $\text{CuNi-Janus}$  during  $\text{NO}_3^-$ RR, Cu yellow, Ni blue, N red, O green, and H light gray atoms. The reaction energy barrier of elementary step  $*\text{NO} + *H \rightarrow *NOH$  (b). Free energy change of  $*H$  at different positions on  $\text{CuNi}$  bimetallics [top right inset, top view of the atomic  $\text{CuNi-SSA}$  and  $\text{CuNi-Janus}$  structure model and labeled  $*H$  spillover path (A  $\rightarrow$  B  $\rightarrow$  C  $\rightarrow$  D)] (c). Schematic of the reaction mechanism of the enhanced  $\text{NO}_3^-$ RR process over  $\text{Cu}_{50}\text{Ni}_{50}\text{-Janus/C}$  (d).

structure could promote the adsorption of nitrogenous species on the catalytic surface.

In the aim to elucidate the preferential adsorption and reduction capabilities of the catalysts for NO, a key intermediate

species in the reaction, in situ electrochemical ATR–FTIR was employed (Figure 4a–d). For all the catalysts as the potential decreases from 0.7 V to –0.3 V, an absorption peak appeared around 1400  $\text{cm}^{-1}$  and was ascribed to the N–H stretching.<sup>35</sup> In addition to this peak, a broad band between 1450 and 1800  $\text{cm}^{-1}$  was also observed. Deconvoluting this band on the spectra obtained at –0.1 V on  $\text{Cu}_{50}\text{Ni}_{50}\text{-SSA/C}$  (Figure 4a) unfolded three distinct bands centered at 1712, 1620, and 1531  $\text{cm}^{-1}$  (Supporting Information, Figure S17). These bands were attributed to three different adsorption modes of the NO species onto a metal surface, *viz.*: (1) At 0.6 V, a bipolar band of a linearly on-top bonded NO ( $\text{NO}_{\text{linear}}$ ) can be observed at 1655–1595  $\text{cm}^{-1}$ .<sup>36–39</sup> The bipolar shape can be attributed to the electrode potential's effect on the N–O stretching frequency,<sup>36</sup> resulting in a downward shift of the adsorbate band as the electrode potential decreases. At lower potentials (below 0.2 V), the band transitions to an upward shape due to the NO reduction; (2) simultaneously, at a lower wavelength, around 1531  $\text{cm}^{-1}$ , another band appeared and was assigned to N–O stretching of a bridge-bonded NO ( $\text{NO}_{\text{bridge}}$ );<sup>38–42</sup> (3) the third band at ca. 1712  $\text{cm}^{-1}$  was attributed to the bisnitrosyl adducts of Ni adlayer  $[\text{Ni}(\text{NO})_2]$ .<sup>43</sup> The integrated intensities of the three bands versus applied potential were subsequently plotted on the basis of curve fitting, as shown in Supporting Information, Figure S18. The proportion of  $\text{NO}_{\text{bridge}}$  was calculated using eq (S1) and compared among  $\text{Cu}_{50}\text{Ni}_{50}\text{-Mix/C}$ ,  $\text{Cu}_{50}\text{Ni}_{50}\text{-Janus/C}$ , and  $\text{Cu}_{50}\text{Ni}_{50}\text{-SSA/C}$  (Figure 4d).  $\text{Cu}_{50}\text{Ni}_{50}\text{-Mix/C}$  and  $\text{Cu}_{50}\text{Ni}_{50}\text{-Janus/C}$  exhibited a higher proportion of  $\text{NO}_{\text{bridge}}$  species on their surface in comparison to  $\text{Cu}_{50}\text{Ni}_{50}\text{-SSA/C}$ . This observation suggests that short-range ordered active sites facilitate the bridge-bonded adsorption of NO, whereas the linear-bonded adsorption configuration predominates on  $\text{Cu}_{50}\text{Ni}_{50}\text{-SSA/C}$ . Meanwhile, the absorption intensity of N–O stretching was significantly greater on Ni/C in comparison to Cu/C (Supporting Information, Figures S19a–c), indicating that Ni sites accommodate a stronger adsorption affinity for NO. These results align well with DFT calculations, where the Gibbs free energy for NO adsorption on Ni atoms (–2.1 eV) was considerably lower than that on Cu atoms (–1.2 eV). Besides,  $\text{NO}_{\text{bridge}}$  displayed a higher intensity than  $\text{NO}_{\text{linear}}$  on Ni/C, while the  $\text{NO}_{\text{linear}}$  intensity was more pronounced on Cu/C (Supporting Information, Figure S19c,d). This indicates a preference for bridge-bonded and linear-bonded NO adsorption on Ni and Cu atoms, respectively. The much higher intensity of NO peaks (including linear- and bridge-bonded NO) proved that the NO formed from  $^*\text{NO}_2$  reduction on the Cu-rich phase spilled over to the Ni-rich phase with a bridge-bonded adsorption (Supporting Information, Figures S16). These results provide a robust explanation for the superior catalytic performance of Ni/C over Cu/C during  $\text{NO}_2^-$ RR and NORR. Moreover, it suggests that during the hydrogenation of the intermediates  $^*\text{NO}_2$  and  $^*\text{NO}$ , the Ni sites in  $\text{Cu}_{50}\text{Ni}_{50}\text{-Janus/C}$  serve not only as providers of  $^*\text{H}$  but also as active catalytic sites for NO adsorption.

Figure 5 provides the Gibbs free energies ( $\Delta G$ ) of  $^*\text{NO}_3$  species and their derivatives on  $\text{Cu}_{50}\text{Ni}_{50}\text{-SSA/C}$  and  $\text{Cu}_{50}\text{Ni}_{50}\text{-Janus/C}$  based on density functional theory (DFT) calculations. On the basis of the thermodynamics data, the RDS on  $\text{Cu}_{50}\text{Ni}_{50}\text{-SSA/C}$  was the hydrogenation of  $^*\text{NOH}$  to  $^*\text{NHOH}$  (0.37 eV), Figure 5a. This step on  $\text{Cu}_{50}\text{Ni}_{50}\text{-Janus/C}$  became spontaneous (–0.54 eV) due to enhanced  $\text{NO}_x$  adsorption in a bridge-bonded configuration. This result highlights the preference for the hydrogenation of bridge-bonded  $\text{NO}_x$  into  $\text{NH}_3$  on

$\text{Cu}_{50}\text{Ni}_{50}\text{-Janus/C}$ . Indeed, it is well acknowledged that  $\text{NO}_{\text{bridge}}$  will cleave more readily than  $\text{NO}_{\text{linear}}$  to produce  $\text{NH}_3$ .<sup>37</sup> Besides, the RDS on  $\text{Cu}_{50}\text{Ni}_{50}\text{-Janus/C}$  became the desorption of  $^*\text{NH}_3$  with a  $\Delta G$  of 0.28 eV that was also lower than the  $\Delta G$  of the RDS on  $\text{Cu}_{50}\text{Ni}_{50}\text{-SSA/C}$  (0.37 eV). The Gibbs free energies of  $^*\text{NO}_3$  and  $^*\text{H}$  on Ni and Cu were subsequently compared. Although the adsorption of  $^*\text{NO}_3$  on Ni (–0.06 eV) was easier than on Cu (0.18 eV) (Figure 5a), the adsorption of  $^*\text{H}$  (–0.32 eV) on Ni was much easier than that of  $^*\text{NO}_3$  and also easier than  $^*\text{H}$  on the Cu site (–0.18 eV), Supporting Information, Figure S20, which suggests that  $^*\text{H}$  will adsorb preferentially on Ni sites on the CuNi bimetallic catalysts. It was also well fitted with the electrochemical in situ FTIR results that the  $^*\text{H}$  signal was observed on Ni/C but vanished on Cu/C in the presence of  $\text{NO}_3^-$ . The calculated results also provide an explanation for the relative inertness of monometallic Ni/C toward the  $\text{NO}_3^-$ RR, as they reveal that the  $^*\text{H}$  coverage on Ni sites is sufficiently high to hinder the adsorption of  $^*\text{NO}_3$ . These theoretical results substantiate the results obtained from in situ electrochemical ATR–FTIR analysis (Figure 1c–e). Additional DFT calculations were performed to elucidate the migration and interaction of  $^*\text{H}$  generated on the Ni sites with the reaction intermediates on the Cu sites. According to the preceding experimental results, the formation of adsorbed  $^*\text{H}$  was crucial for  $\text{NO}_x$  hydrogenation, and the Gibbs free energy for H adsorption ( $\Delta G_{\text{H}}$ ) emerged as a significant descriptor for the hydrogenation process. Hydrogen spillover usually exists in binary composite materials, with one site (denoted as A) featuring a negative  $\Delta G_{\text{H}}$  value ( $\Delta G_{\text{H}(1)}$ ) and thus a strong H adsorption (such as Ni in this work), and the other site (denoted as D) featuring a positive  $\Delta G_{\text{H}}$  value ( $\Delta G_{\text{H}(2)}$ ) and thus for efficient desorption and further hydrogenation process (such as Cu).<sup>44</sup> Figure 5c provides a summary of the  $\Delta G_{\text{H}}$  values on various sites within the two theoretical models,  $\text{Cu}_{50}\text{Ni}_{50}\text{-Janus/C}$  and  $\text{Cu}_{50}\text{Ni}_{50}\text{-SSA/C}$ , and suggests an energetically favorable  $^*\text{H}$ -spillover process over the Janus-type catalyst. For  $\text{Cu}_{50}\text{Ni}_{50}\text{-SSA/C}$ , the  $^*\text{H}$  spillover was more inclined to occur on Ni sites and the  $\Delta G_{\text{H}}$  values remained relatively constant from site A to site D, around –0.41 eV. The Gibbs free energy of  $^*\text{H}$  desorption from site D was as high as 0.41 eV. In contrast, for  $\text{Cu}_{50}\text{Ni}_{50}\text{-Janus/C}$ , the  $\Delta G_{\text{H}}$  values are –0.35 eV (site A in Ni-rich phase); –0.44 eV (site B in Ni-rich phase); –0.20 eV (site C in Cu-rich phase); and –0.09 eV (site D in Cu-rich phase), and the Gibbs free energy of  $^*\text{H}$  desorption is significantly lower (0.09 eV). We conducted an analysis of the energy change for hydrogenation process ( $^*\text{NO} \rightarrow ^*\text{NOH}$ ) (Figure 5b) and find that the activation barrier and reaction energy of the hydrogenation on  $\text{Cu}_{50}\text{Ni}_{50}\text{-Janus/C}$  (2.5 and 0.5 eV respectively) were lower than that on  $\text{Cu}_{50}\text{Ni}_{50}\text{-SSA/C}$  (2.8 and 0.9 eV), suggesting that hydrogen spillover and bridge-bonded NO on  $\text{Cu}_{50}\text{Ni}_{50}\text{-Janus/C}$  were energetically more favorable for intermediates hydrogenation process, which gave a dramatic leap of the  $Y_{\text{NH}_3}$  on  $\text{Cu}_{50}\text{Ni}_{50}\text{-Janus/C}$  (1127  $\text{mmol}^{-1} \text{h}^{-1} \text{g}^{-1}$ ) compared to that on  $\text{Cu}_{50}\text{Ni}_{50}\text{-SSA/C}$  (264  $\text{mmol}^{-1} \text{h}^{-1} \text{g}^{-1}$ ).

Drawing from the comprehensive results obtained through in situ electrochemical ATR–FTIR analysis and DFT calculations, we are able to put forth a proposed reaction mechanism for  $\text{NO}_3^-$ RR on  $\text{Cu}_{50}\text{Ni}_{50}\text{-Janus/C}$ . This mechanism is illustrated in Figure 5d. Initially, the electron distribution within Janus Cu@Ni structure favors the activation of  $\text{NO}_3^-$  to form  $^*\text{NO}_2$  species on the Cu-rich phase and  $^*\text{H}$  generation through Volmer step on the Ni-rich phase, respectively. During the  $^*\text{H}$ -spillover process, the generated  $^*\text{H}$  on Ni spontaneously migrates and

accumulates at the Cu@Ni interface.<sup>45,46</sup> Simultaneously, \*NO<sub>2</sub> would desorb from Cu atoms and would readsorb onto either Ni or Cu atoms, where the NO<sub>bridge</sub> and NO<sub>linear</sub> intermediates were formed, respectively. The NO bridge adsorption would then promote cleavage of the N–O bond. Additional hydrogen-bond interactions between spillover \*H and intermediates lead to the desorption of spillover \*H from the Cu@Ni interface, enabling it to directly participate in the hydrogenation of bridge-bonded intermediates. This, in turn, enhances the NO<sub>3</sub><sup>−</sup>RR activity of Janus Cu@Ni/C for the conversion of NO<sub>3</sub><sup>−</sup> into NH<sub>3</sub>.

## CONCLUSIONS

In our study, we provide valuable insights into the process of optimizing catalysts into a phase-separated structure for enhancing their performance against the NO<sub>3</sub><sup>−</sup>RR by a phase-dependent mechanism. By conducting this research, we shed light on the factors and parameters that can be adjusted to improve the catalytic activity by constructing two active sites adjacent to each other. While acknowledging that certain structural features of the Cu@Ni catalyst with different metal ratios remain unexplored and these variations may also lead to different catalytic activities. We believe that the tandem cooperation between adjacent active sites on the Cu-rich and Ni-rich phases, as described in our mechanistic study with a ratio of 50:50, offers insights for the design of multicomponent heterogeneous catalysts. Understanding and providing alternative explanations on how to fine-tune catalysts is crucial because it can prompt more efficient and effective systems (rather than a homogeneous alloy) for reducing NO<sub>3</sub><sup>−</sup> into valuable product such NH<sub>3</sub>, ultimately contributing to cleaner and more sustainable energy technologies and environmental protection.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.4c00479>.

XRD patterns; XPS spectra; electrocatalytic performance data over catalysts of Cu<sub>50</sub>Ni<sub>50</sub>-Janus/C, Cu<sub>50</sub>Ni<sub>50</sub>-SSA/C, Cu<sub>50</sub>Ni<sub>50</sub>-Mix/C, Cu/C, and Ni/C; TEM images with particle size distribution; EPR spectra; EXAFS spectra; in situ FTIR spectra; and their quantitative analysis (PDF)

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Y.Y.L. and Q.Z.Z. contributed equally to this work. Y.Y.L., X.Y.H., and S.G.S. contributed to the design of the study; Y.Y.L., S.Y.Z., J.Y.F., X.Y.H., and X.Y.D. conducted experiments and data analysis. Q.Z.Z. conducted the DFT calculations. Y.Y.L., O.A., and X.Y.H. conceived the mechanism; Y.Y.L., R.O., G.P., and S.S.G. provided technical support, conceptual advice, and result interpretation. Y.Y.L., X.Y.H., O.A., and R.O. wrote the manuscript and the Supporting Information. All authors commented on- and amended both documents. All authors discussed and contributed to the work.

## Notes

The authors declare no competing financial interest.

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