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# High yield ammonia production via glucose oxidation assisted electrochemical nitrate reduction†

Akansha Chaturvedi,‡ Sukhjot Kaur,‡ Kalpana Garg and Tharamani C. Nagaiah \*

The electrocatalytic nitrate ( $\text{NO}_3^-$ ) reduction reaction ( $\text{NO}_3\text{RR}$ ) provides a potential route for the synthesis of value-added ammonia ( $\text{NH}_3$ ) and removal of nitrate pollutants. However, this reaction is limited by nitrate adsorption and slow kinetics involving multiple proton and electron transfer steps. The sluggish OER can hinder  $\text{NO}_3\text{RR}$  performance, but replacing it with a more facile oxidation process enhances performance. Herein, we have demonstrated the glucose oxidation assisted  $\text{NO}_3\text{RR}$ , utilizing  $\text{CuNi}(1:2)\text{S}$  as a bifunctional catalyst demonstrating a high  $\text{NH}_3$  faradaic efficiency (F.E.) of 93.44% with a yield rate of  $4.7 \text{ mg h}^{-1} \text{ cm}^{-2}$  or  $280.47 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$  at  $-0.4 \text{ V vs. RHE}$  along with achieving high current densities of  $\sim 118 \text{ mA cm}^{-2}$  and its high activity compared to monometallic variants was explained using the ultraviolet photoelectron spectroscopy (UPS) technique. Furthermore, a mechanistic study using *in situ* electrochemical Raman spectroscopy, illustrates the hydrogenation of  $\text{NO}_3^-$  to  $\text{NH}_3$  via a  $\text{NO}_2^-$  intermediate. Moreover, replacing the OER with the glucose oxidation reaction (GOR) in a full cell system could decrease the total energy input by 200 mV and increase the  $\text{NH}_3$  yield from  $120.95 \text{ } \mu\text{g h}^{-1} \text{ cm}^{-2}$  to  $259.46 \text{ } \mu\text{g h}^{-1} \text{ cm}^{-2}$ . Furthermore, high value-added products were obtained at both the anode and cathode at a low cell voltage. More interestingly, we demonstrate the practical extraction of high-purity  $\text{NH}_4\text{Cl}(\text{s})$  and  $\text{NH}_3$  aqueous products from electro-reduced  $\text{NO}_3^-$  after electrolysis at  $100 \text{ mA cm}^{-2}$  for 50 h, with a collection efficacy of 89.84% for the condensed  $\text{NH}_3(\text{aq})$  solution.

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## Introduction

Hydrogen energy is being touted as an appealing substitute for fossil fuels in light of the rising need to reduce carbon emissions.<sup>1</sup> However, challenges with  $\text{H}_2$  storage and transportation hinder its scalability.<sup>2</sup> Amidst these challenges, ammonia ( $\text{NH}_3$ ) emerges as a key player in clean hydrogen deployment due to its high volumetric energy density ( $12.92\text{--}14.4 \text{ MJ L}^{-1}$ ), high hydrogen content (17.65%), and easy liquefaction.<sup>3–8</sup>  $\text{NH}_3$  is also crucial for fertilizer production, addressing the UN's Sustainable Development Goal of Zero Hunger.<sup>9,10</sup> With an annual demand exceeding 200 million metric tonnes,  $\text{NH}_3$  is the second most synthesized feedstock globally.<sup>11</sup> Currently,  $\text{NH}_3$  production relies on the energy-intensive Haber–Bosch process, consuming about 1% of the world's fossil-fuel energy and emitting over 400 million metric tons of  $\text{CO}_2$  annually.<sup>4,12–16</sup> Recently, electrochemical nitrogen reduction (NRR) to ammonia has emerged as a sustainable alternative.<sup>4,17,18</sup> However, challenges such as the activation of the inert

dinitrogen triple bond, low water solubility of  $\text{N}_2$ , and the competing hydrogen evolution reaction (HER) result in low faradaic efficiency (F.E.) and  $\text{NH}_3$  yield, falling short of the U.S. Department of Energy's targets (DoE, F.E.: 50% and an  $\text{NH}_3$  yield rate of over  $1700 \text{ } \mu\text{g h}^{-1} \text{ cm}^{-2}$ ).<sup>19–24</sup> The electrochemical nitrate reduction reaction ( $\text{NO}_3\text{RR}$ ) to ammonia offers a glimmer of hope, due to the lower bond dissociation energy of the  $\text{N}=\text{O}$  bond ( $204 \text{ kJ mol}^{-1}$ ) compared to  $\text{N}\equiv\text{N}$  ( $941 \text{ kJ mol}^{-1}$ ) and higher water solubility ( $316 \text{ g L}^{-1}$  at  $20 \text{ }^\circ\text{C}$ ).<sup>25–27</sup> Moreover the  $\text{NO}_3\text{RR}$  has the potential to generate  $\text{NH}_3$  from polluted industrial and agricultural wastewater, aiding in environmental remediation.<sup>25,26,28,29</sup>

Furthermore, the overall nitrate electrolysis pairs up with the  $\text{NO}_3\text{RR}$  ( $\text{NO}_3^- + 7\text{H}_2\text{O} + 8\text{e}^- \rightarrow \text{NH}_4\text{OH} + 9\text{OH}^-$ ) at the cathode and the OER ( $4\text{OH}^- \rightarrow \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$ ) at the anode. However, the slow kinetics associated with the O–O bond formation and the requirement of four proton-coupled electron transfer demand high energy input making  $\text{NO}_3^-$  electrolysis in the  $\text{NO}_3\text{RR}$ –OER pair an energy intensive process.<sup>30,31</sup> Moreover, the OER doesn't provide us with an industrially relevant product. Hence, replacing the OER with alternative anodic reactions which are thermodynamically favourable has become an emerging solution to address the “energy-saving” issue in the  $\text{NO}_3\text{RR}$ –OER electrolysis. Therefore, owing to lower overpotential required compared to the OER, the GOR ( $\text{C}_6\text{H}_{12}\text{O}_6 + 2\text{OH}^- \rightarrow \text{C}_6\text{H}_{12}\text{O}_7 + 2\text{H}_2\text{O} + 2\text{e}^-$  and

Department of Chemistry, Indian Institute of Technology Ropar, Rupnagar-140001, Punjab, India. E-mail: tharamani@iitrpr.ac.in

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‡ These authors contributed equally.



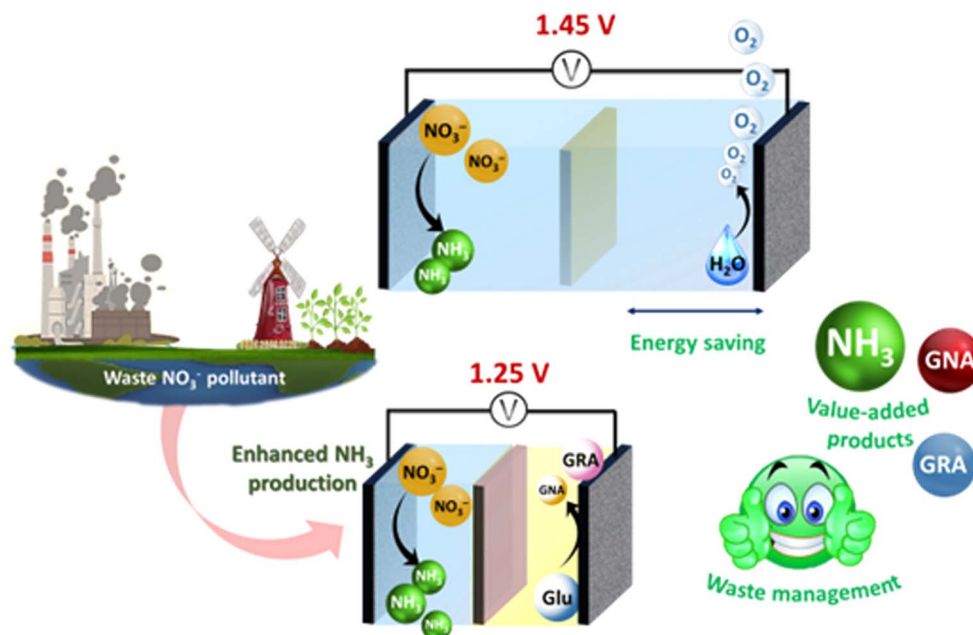


Fig. 1 Schematic representation of the replacement of anodic OER with GOR during ammonia production using CuNi(1:2)S as a bifunctional electrocatalyst.

$C_6H_{10}O_7 + 2OH^- \rightarrow C_6H_{12}O_8 + 2H_2O + 2e^-$ ) is a potential candidate to pair with the  $NO_3RR$  to produce useful chemical commodities such as glucaric acid, gluconic acid and gluconolactone, used in polymer synthesis, the pharmaceutical industry, food and beverage production, and agriculture.<sup>32–37</sup> Glucaric acid (GRA) is known as a “top valuable compound” derived from biomass.<sup>38</sup> It serves as an essential intermediate in the production of biodegradable polymers, eco-friendly detergents, and metal chelating agents.<sup>35,39</sup> A market report from Grand View Research, Inc. indicates that the global GRA market size was approximately USD 550.4 million in 2016, with projections to reach USD 1.30 billion by 2025.<sup>35</sup> The substitution of the  $NO_3RR$ –OER pair with the  $NO_3RR$ –GOR pair in  $NO_3^-$  electrolysis could be a game changing strategy which provides value-added products in both anodic and cathodic reactions while simultaneously reducing the total energy demand required for efficient  $NH_3$  production.<sup>40–44</sup> Designing a bifunctional catalyst for the  $NO_3RR$  and GOR is challenging, as it must facilitate both reactions with distinct mechanisms. Noble metals like Pt, Ru, Rh, and Pd are efficient but costly and scarce, prompting the search for earth-abundant, cost-effective alternatives.<sup>40–46</sup> Transition metal catalysts, particularly Cu-based ones, are promising for the  $NO_3RR$  to  $NH_3$  due to the similar energies of the Cu d orbital and the  $\pi^*$  (LUMO) molecular orbital of  $NO_3^-$ .<sup>47–50</sup> Although Cu-based catalysts have weak proton adsorption, which minimizes the competitive HER, insufficient hydrogen adsorption species hinder intermediate ( $NO_2^-$ , NO, etc.) hydrogenation, which is critical for  $NH_3$  formation.<sup>47–50</sup> Nickel (Ni) exhibits significant O–H activation and a strong affinity for the adsorption of hydrogen ( $H^*$ ) species.<sup>51</sup> Incorporating Ni into Cu-based catalysts optimizes the hydrogen species supply for nitrate reduction while minimizing the superfluous HER.<sup>52</sup> Additionally, Ni and Cu-based catalysts have

shown notable success in electrochemical glucose oxidation.<sup>53–55</sup> Herein, we investigated a cost-effective transition metal-based bifunctional catalyst CuNi(1:2)S for glucose-assisted electrochemical nitrate reduction for ammonia production at room temperature (Fig. 1). The proposed catalyst demonstrated superior  $NO_3RR$  electrocatalytic activity for  $NH_3$  production with a high  $NH_3$  yield rate of  $4.76 \text{ mg h}^{-1} \text{ cm}^{-2}$  and a F.E. of 93.44%. Under full cell conditions, the  $NH_3$  yield rate improved from  $120.95 \text{ } \mu\text{g h}^{-1} \text{ cm}^{-2}$  to  $259.46 \text{ } \mu\text{g h}^{-1} \text{ cm}^{-2}$  in the presence of glucose.

## Results and discussion

### Synthesis and characterization

The CuNi(*x*:*y*)S catalyst along with the control catalysts, NiS and  $Cu_xS$ , were synthesized using a one-step hydrothermal method (detailed in the ESI†), and its microstructure was assessed using the powder X-ray diffraction (P-XRD) pattern. The P-XRD pattern (Fig. 2a) of the synthesized NiS demonstrated diffraction peaks at  $2\theta = 30.168^\circ$ ,  $34.743^\circ$ ,  $46.035^\circ$ , and  $53.547^\circ$ , which are attributed to the (100), (101), (102) and (110) planes of NiS matching with JCPDS no. 02-1280. Furthermore, the P-XRD pattern of  $Cu_xS$  revealed a combination of peaks that corresponded to CuS (JCPDS no. 06-0464) and  $Cu_2S$  (JCPDS no. 53-0522), with the most prominent peak at  $31.785^\circ$ , which can be attributed to the (103) plane of CuS and a major peak at  $46.105^\circ$  corresponding to the (220) plane of  $Cu_2S$ . Thus, the P-XRD pattern of the designed CuNi(*x*:*y*)S catalysts demonstrated the coexistence of NiS, CuS and  $Cu_2S$  in all the synthesised variants, matching well with their respective standard JCPDS data (Fig. 2a and S1†). CuNi(1:2)S, as revealed by the field emission scanning electron microscopy (FE-SEM) image,



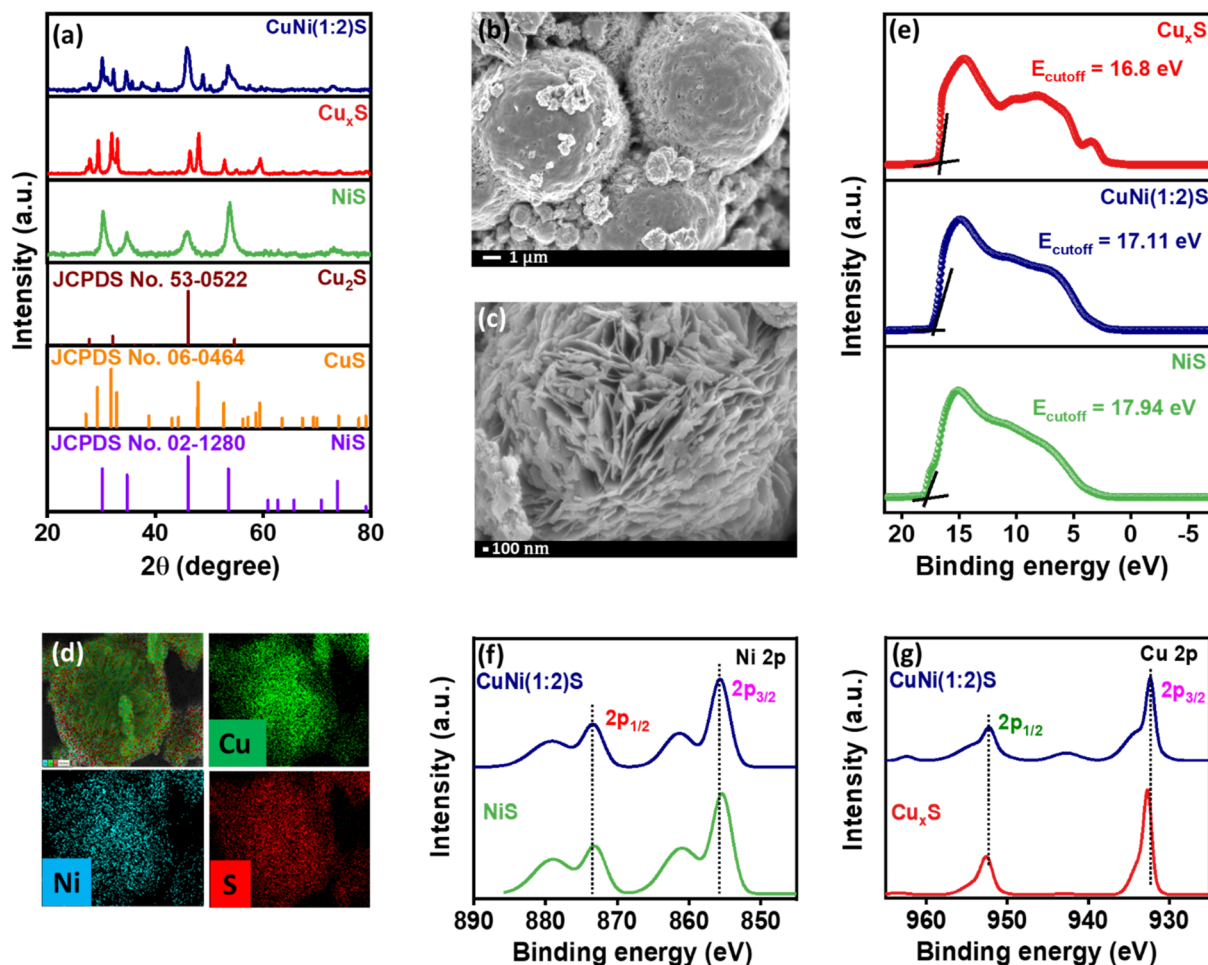


Fig. 2 (a) P-XRD pattern of NiS,  $\text{Cu}_x\text{S}$ , and  $\text{CuNi}(1:2)\text{S}$  catalysts, (b) and (c) FE-SEM at 1  $\mu\text{m}$  and 100 nm magnification for the  $\text{CuNi}(1:2)\text{S}$  catalyst, and (d) elemental dot mapping showing the uniform distribution of Cu, Ni and S elements over the scanned area of  $\text{CuNi}(1:2)\text{S}$ . (e) UPS spectra of  $\text{Cu}_x\text{S}$ , NiS and  $\text{CuNi}(1:2)\text{S}$  catalysts. Comparison of XPS spectra for (f) Ni 2p and (g) Cu 2p of  $\text{CuNi}(1:2)\text{S}$  with NiS and  $\text{Cu}_x\text{S}$ , respectively.

exhibited a spherical morphology wherein the flakes aggregated into microspheres (Fig. 2b and c). Similarly, NiS and  $\text{Cu}_x\text{S}$  showed a slightly distorted morphology with microspheres of varying sizes (Fig. S2†). In addition, energy dispersive X-ray spectroscopy (EDS) elemental dot mapping validated the coexistence and uniform distribution of Cu, Ni and S within the sphere (Fig. 2d). Besides, UPS was utilized to understand the interactions between NiS and  $\text{Cu}_x\text{S}$  in the  $\text{CuNi}(1:2)\text{S}$  catalyst. Fig. 2e reveals the secondary electron cutoff energy<sup>56,57</sup> ( $E_{\text{cutoff}}$ ) at a binding energy (BE) of ca. 17.94 eV, 16.8 eV and 17.11 eV for NiS,  $\text{CuS}$  and  $\text{CuNi}(1:2)\text{S}$ , respectively. The work function (WF) of  $\text{CuNi}(1:2)\text{S}$  was computed to be 6.33 eV which lies between the WFs of NiS (5.8 eV) and  $\text{CuS}$  (6.59 eV) signifying electron transfer from Ni to Cu in the  $\text{CuNi}(1:2)\text{S}$  catalyst (Table S1, detailed calculation in the ESI†). Additionally, X-ray photoelectron spectroscopy (XPS) analysis was carried out to comprehend the oxidation states of the elements in the  $\text{CuNi}(1:2)\text{S}$  catalyst. The XPS survey spectrum shows the presence of all the expected elements Cu, Ni and S in the  $\text{CuNi}(1:2)\text{S}$  catalyst (Fig. S3a†). The deconvoluted Ni 2p XP spectra exhibited peaks at BEs of 873.3 eV and 855.65 eV, which are separated by 17.65 eV,

corresponding to Ni 2p<sub>1/2</sub> and Ni 2p<sub>3/2</sub>, respectively, with satellite peaks at 879.07 eV and 861.3 eV ascribed to Ni in the +2 oxidation state (Fig. S3b†).<sup>58</sup> The deconvoluted Cu 2p XPS pattern shown in Fig. S3c† revealed BE peaks at 932.3 eV and 952.2 eV corresponding to 2p<sub>3/2</sub> and 2p<sub>1/2</sub>, respectively, of Cu<sup>+</sup>. Furthermore, peaks at 933.67 eV and 953.48 eV correspond to 2p<sub>3/2</sub> and 2p<sub>1/2</sub> of Cu<sup>2+</sup>.<sup>59,60</sup> Thus, we can conclude that Cu is present in both Cu(I) and Cu(II) oxidation states in the  $\text{CuNi}(1:2)\text{S}$  catalyst. Two satellite peaks were also observed at 942.72 eV and 962.42 eV, which are ascribed to Cu<sup>2+</sup>.<sup>59</sup> Furthermore, the deconvoluted S 2p XP spectrum revealed peaks at 161.21 eV and 162.15 eV corresponding to S 2p<sub>3/2</sub> and S 2p<sub>1/2</sub> bonded with metal, while the peaks at 163.29 eV and 168.02 eV represented divalent sulphide and sulphate, respectively (Fig. S3d†).<sup>61</sup> Furthermore, the increase in BE of Ni 2p by 0.3 eV in  $\text{CuNi}(1:2)\text{S}$  and the decrease in BE of Cu 2p by 0.3 eV in  $\text{CuNi}(1:2)\text{S}$  relative to  $\text{Cu}_x\text{S}$  indicate successful Cu–Ni binding in  $\text{CuNi}(1:2)\text{S}$  (Fig. 2f and g). All the aforementioned observations from UPS and XPS indicate close chemical interaction between Cu and Ni, involving the transfer of electrons from Ni to Cu atoms within  $\text{CuNi}(1:2)\text{S}$ .<sup>62–64</sup>



Electrochemical nitrate reduction (NO<sub>3</sub>RR)

The electrocatalytic activity of the designed CuNi(*x*:*y*)S catalysts towards the NO<sub>3</sub>RR was investigated using various electrochemical and spectroscopic techniques. Initially, linear sweep voltammetric (LSV) experiments were conducted in Ar-saturated 1 M KOH + 100 mM KNO<sub>3</sub> (Fig. S4A†) at a scan rate of 25 mV s<sup>-1</sup>. As observed in Fig. 3a, the reduction current was observed at a potential of -0.095 V, reaching the highest current density of 270 mA cm<sup>-2</sup> @ -0.6 V vs. RHE. While a shift in the reduction current to more negative potentials was observed in the absence of KNO<sub>3</sub> signifying that the designed catalyst is active towards nitrate reduction. To gain a deeper understanding of the role of dual metal catalysts in NO<sub>3</sub>RR activity, control experiments were performed using monometallic catalysts *viz.* NiS and Cu<sub>x</sub>S. The comparison of LSV curves (Table S2†) for the synthesized monometallic catalysts *viz.* NiS and Cu<sub>x</sub>S is shown in Fig. 3a. As expected, the onset potentials were observed at more negative values of -0.25 V and -0.22 for Cu<sub>x</sub>S and NiS, respectively, which are higher than that of the CuNi(1:2)S catalyst (-0.095 V). The current density @ -0.6 V vs. RHE was found to be 194 mA cm<sup>-2</sup> and 155 mA cm<sup>-2</sup> for Cu<sub>x</sub>S and NiS, respectively, both of which are lower than that of the CuNi(1:2)S catalyst indicating its superior NO<sub>3</sub>RR activity. Hence, to understand the role of the Cu to Ni ratio in the CuNi(*x*:*y*)S catalyst, further experiments were performed with other variants. As observed in Fig. S4B,† the onset potential for CuNi(1:1)S and CuNi(2:1)S was almost similar which is -0.14 V vs. RHE, reaching current densities of 248 mA cm<sup>-2</sup> and 237 mA cm<sup>-2</sup> respectively @ -0.6 V vs. RHE. Furthermore, to quantify the ammonia produced during nitrate reduction, chronoamperometric

measurements were conducted in an Ar-saturated 100 mM KNO<sub>3</sub> + 1 M KOH solution at various potentials ranging from -0.2 V to -0.6 V vs. RHE for 1 h each (Fig. 3b). The electrolyte was collected after 1 h of chronoamperometric electrolysis at different potentials and subjected to UV-Vis studies using the indophenol blue method (Fig. S5 and S6†). As observed in Fig. 3c, the NH<sub>3</sub> yield rate increased as the potential moved towards more negative values during the NO<sub>3</sub>RR, indicating higher NH<sub>3</sub> synthesis at larger negative potential. The highest NH<sub>3</sub> yield rate of 8.05 mg h<sup>-1</sup> cm<sup>-2</sup> was attained at -0.6 V vs. RHE. Furthermore, the F.E. of NH<sub>3</sub> was calculated at various potentials, revealing 93.44% F.E. at -0.4 V vs. RHE with an NH<sub>3</sub> yield rate of 4.76 mg h<sup>-1</sup> cm<sup>-2</sup> (Fig. 3c) and a turn over frequency (TOF) of 11.92 h<sup>-1</sup> suggesting the efficient performance of CuNi(1:2)S towards the NO<sub>3</sub>RR to ammonia (Table S3†). The validation of generated NH<sub>3</sub> and reliability of the data for the same have emerged as critical and significant criteria. As a result, a strict methodology was followed, including cleaning of cell components.<sup>65</sup> Moreover, prior to the electrochemical experiments, the feeding Ar gas was passed through an alkaline KMnO<sub>4</sub> scrubbing solution to remove the impurities of reducible and labile N-containing compounds, namely NO<sub>x</sub>.<sup>66</sup> The use of Ni foam as a substrate for the working electrode was mainly due to its higher surface area and high conductivity.<sup>67</sup> Meanwhile, it has been proven that Ni foam is a relatively inert material for the NO<sub>3</sub>RR, while maintaining the catalyst's performance.<sup>67,68</sup> Thus, similar control experiments were performed on the bare Ni foam electrode at -0.4 V vs. RHE and in the absence of NO<sub>3</sub><sup>-</sup> using CuNi(1:2)S. As can be seen in the UV-Vis spectra (Fig. 3d) negligible absorbance was observed in

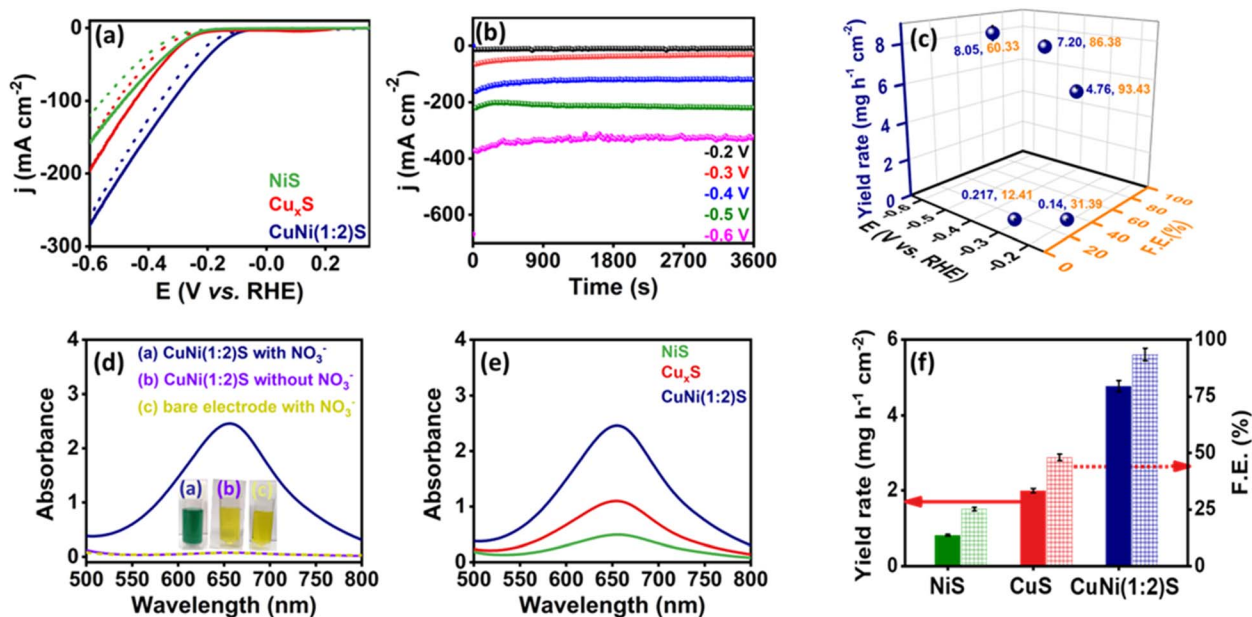


Fig. 3 (a) LSV for NiS, Cu<sub>x</sub>S and CuNi(1:2)S catalysts in Ar saturated 1 M KOH solution in the presence (solid line) and absence (dashed line) of 100 mM KNO<sub>3</sub>, (b) chronoamperometric curves for the CuNi(1:2)S catalyst in Ar saturated 1 M KOH in the presence of 100 mM KNO<sub>3</sub> at different potentials and (c) graph representing the corresponding NH<sub>3</sub> yield rate and F.E. (d) UV-Vis spectra obtained by the indophenol blue method for CuNi(1:2)S under various conditions and (e) comparison of UV-Vis spectra of NiS, Cu<sub>x</sub>S and CuNi(1:2)S at -0.4 V vs. RHE. (f) Bar diagram representing the corresponding NH<sub>3</sub> yield rate and F.E. (WE: Ni foam; RE: Hg/HgO/1 M NaOH; CE: graphite rod).



both the cases and the quantification clearly indicates that a negligible amount of  $\text{NH}_3$  was produced (Fig. S7†). Thus, it is affirmed that the source of  $\text{NH}_3$  is exclusively from the added  $\text{NO}_3^-$  and there are no potential interferences. Furthermore monometallic variants ( $\text{NiS}$  and  $\text{Cu}_x\text{S}$ ) were also compared with  $\text{CuNi}(1:2)\text{S}$  under similar experimental conditions (Fig. 3e and S8†). It was observed that  $\text{CuNi}(1:2)\text{S}$  exhibited a considerably enhanced  $\text{NH}_3$  yield rate ( $4.76 \text{ mg h}^{-1} \text{ cm}^{-2}$ ) and F.E. (93.44%) compared to monometallic  $\text{NiS}$  ( $0.81 \mu\text{g h}^{-1} \text{ cm}^{-2}$ , 25.02%) and  $\text{Cu}_x\text{S}$  ( $2.00 \text{ mg h}^{-1} \text{ cm}^{-2}$ , 48.02%) at a potential of  $-0.4 \text{ V vs. RHE}$  (Fig. 3f). The superior performance of  $\text{CuNi}(1:2)\text{S}$  benefited from the advantageous synergy between  $\text{Cu}$  and  $\text{Ni}$  in  $\text{CuNi}(1:2)\text{S}$ . More importantly, all the three variants of  $\text{CuNi}(x:y)\text{S}$  with different metal ratios exhibited a high F.E. of more than 80%, with  $\text{CuNi}(1:2)\text{S}$  showing the highest  $\text{NH}_3$  yield rate and F.E., indicating its superior  $\text{NO}_3\text{RR}$  activity (Fig. S9†). This superior activity of  $\text{CuNi}(1:2)\text{S}$  was further justified by various electrochemical characterization techniques including Tafel analysis, electrochemical impedance spectroscopy (EIS) and electrochemical surface area (ECSA) analysis. First, the Tafel slopes were obtained from LSV curves shown in Fig. 3a for the catalysts in the presence of  $\text{NO}_3^-$ . The lower Tafel slope of  $102 \text{ mV dec}^{-1}$  for  $\text{CuNi}(1:2)\text{S}$  as compared to other controlled synthesized catalyst variants (Fig. S8b, S10 and Table S4†), indicated its faster kinetics towards the  $\text{NO}_3\text{RR}$ . Furthermore, the Tafel slope slightly less than  $120 \text{ mV dec}^{-1}$  signifies that the rate determining step is the first one electron transfer that occurs during the  $\text{NO}_3^-$  to  $\text{NO}_2^-$  conversion.<sup>69,70</sup> Furthermore, to confirm the conclusions from Tafel analysis, electrochemical impedance spectroscopic (EIS) analysis was conducted by recording Nyquist plots at  $-0.4 \text{ V}$  in the presence of  $\text{NO}_3^-$  over the frequency range of  $7 \text{ mHz}$  to  $3 \text{ MHz}$ . As shown in Fig. S11,† a lower charge transfer resistance ( $R_{\text{ct}}$ ) was observed for  $\text{CuNi}(1:2)\text{S}$  (Table S5†), signifying a fast charge transfer at the electrode-electrolyte interface during the electrochemical reaction. To further validate this, we estimated the exchange current density and rate constant from the  $R_{\text{ct}}$  values using the following equations.<sup>71-73</sup>

$$R_{\text{ct}} = RT/nFi_0 \quad (1)$$

$$R_{\text{ct}} = RT/n^2F^2Ack_0 \quad (2)$$

where,  $R_{\text{ct}}$  is the charge transfer resistance,  $R$  is the universal gas constant,  $T$  is the temperature,  $n$  is the number of electrons,  $F$  is Faraday's constant,  $i_0$  is the exchange current density,  $A$  is the surface area,  $c$  is the concentration, and  $k_0$  is the rate constant. The  $i_0$  and  $k_0$  values were determined to be  $3.55 \text{ mA cm}^{-2}$  and  $5.78 \times 10^{-9} \text{ cm s}^{-1}$ , respectively, for the  $\text{CuNi}(1:2)\text{S}$  catalyst. These values are higher than those for  $\text{Cu}_x\text{S}$  ( $2.80 \text{ mA cm}^{-2}$ ,  $4.56 \text{ cm s}^{-1}$ ) and  $\text{NiS}$  ( $2.72 \text{ mA cm}^{-2}$ ,  $4.43 \times 10^{-9} \text{ cm s}^{-1}$ ), indicating an enhanced rate of reaction. Furthermore, the  $i_0$  and  $k_0$  values for  $\text{CuNi}(1:1)\text{S}$  and  $\text{CuNi}(2:1)\text{S}$  catalysts were found to be  $3.48 \text{ mA cm}^{-2}$ ,  $5.67 \times 10^{-9} \text{ cm s}^{-1}$  and  $3.34 \text{ mA cm}^{-2}$ ,  $5.44 \times 10^{-9} \text{ cm s}^{-1}$  respectively. This facile kinetics could also be attributed to the increased number of accessible electrochemically active sites on the catalyst surface, as measured

using the double layer capacitance ( $C_{\text{dl}}$ ) in the non-faradaic region. The electrochemical surface area (ECSA) of the  $\text{CuNi}(1:2)\text{S}$  catalyst was found to be  $37.5 \text{ cm}^2$  which is superior to that of other variants (Fig. S12 and Table S6†). Thus, the superior activity of the  $\text{CuNi}(1:2)\text{S}$  catalyst towards the  $\text{NO}_3\text{RR}$  was substantially justified by its lower charge transfer resistance ( $R_{\text{ct}}$ ) and higher ECSA.

To confirm that the ammonia generated herein is a result of the  $\text{NO}_3\text{RR}$  only, the most consistent control isotope labelling experiments were performed using  $^{14}\text{NO}_3^-$  and  $^{15}\text{NO}_3^-$  potassium salts as the N source (Fig. 4a). For the quantitative analysis of  $^{15}\text{NH}_4^+ / ^{14}\text{NH}_4^+$  acquired from the isotope labelling studies, the calibration curves were extracted for different known concentrations of  $^{14}\text{NH}_4^+$  and  $^{15}\text{NH}_4^+$  using  $^1\text{H}$  NMR spectra (Fig. S13 and S14†). After electrolysis of the  $^{14}\text{NO}_3^-$  aqueous solution,  $^1\text{H}$  NMR spectra were acquired exhibiting a triplet with peaks present at 7.06, 6.93 and 6.8 ppm corresponding to a coupling constant of  $\sim 52 \text{ Hz}$ , which were attributed to  $^{14}\text{NH}_4^+$  signals. On the other hand, the  $^1\text{H}$  NMR spectrum of the  $^{15}\text{NO}_3^-$  aqueous solution upon electrolysis showed a doublet at 7.02 and 6.84 ppm with a coupling constant of  $\sim 72 \text{ Hz}$  and no doublet or triplet was observed in the absence of  $\text{NO}_3^-$ , indicating that the chemical origin of the produced  $\text{NH}_3$  during the  $\text{NO}_3\text{RR}$  is due to the supplied  $\text{NO}_3^-$  (Fig. 4a). Quantification of  $\text{NH}_3$  for both  $^{15}\text{NH}_4^+$  and  $^{14}\text{NH}_4^+$  obtained by  $^1\text{H}$  NMR is consistent with the indophenol blue method (Fig. 4b and Table S7†). Similarly, quantification of  $\text{NH}_3$  produced by the electrochemical  $\text{NO}_3\text{RR}$  using the  $\text{CuNi}(1:2)\text{S}$  catalyst was further validated by Nessler's reagent test and Fig. 4c shows almost similar  $\text{NH}_3$  yield values obtained from all the three methods (Fig. 4c, S15 and Table S8†).

To corroborate whether any intermediate/by products *viz.*, nitrites ( $\text{NO}_2^-$ ), hydrazine ( $\text{N}_2\text{H}_4$ ), and hydroxyl amine ( $\text{NH}_2\text{OH}$ ) were produced during the  $\text{NO}_3\text{RR}$ , they were also quantified after chronoamperometric analysis under similar experimental conditions.  $\text{NO}_2^-$  was quantified using the Griess method<sup>74</sup> at potentials similar to those used for  $\text{NH}_3$  quantification and it was found that a maximum F.E. of 6.52% was achieved at  $-0.4 \text{ V vs. RHE}$  (Fig. S16 and S17†).

Furthermore,  $\text{N}_2\text{H}_4$  and  $\text{NH}_2\text{OH}$  by products were also quantified using various colorimetric and UV-Vis spectroscopy techniques (Fig. S18 and S19 detailed in the ESI†). It is worth noting that  $\text{N}_2\text{H}_4$  and  $\text{NH}_2\text{OH}$  were not detected as revealed by the UV-Vis spectra (Fig. S18c and S19c†), thus indicating a relatively high selectivity for  $\text{NH}_3$  synthesis by  $\text{CuNi}(1:2)\text{S}$ . The total F.E. for the  $\text{NO}_3\text{RR}$  at a potential of  $-0.4 \text{ V vs. RHE}$  was found to be 99.96% ( $\sim 100\%$ ) with the F.E. for  $\text{NH}_3$ , and  $\text{NO}_2^-$  being 93.44% and 6.52%, respectively (Fig. S20†). The energy efficiency was found to be 30.95% at a potential of  $-0.4 \text{ V vs. RHE}$  (details in ESI†).

This was further confirmed by *in situ* electrochemical Raman spectroscopy (Fig. 4d). The Raman spectra was recorded over the range of  $980$  to  $1600 \text{ cm}^{-1}$  under an applied potential of  $-0.4 \text{ V vs. RHE}$ . Initially, the only prominent peak was observed at around  $1043 \text{ cm}^{-1}$ , which is attributed to the presence of nitrate ions ( $\text{NO}_3^-$ ).<sup>67</sup> As the electrochemical reaction progressed, a new peak emerged at approximately  $1056 \text{ cm}^{-1}$ ,



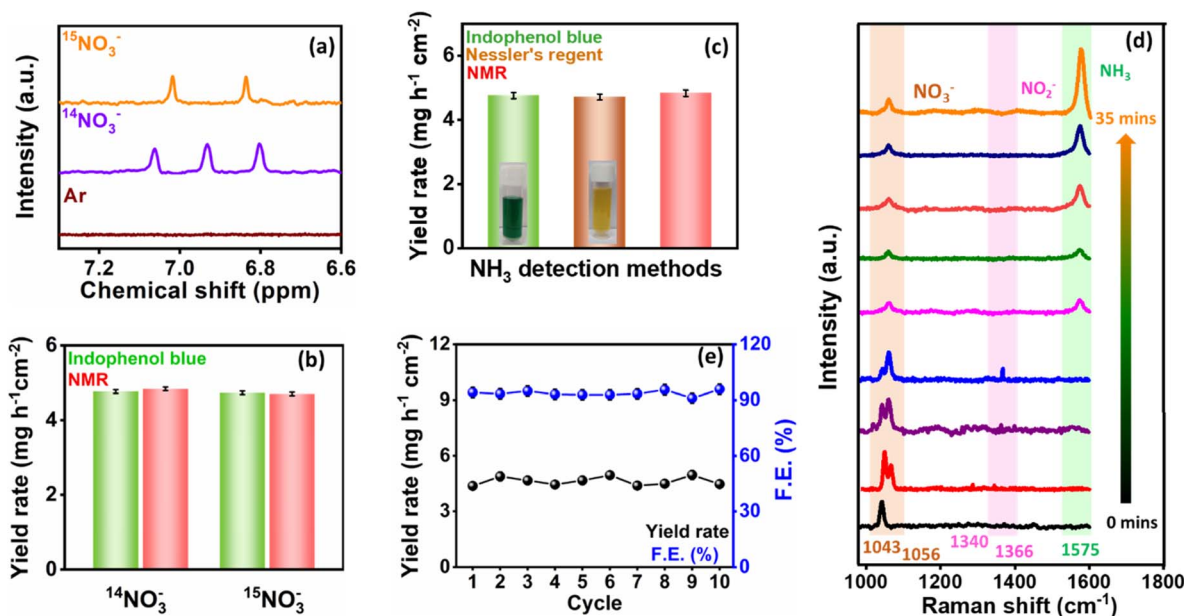


Fig. 4 (a)  $^1\text{H}$  NMR spectra obtained after the  $\text{NO}_3\text{RR}$  for  $\text{CuNi}(1:2)\text{S}$  in Ar saturated,  $^{14}\text{NO}_3^-$ , and  $^{15}\text{NO}_3^-$ -containing electrolyte solutions. A bar diagram representing the comparison of the  $\text{NH}_3$  yield calculated from calibrated data by the (b) indophenol method, and NMR for  $^{14}\text{NH}_4^+$  and  $^{15}\text{NH}_4^+$  produced during the  $\text{NO}_3\text{RR}$ , and (c)  $^{14}\text{NH}_3$  detection by the indophenol blue method, Nessler's reagent test and NMR. (d) Time dependent *in situ* electrochemical Raman spectra of the  $\text{CuNi}(1:2)\text{S}$  catalyst at  $-0.4\text{ V}$  vs. RHE. (e)  $\text{NH}_3$  yield and F.E. for consecutive 10 cycles at  $-0.4\text{ V}$  vs. RHE using the  $\text{CuNi}(1:2)\text{S}$  catalyst.

corresponding to the stretching vibrations of the  $\text{NO}_3^-$  ions.<sup>75</sup> This suggests the formation of an intermediate or a slight change in the chemical environment of the  $\text{NO}_3^-$  ions, indicating  $\text{NO}_3^-$  reduction. Additionally, peaks at  $1340\text{ cm}^{-1}$  and  $1366\text{ cm}^{-1}$  were observed at the onset of the reaction in the measurements, representing symmetric and antisymmetric stretching of  $\text{NO}_2$  in  $\text{NO}_3^-$ , respectively.<sup>76,77</sup> This indicates the reduction of  $\text{NO}_3^-$  *via*  $\text{NO}_2$ . As the reaction time increases, the intensity of the peak corresponding to  $\text{NO}_3^-$  (initially at  $1043\text{ cm}^{-1}$ ) decreases, indicating the consumption or transformation of nitrate ions during the reduction process. Simultaneously, a new peak emerges at around  $1575\text{ cm}^{-1}$ . This peak is attributed to the antisymmetric bending vibrations of the HNH moiety in ammonia ( $\text{NH}_3$ ).<sup>67,78</sup> The increasing intensity of this peak over time suggests a greater formation of ammonia as the reaction progresses. Thus, the Raman spectral changes observed during the electrochemical nitrate reduction provide insights into the formation of intermediate species and the conversion of nitrate ions to ammonia. Thus, based on our electrochemical results and previous studies, we conclude that the electrochemical reaction  $\text{NO}_3^- + 6\text{H}_2\text{O} + 8\text{e}^- \rightarrow \text{NH}_3 + 9\text{OH}^-$  is characterized by a sequence of deoxidation reactions ( $^*\text{NO}_3^- \rightarrow ^*\text{NO}_2 \rightarrow ^*\text{NO} \rightarrow ^*\text{N}$ ), followed by hydrogenation steps ( $^*\text{N} \rightarrow ^*\text{NH} \rightarrow ^*\text{NH}_2 \rightarrow ^*\text{NH}_3$ ).<sup>25,79</sup>

Along with electrochemical activity, stability is an important parameter for evaluating the performance of catalyst. The electrochemical stability of  $\text{CuNi}(1:2)\text{S}$  towards the  $\text{NO}_3\text{RR}$  was then investigated through electrolysis for 10 consecutive cycles (1 h each) at the potential of  $-0.4\text{ V}$  vs. RHE. The chronoamperometric curves revealed a negligible change in the current response and the corresponding UV-Vis spectra for

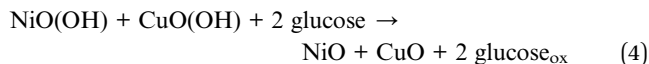
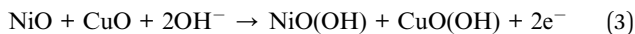
consecutive 10 cycles of 1 h each remained consistent (Fig. S21<sup>†</sup>). A steady F.E. and  $\text{NH}_3$  yield were maintained throughout the 10-h stability test (Fig. 4e). Moreover, post analysis of the catalyst after prolonged chronoamperometric measurement was further investigated by P-XRD, FE-SEM and XPS. The P-XRD pattern and FE-SEM image showed that the crystalline structure and morphology are well preserved (Fig. S22a and b<sup>†</sup>). Furthermore, post XPS analysis (Fig. S23<sup>†</sup>) showed no change in the chemical composition of elements present in  $\text{CuNi}(1:2)\text{S}$  confirming the high stability of the catalyst towards the  $\text{NO}_3\text{RR}$ . The aforementioned results show the appreciable activity and robust nature of  $\text{CuNi}(1:2)\text{S}$  towards the  $\text{NO}_3\text{RR}$  in alkaline media and its superiority compared to the reported literature (Table S9<sup>†</sup>).

### Glucose oxidation reaction (GOR)

To probe the catalytic activity of  $\text{CuNi}(x:y)\text{S}$  towards the glucose oxidation reaction (GOR), LSV curves were recorded for all variants in the absence (*i.e.*, OER) and presence of glucose (*i.e.*, GOR) in 1 M KOH at a scan rate of  $5\text{ mV s}^{-1}$  in a 3-electrode assembly, with catalyst-coated Ni foam serving as the working electrode (WE), graphite rod as the counter electrode (CE), and Hg/HgO/1 M NaOH as the reference electrode (RE). The catalyst was activated prior to the LSV measurements by recording cyclic voltammetry patterns at a scan rate of  $50\text{ mV s}^{-1}$  for 50 cycles. Cyclic voltammetry patterns in Fig. S24<sup>†</sup> illustrate the behaviour of  $\text{CuNi}(1:2)\text{S}$  for 50 cycles in 1 M KOH where both the anodic and cathodic peak current displayed an exponential increase in the current w.r.t cycles, indicating the formation of a metal oxide layer. The plausible mechanism involved in the GOR is as



follows: Cu and Ni atoms are initially oxidised and then they take part in the GOR as described by reactions (3) and (4):<sup>55</sup>



Among the several variants of synthesised catalysts examined, CuNi(1:2)S exhibited the highest GOR activity, with an onset potential of 1.35 V vs. RHE as observed in Fig. 5a and S25.† The comparison of LSV for OER and GOR activity of CuNi(1:2)S in Fig. 5a depicts that the GOR occurs at a lower potential of 1.35 V vs. RHE as compared to the OER (1.55 V vs. RHE). In addition, a lower Tafel slope value of 78 mV dec<sup>-1</sup> in the presence of glucose was obtained, compared to that for OER (146 mV dec<sup>-1</sup>) for CuNi(1:2)S (Fig. S26†), pointed towards faster kinetics for glucose oxidation in comparison to oxygen evolution.<sup>31</sup> To determine the precise onset potential for the GOR, sequential chronoamperometric measurements were performed at potentials ranging from 1.1 V to 1.6 V vs. RHE with a 0.05 V interval for 4 minutes each. As shown in Fig. S27,† the current density showed a sudden increase for the GOR at 1.35 V vs. RHE, whereas for the OER, the current density increased only after 1.55 V vs. RHE. Furthermore, the catalytic performance of CuNi(1:2)S was assessed by recording LSV curves across various concentrations from 0 to 250 mM (Fig. S28†). Interestingly, an increasing trend in current density was observed up to 100 mM glucose concentration and upon further increasing the glucose concentration, a decline in current density was observed which could be potentially attributed to the attainment of complete coverage of

the catalyst surface by glucose.<sup>31</sup> Furthermore, to examine the products obtained during the GOR, chronopotentiometry measurement at 50 mA cm<sup>-2</sup> was performed for 4 h (Fig. 5b) and the electrolyte was analysed using high resolution mass spectrometry (HRMS, Fig. S29†). Table S10† depicts the successful formation of gluconic acid, glucaric acid, guluronic acid and their adducts. Moreover, long-term chronopotentiometry tests were performed at 50 and 100 mA cm<sup>-2</sup> for 15 h, displaying good stability of the catalyst with a negligible decrease in current density (Fig. S30†). Table S11† shows the comparable performance of our catalyst to that reported in the literature. Thus, CuNi(1:2)S demonstrates remarkable bifunctional activity towards the electrocatalytic NO<sub>3</sub>RR and GOR for the production of value added products from both reactions.

### Glucose oxidation assisted NH<sub>3</sub> production

The outstanding bifunctional catalytic activity of CuNi(1:2)S towards both the cathodic NO<sub>3</sub>RR and anodic GOR, inspired us to investigate its practical applicability for glucose oxidation assisted NH<sub>3</sub> generation. We assembled a full cell using CuNi(1:2)S as both the anode and cathode electrocatalysts in a homemade H-type cell separated by a Nafion membrane. The anodic chamber was filled with a solution of 1 M KOH + 100 mM glucose. On the other hand, the cathodic chamber was filled with a solution containing 1 M KOH + 100 mM KNO<sub>3</sub>, to facilitate the reduction of nitrate. Initially the LSV curve was recorded in the presence of glucose, which showed an increase in the current density at a potential of 1.25 V, whereas a voltage of 1.45 V was observed in the absence of glucose, which is 200 mV higher (Fig. 5d). Moreover, the NO<sub>3</sub>RR-OER cell configuration

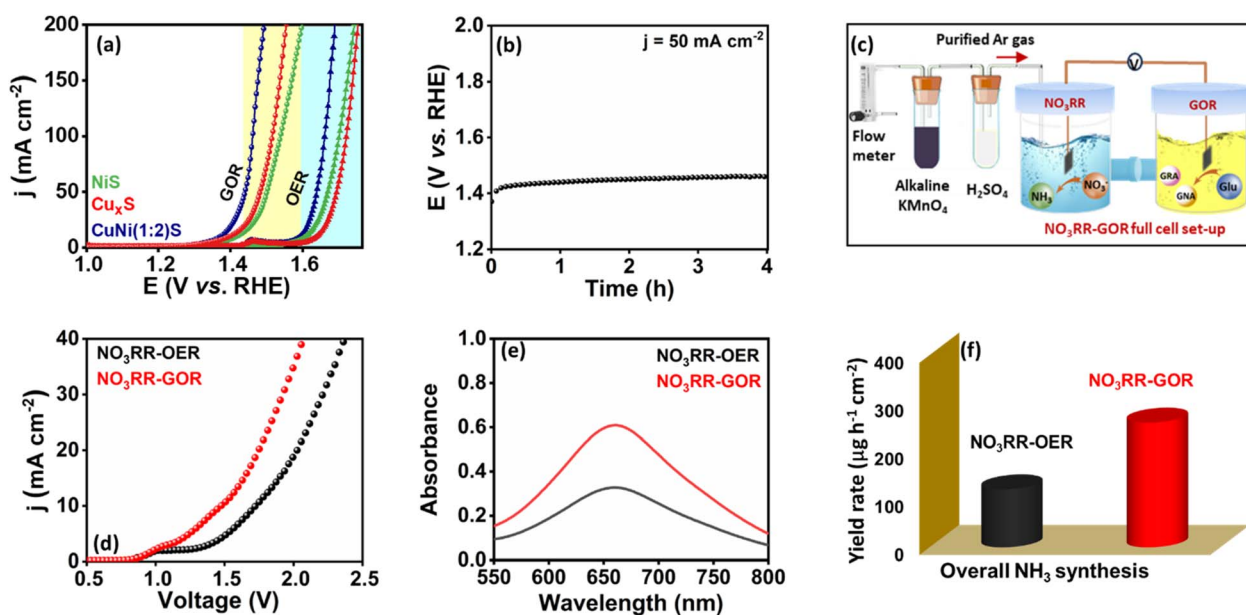


Fig. 5 (a) LSV for the GOR and OER for NiS, Cu<sub>x</sub>S, and CuNi(1:2)S at a scan rate of 5 mV s<sup>-1</sup>, (b) chronopotentiometry measurement at 50 mA cm<sup>-2</sup> for glucose oxidation, and (c) Schematic representation for the gas-purification set-up during the NO<sub>3</sub>RR-GOR full cell experiment for purification of the gas-supply. (d) Comparison of LSV for NO<sub>3</sub>RR-OER and NO<sub>3</sub>RR-GOR for full cell studies, and (e) UV-Vis spectra after chronoamperometry at a potential of 1.5 V in the absence and presence of glucose and (f) bar diagram showing the NH<sub>3</sub> yield rate in NO<sub>3</sub>RR-OER and NO<sub>3</sub>RR-GOR after electrolysis at 1.5 V.



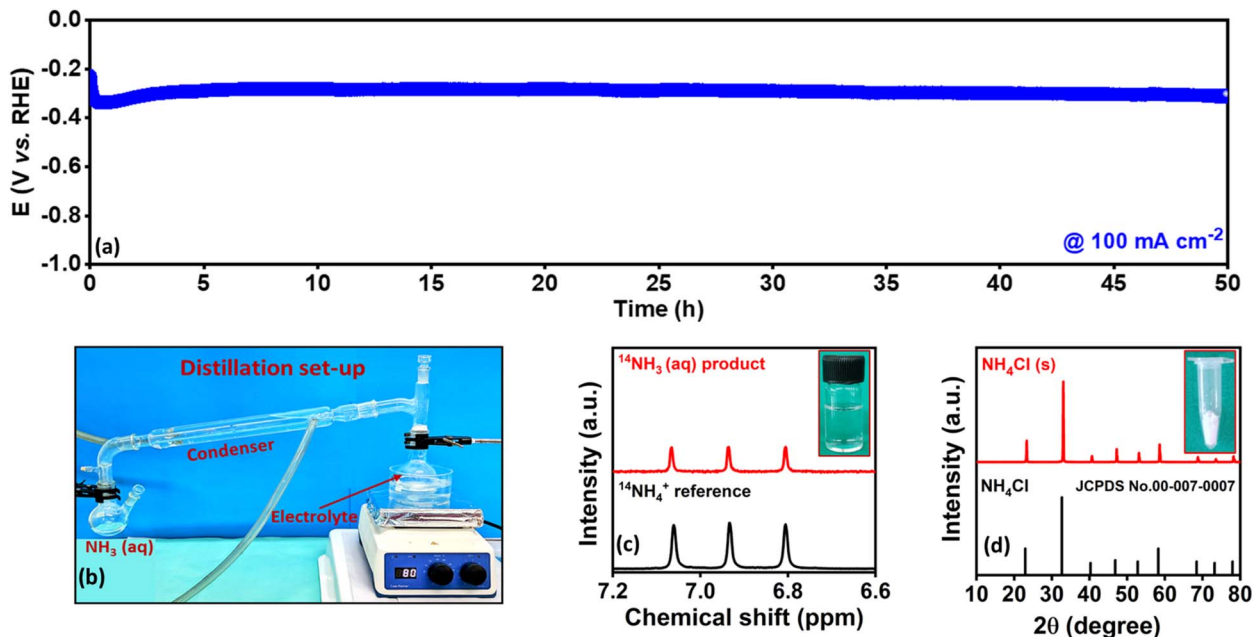


Fig. 6 (a) Chronopotentiometry of CuNi(1 : 2)S at  $100 \text{ mA cm}^{-2}$  in 1 M KOH with 100 mM  $\text{KNO}_3$  for 50 h and (b) photograph showing the distillation set-up for the extraction of condensed  $\text{NH}_3(\text{aq})$  from the electrolyte solution after 50 h of electrolysis. (c)  $^{15}\text{N}$  NMR spectra with the inset showing the photograph of condensed  $\text{NH}_3(\text{aq})$  and (d) XRD pattern with the inset showing the photograph of the extracted  $\text{NH}_4\text{Cl}(\text{s})$ .

requires a voltage of 1.72 V to reach a current density of  $10 \text{ mA cm}^{-2}$ . However, when the OER is substituted with the GOR at the anode during  $\text{NH}_3$  production, a voltage of 1.48 V is enough to accomplish the same current density. After electrolysis for 1 h at a potential of 1.5 V, a further evaluation of the  $\text{NH}_3$  generation yield was carried out using UV-Vis spectroscopy (Fig. S31† and 5e). The  $\text{NH}_3$  yield rate of  $259.46 \mu\text{g h}^{-1} \text{ cm}^{-2}$  for the  $\text{NO}_3\text{RR-GOR}$  cell was determined, which is higher than the  $\text{NH}_3$  yield rate for the  $\text{NO}_3\text{RR-OER}$  cell system ( $120.95 \mu\text{g h}^{-1} \text{ cm}^{-2}$ ), as shown in Fig. 5f. This strengthens the relevance of our conceptualization. Therefore, this work may delve into the implementation of metal sulphides for overall  $\text{NH}_3$  production at decreased cell voltage by substituting the anodic OER with GOR for practical application.

### Extraction of pure ammonia

With our catalyst's noteworthy  $\text{NO}_3\text{RR}$  performance, we further illustrate the practical recovery of high-purity ammonia products. A catalyst's good stability is essential at industrially relevant current densities for real applications. Thus, we performed a long-term chronopotentiometry (CP) stability test of CuNi(1 : 2)S in an H-cell at a current density of  $100 \text{ mA cm}^{-2}$  for 50 h for the  $\text{NO}_3\text{RR}$  (Fig. 6a). After that, ammonia was extracted from the electrolyte solution *via* the distillation process, which resulted in ammonia condensation in the receiver flask while leaving the remaining reaction mixture in the distilling flask (Fig. 6b and Scheme S1, detailed in the ESI†). The condensed  $\text{NH}_3(\text{aq})$  was verified using  $^1\text{H}$  NMR spectroscopy as shown in Fig. 6c and the inset shows the condensed  $\text{NH}_3$ . The condensed  $\text{NH}_3$  was quantified by UV-Vis spectroscopy, with a condensation collection efficiency of 89.84% (detailed in the ESI†). The condensed

$\text{NH}_3(\text{aq})$  solution was further treated with HCl to finally form  $\text{NH}_4\text{Cl}$ .<sup>80</sup> High-purity  $\text{NH}_4\text{Cl}(\text{s})$  powder was obtained through rotary evaporation at a temperature of  $40 \text{ }^\circ\text{C}$ , and its formation was confirmed by the XRD pattern that matches with standard JCPDS ICDD no. 00-007-0007, with no extra peak (Fig. 6d). The collection efficiency of solid  $\text{NH}_4\text{Cl}$  was also calculated to be 82.27%. This practical illustration shows the entire process for electrochemically converting nitrate to an advantageous, high-purity ammonia product.

## Conclusion

In summary, we successfully synthesised a CuNi binary metal sulphide CuNi(x : y)S catalyst using a one-step hydrothermal approach with flakes aggregated into a microsphere-like morphology for the glucose assisted  $\text{NO}_3\text{RR}$  in alkaline media. A high  $\text{NH}_3$  yield of  $4.76 \text{ mg h}^{-1} \text{ cm}^{-2}$  ( $280.47 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ ) and a F.E. of 93.44% at a potential of  $-0.4 \text{ V (vs. RHE)}$  with a high current density of  $\sim 118 \text{ mA cm}^{-2}$  was achieved for the CuNi(1 : 2)S catalyst, which is superior to the yield obtained in the industrial Haber-Bosch process ( $< 200 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ ).<sup>40</sup> Moreover, the successful  $\text{NO}_3\text{RR}$  to  $\text{NH}_3$  conversion was studied by *in situ* electrochemical Raman spectroscopy. The full-cell studies reveal 2.14 times higher  $\text{NH}_3$  yield for the  $\text{NO}_3\text{RR-GOR}$  system compared to the  $\text{NO}_3\text{RR-OER}$  system. This work unveils the synergistic effect of Cu and Ni for efficient  $\text{NO}_3\text{RR}$  and GOR and contributes to a better understanding and design of effective bimetallic catalysts for the  $\text{NO}_3\text{RR}$  and other applications. This study significantly broadens the area of research for the glucose-assisted  $\text{NH}_3$  generation at lower cell potential with high  $\text{NH}_3$  yield, which is accomplished by substituting the sluggish oxygen evolution reaction with the GOR. Furthermore,



we extracted a pure  $\text{NH}_3$  aqueous product and  $\text{NH}_4\text{Cl}$  for large-scale industrial application.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Conflicts of interest

There are no conflicts to declare.

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