**Diagram of a gas-powered device

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**Supplementary Figure S1** Schematic diagram of electrochemical setup for NO3- reduction

Figure S2 displays the SEM images of pristine 25 nm Cu-Ni electrode at 370× and 4000× magnification. The images reveal the presence of pits on the Ni plate, with widths of ~1 μm.

A close-up of a rock formation

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**Supplementary Figure S2** SEM micromorphology of 25 nm Cu-Ni electrode at (A) 370x, and (B) 4000x

Figure S3 displays the elemental EDX mapping and EDX spectrum, which demonstrates the complete coverage of the Ni plate with Cu, a finding that is consistent with the XPS results (shown in the next section).

A screenshot of a computer

Description automatically generated

**Supplementary Figure S3** EDX images with elemental mapping and EDX spectrum of 25 nm Cu-Ni electrode

XPS spectra of the Ni plate used in this study is shown in Figure S4. The survey spectrum of Ni plate showed the elements like C, Ni, O present on the surface (Figure S4A). High resolution spectrum of Ni 2p is curve fitted as shown in Figure S4B. In Ni 2p3/2 region, the peak at 852.39 eV corresponds to Ni metal (Ni0) (Hu et al., 2019), the peaks at 855.13 eV and 857.14 eV correspond to Ni oxides, NiO and Ni2O3, respectively. The Ni 2p1/2 region, the peak at 870 eV corresponds to Ni metal (Ni0), the peaks at 872.8 eV and 874.89 eV correspond to Ni oxides, NiO and Ni2O3, respectively (Cheng et al., 2017). All other peaks are satellite peaks. Figure S4C shows the O 1s spectrum with three subpeaks at 529.09, 531.26 and 532.99 eV are corresponding to oxygen in nickel oxides (NiO and Ni2O3), Ni(OH)2 and water adsorbed on Ni plate, respectively (Cheng et al., 2017).

A diagram of different energy levels

AI-generated content may be incorrect.**Supplementary Figure S4** XPS spectra of Ni plate (A) Survey, (B) Ni 2p, (C) O 1s

XPS spectra of 25 nm thick Cu coated on Ni plate (Pristine) is shown in Figure S5. The survey spectrum of 25 nm Cu-Ni plate showed the elements like C, Cu, and O present on the surface (Figure S5A). The peaks corresponds Ni in high resolution Ni 2p spectrum (Figure S5B) is negligible, due to complete coverage of Cu coating on Ni plate using PVD. High resolution spectrum of Cu 2p is curve fitted as shown in Figure S5C. The peaks at 931.83 and 951.70 eV correspond to Cu metal (Cu0), the peaks at 933.59 and 954.42 eV correspond to Cu2+ (Cu2O), respectively (Jiang et al., 2021). Figure S5D shows the O 1s spectrum with three subpeaks at 529.80, 531.87 and 534.0 eV are corresponding to oxygen in CuO, Cu(OH)2 and adsorbed water molecules, respectively (Jiang et al., 2021).

A diagram of different energy levels

AI-generated content may be incorrect.**Supplementary Figure S5** XPS spectra of pristine 25 nm Cu coated on Ni. (A) Survey, (B) Ni 2p, (C) Cu 2p, (D) O 1s

XPS spectra of spent 25 nm Cu-Ni cathode is shown in Figure S6. The survey spectrum of spent 25 nm Cu-Ni cathode showed the elements like C, Ni, N, Cu, and O present on the surface (Figure S6A). The Ni peaks in high resolution Ni 2p spectrum (Figure S6B) is barely visible. This could be due the removal of Cu from cathode plate during NO3- reduction, most likely from the area of pits on the surface (Eiler et al., 2020). High resolution spectrum of Cu 2p is curve fitted as shown in Figure S6C. The peaks at 933.59 and 951.70 eV correspond to Cu metal (Cu0). The peaks at 933.59 and 954.42 eV correspond to Cu2+ (Cu2O), respectively (Jiang et al., 2021). The small shift in the position of Cu2+ peaks is due to the adsorption of nitrogen compounds from the electrolyte on the surface of the cathode. Figure S6D shows the O 1s spectrum with three subpeaks at 529.8, 531.87, and 534.0 eV correspond to oxygen in CuO, Cu(OH)2, and adsorbed water, respectively (Jiang et al., 2021). Figure S6E shows the N 1s spectrum with two subpeaks at 399.5 and 396.0 eV corresponding to \*NH3 and N3- adsorbed on the Cu-Ni cathode plate, respectively (Baltrusaitis et al., 2009; Kehrer et al., 2019; Yoon et al., 2019).

A collection of diagrams showing different types of energy

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**Supplementary Figure S6** XPS spectra of spent 25 nm Cu coated on Ni. (A) Survey, (B) Ni 2p, (C) Cu 2p, (D) O 1s, (E) N 1s

Figure S7 depicts a comparison of XPS spectra of Ni 2p for Ni plate without coating (Figure S7A), 25 nm Cu-Ni electrode (pristine) (Figure S7B), and 25 nm Cu-Ni electrode (spent) (Figure S7C). A noticeable difference in peaks can be observed for all three electrodes. The Ni plate without a coating exhibits the highest peaks, corresponding to Ni0, Ni2+, and Ni3+, whereas no peaks were detected for the Cu-Ni electrode (pristine). For the Cu-Ni electrode (spent), Ni peaks are barely visible, indicating that some Cu has been removed, exposing the Ni surface during NO3RR facilitating the NO3- reduction

**A graph of a graph showing the value of a stock market

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**Supplementary Figure S7** XPS spectra of Ni 2p of (A) Ni plate without coating, (B) 25 nm Cu-Ni electrode (pristine), (C) 25 nm Cu-Ni electrode (spent)

A schematic diagram depicting the mechanism of Cu removal from the cathode during NO3- reduction is illustrated in Figure S8. The Cu particles detach from the electrode during the electrocatalytic process of NO3- reduction, revealing the Ni plate and forming pits.

A diagram of a structure

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**Supplementary Figure S8** Schematic of Cu removal mechanism on Cu-Ni cathode during NO3- reduction

The comparison of reduction curves for 25 nm, 50 nm, and 100 nm Cu-Ni electrodes is illustrated in Figure S9. It is evident from the figure that as the thickness of Cu is increased, the current density decreases because as film thickness increases there is a evolution of microstructure and increased surface roughness (Lin et al., 2017), structural deterioration (Nguyen et al., 2024), and increased resistivity caused due to variations in bonding mechanisms and interface voids in thicker films which impedes current flow (Lu et al., 2024).

A group of different colored lines

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**Supplementary Figure S9** Comparison of reduction curves for 25 nm, 50 nm, and 100 nm Cu-Ni electrodes with different catholyte concentration of (A): 2.5 mM KNO3 + 3.5 mM Na2SO4 , (B): 2.5 mM KNO3 + 9.8 mM Na2SO4 , (C): 5.9 mM KNO3 + 9.8 mM Na2SO4, and (D): 3.5 mM Na2SO4