Supplementary Information (SI) for Nanoscale.
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Supporting information

Closing the nitrogen loop: Sustainable ammonia production from industrial nitrate waste using a stacked electrolyzer

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Materials and methods

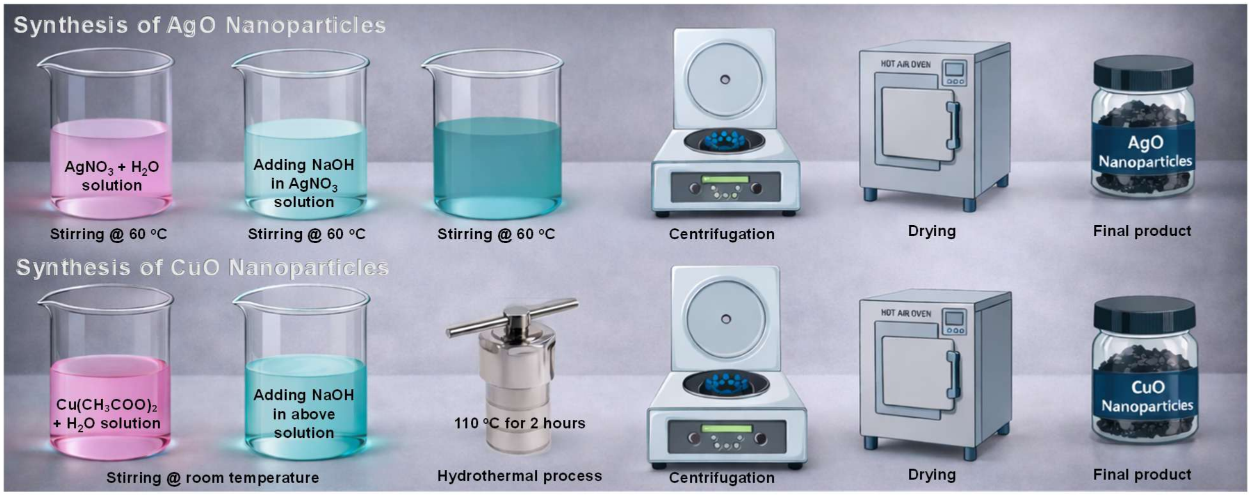
Materials

Aqueous silver nitrate ($AgNO_3$) solution *(Sigma-Aldrich)*, Sodium hydroxide (NaOH, 99%) *(Sigma-Aldrich)*, copper (II) acetate monohydrate ($Cu(CH_3COO)_2{\cdot}H_2O$, 99%) *(Sigma-Aldrich)*, Ethanol *(Merck)*, Nafion-perfluorinated resin solution about 5 wt % *(Sigma-Aldrich),* Sustainion XA-9.5% - Dioxide materials, salicylic acid – 98% *(Sigma-Aldrich)*, sodium citrate ($HOC(COONa)(CH_2COONa)_2{\cdot}2H_2O$, 99%) *(Merck)*, Sodium hypochloride (NaClO) *(Merck)*, Sodium nitroprusside *(Sigma-Aldrich)*, p-aminobenzene sulfonamide *(Merck)*, ethylenediamine dihydrochloride *(Merck)*, phosphoric acid (99.99%) *(Merck)*, Sulfamic acid (NH_2SO_3HACS Reagent, 99%) *(Merck)*, Hydrochloric acid (HCl, 37%) *(Merck)*, Potassium hydroxide (KOH) (Merck), Sodium Nitrate ($NaNO_3$) *(Sigma-Aldrich)*.

Synthesis of CuO/AgO

AgO and CuO nanoparticles (NPs) were prepared using the wet chemical method and hydrothermal method based on the earlier reports[1-2]. For AgO NPs synthesis, 80 mL of an aqueous silver nitrate ($AgNO_3$) solution (5 mM) was heated to 60 °C. Subsequently, 20 ml of a 0.025 M NaOH solution was slowly added dropwise to the $AgNO_3$ solution under stirring at 60 °C for 2 hours. After the reaction mixer had cooled to room temperature, the resulting precipitate was separated via centrifugation at 3000 rpm. The collected solid was washed multiple times with ethanol and water, and dried at 50 °C for 24 hours under vacuum to get AgO NPs.

For CuO NPs synthesis, 4 g of copper (II) acetate monohydrate ($Cu(CH_3COO)_2{\cdot}H_2O$) was dissolved in 50 mL of deionized water under continuous stirring until a clear solution formed. Next, 40 mL of a 1 M NaOH solution was added dropwise to the above-mentioned solution while stirring. The resulting mixture (90 mL total volume) was then transferred into a Teflon-lined stainless-steel autoclave, sealed, and heated at 110 °C for 2 hours. After the reaction, the autoclave was allowed to cool naturally to room temperature. The black precipitate obtained was collected after centrifuging, washed repeatedly with deionized water and ethanol, and dried at 90 °C in air to get CuO NPs.



Scheme S1: Schematic representation of the synthesis of AgO and CuO nanoparticles

Electrode Preparation:

20 mg of CuO NPs and 20mg of AgO NPs were mixed with 5mg of carbon black in a 70% ethanol solution (2 mL) and 50 µL of Nafion. The prepared solution was sonicated for 30 minutes and coated on a 5 cm^2 carbon paper using the spray coating approach. The same procedure was followed for the electrolyzer GDL preparation, instead of Nafion, we used ionomer (Sustainion XA-9.5% - Dioxide materials). The mass loading of the CuO/AgO catalyst on carbon paper is 1mg cm^{-1}.[3-5]

Electrochemical measurements:

All electrochemical measurements were carried out using a Biologic SP 150 Potentiostat, and long-term measurements were carried out using a Rigol Power supply. Initial three-electrode measurements were conducted with CuO/AgO as the working electrode, Ag/AgCl as the reference electrode, and a graphite rod as the counter electrode, respectively. The LSV measurements were done with scan rate of 5 mVs^{-1}. Two-electrode measurements were carried out using an electrolyzer with CuO/AgO as the cathode and IrO_2/C as the anode catalyst with a PTFE-supported proton exchange membrane (PEM). All the measurements are carried out in deionized water with various concentrations of $NaNO_3$ and unless it is mentioned as industrial wastewater. Flow rate was precisely maintained using a peristaltic pump. In the fabrication of a 50 cm^2 stacked electrolyzer (25 cm^2 × 2), a custom unit was made using an acrylic sheet body, Ni sheet contact, 5% Pd on carbon as anode, CuO/AgO coated gas diffusion layer as cathode, and PTFE-supported proton exchange membrane.

Product Quantification:

Ammonia Quantification:

For ammonia quantification, we have followed the Indophenol Blue method. Briefly, 2ml of the post electrolyte solution is mixed with 2ml of coloring solution (4 gm of sodium hydroxide, 5 gm of salicylic acid and 5 gm of sodium citrate in 100 ml of DI water) and 1 ml of oxidation solution (1.8 ml of Sodium hypochloride in 48.2 ml of DI water) and 0.2 ml of catalyst sodium nitroprusside (20 mg in 2 ml). The solution is mixed well and tested after 20 minutes using UV-Vis absorption spectroscopy. The calibration curve was obtained through the NH_4Cl standard and is given below Figure S1.

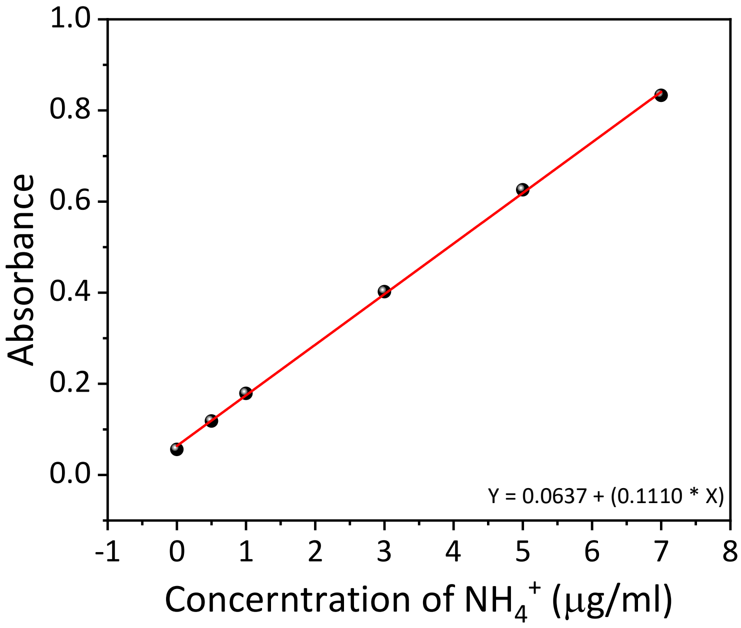


Figure S1: Ammonia calibration curve obtained with NH_4Cl standard.

The NH_3 yield can be found using the following relation

$$NH_3\ yield\ (\mu g) = ((NH_3\ yield\ \ ml^{-1}) * Dilution\ factor * Electrolyt\ Volume) \text{ ---(Eq.1)}$$

Nitrite Quantification:

Nitrite quantification was conducted through UV-Vis absorbance spectroscopy. Briefly, 2 ml of post-electrolyte was mixed with 0.06 ml of coloring agent (4g of p-aminobenzene sulfonamide, 0.2 g of N-(1-naphthyl) ethylenediamine dihydrochloride, and 10 ml of phosphoric acid with 50 ml of DI water) and kept undisturbed for 30 minutes. A calibration curve for NO_2 was obtained with $NaNO_2$ and provided in Figure S2.

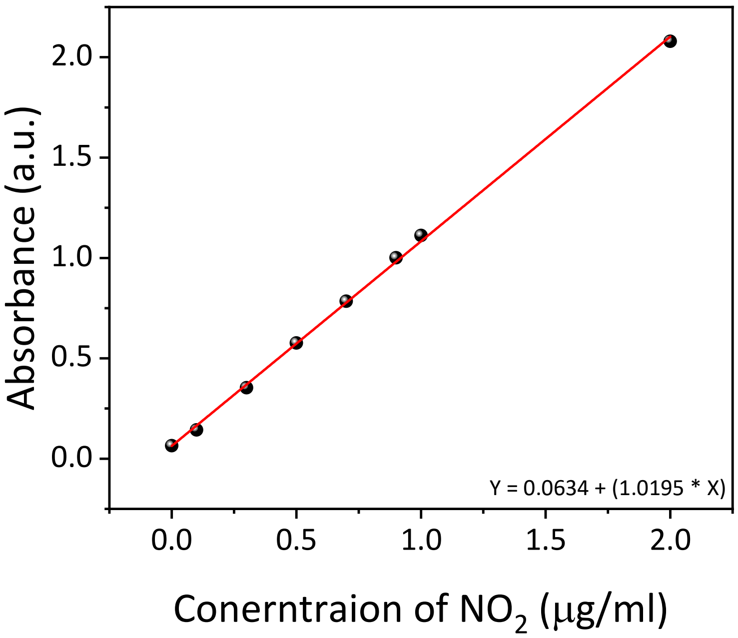


Figure S2: Nitride calibration curve obtained with $NaNO_2$ standard.

The NO_2 yield can be found using the following relation

$$NO_2\ yield\ (\mu g) = ((NO_2\ yield\ ml^{-1}) * Dilution\ factor * Electrolyt\ Volume)$$ ---(Eq.2)

Nitrate Quantification:

Nitrate quantification was conducted through UV-Vis absorbance spectroscopy. Briefly, 6 μL of 0.8 Wt% of sulfamic acid (8 mg in 1 mL DI water) and 60 μL of 1M hydrochloric acid was shaken well with 3 mL of post-reaction electrolyte. After being undisturbed for 30 minutes, absorbance spectra were obtained. The calibration curve was obtained with $NaNO_3$ (absorbance 220 nm - absorbance 275 nm) and provided in Figure S3.

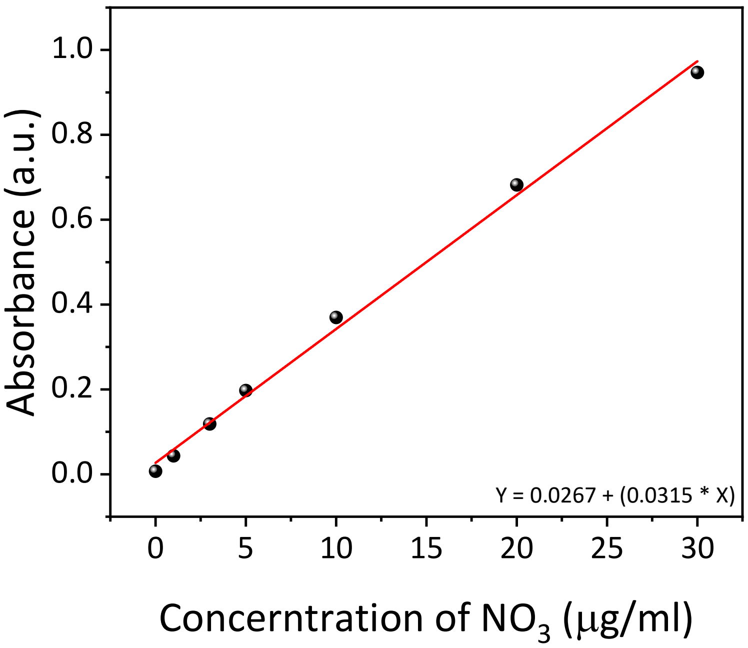


Figure S3: Nitrate calibration curve obtained with $NaNO_3$ standard.

The NO_3 yield can be found using the following relation

$$NO_3\ yield\ (\mu g) = ((NO_3\ yield\ ml^{-1}) * Dilution\ factor * Electrolyt\ Volume) \text{ ---(Eq.3)}$$

Faradic Efficiency calculation:

Faradic efficiency was estimated using the formula

$$Faradic\ Efficiency\ (\%) = \frac{F*n*z}{T*A*I}(100\%) \text{---(Eq.4)}$$

Where F is the Faradic constant 96485 C/mol, n is the number of electrons for the reaction (n=2 for NO_2 and n=8 for NH_3), z is the no. of moles of product (mol), T is the duration (seconds), A is the area (cm^2), and J is the current density (A/cm^2).

Energy conversion efficiency (ECE):

Full-cell ECE was calculated using the formula

$$ECE_{Full-cell} = \frac{(1.23 - E_0) * FE_{NH}}{Applied\ potential\ (V)} \text{ ---(Eq.5)}$$

Where E_0 for NO3RR is -0.69V, and FE_{NH3} is the Faradic efficiency of NH_3.

Nitrate conversion efficiency:

$$Nitrate\ conversion\ \% = \left(\frac{No.of\ moles\ of\ NO_2 + No.of\ moles\ of\ NH_3}{No.of\ moles\ of\ NO_3}\right) \times\ 100\% \text{ ---(Eq.6)}$$

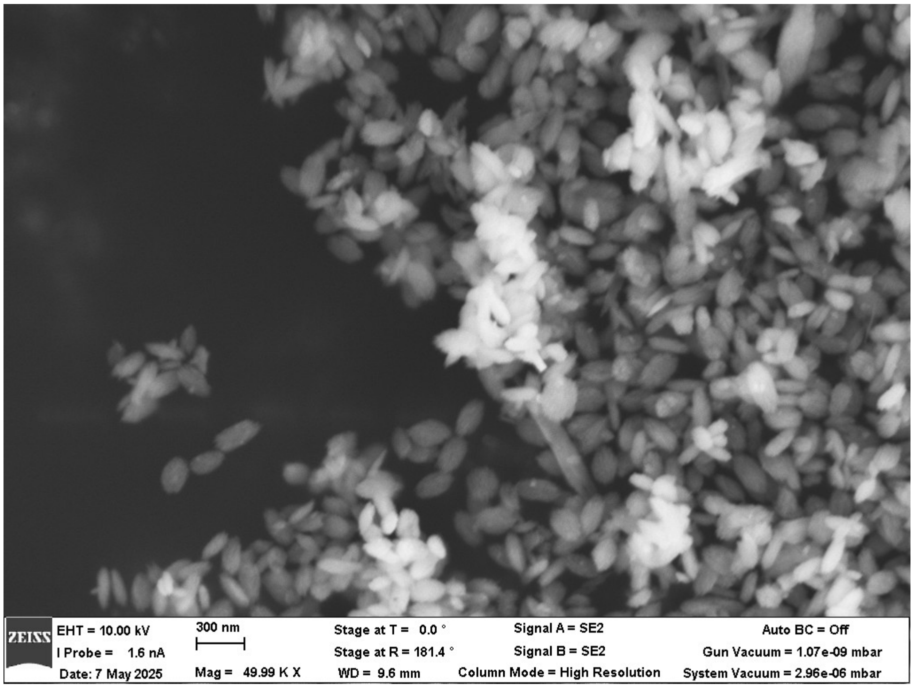


Figure S4: FESEM image of CuO NPs.

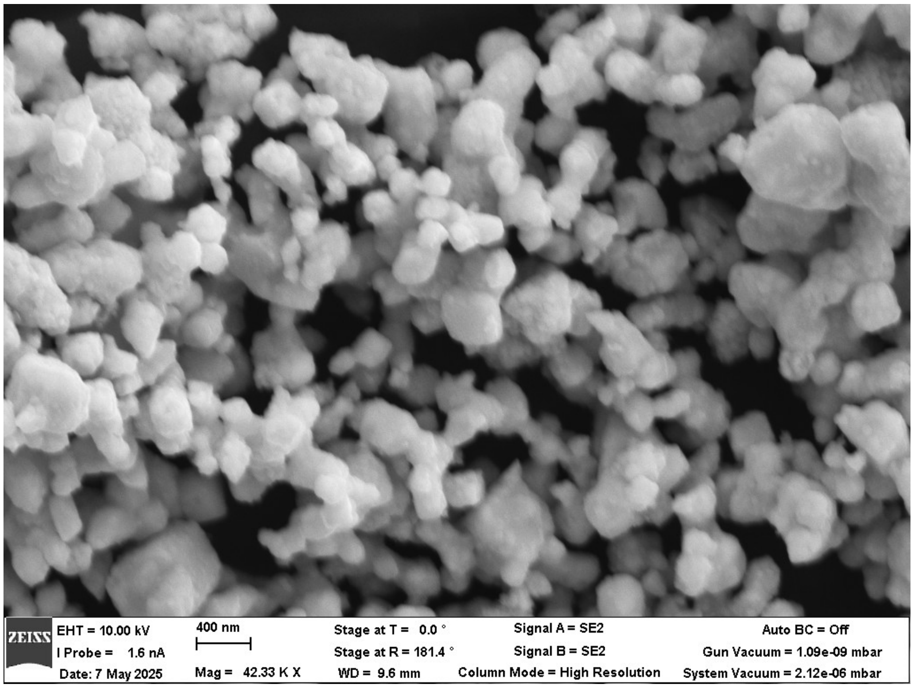


Figure S5: FESEM image of AgO NPs.

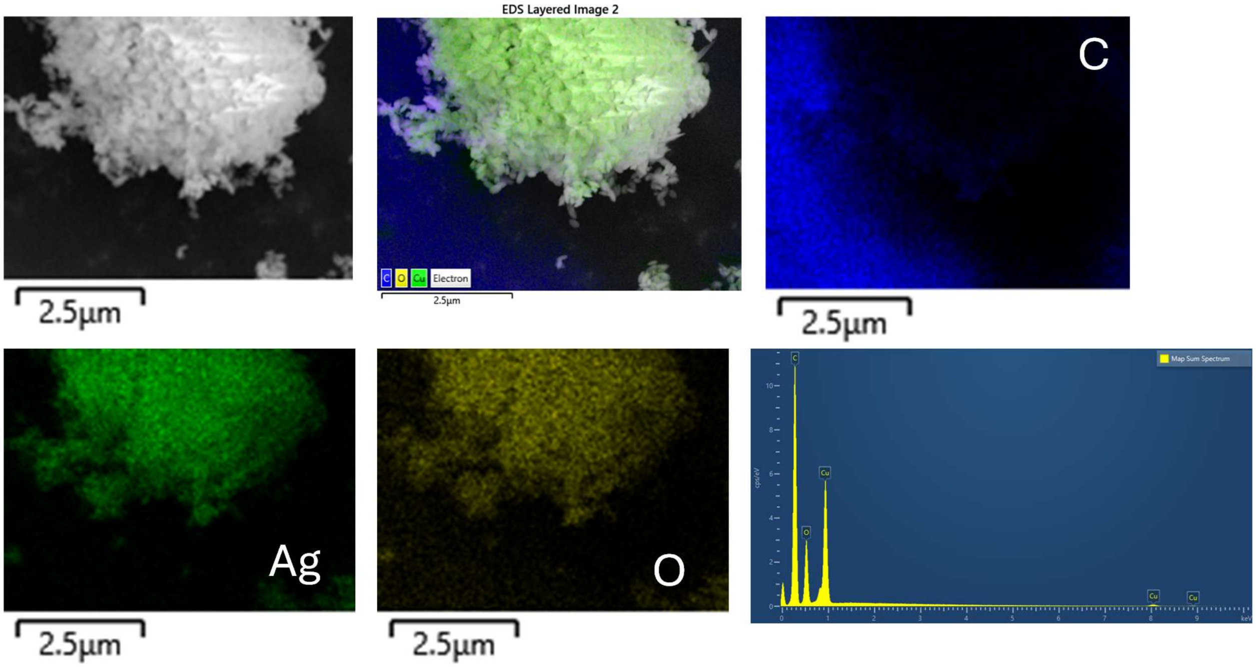


Figure S6: EDS elemental mapping of CuO NPs.

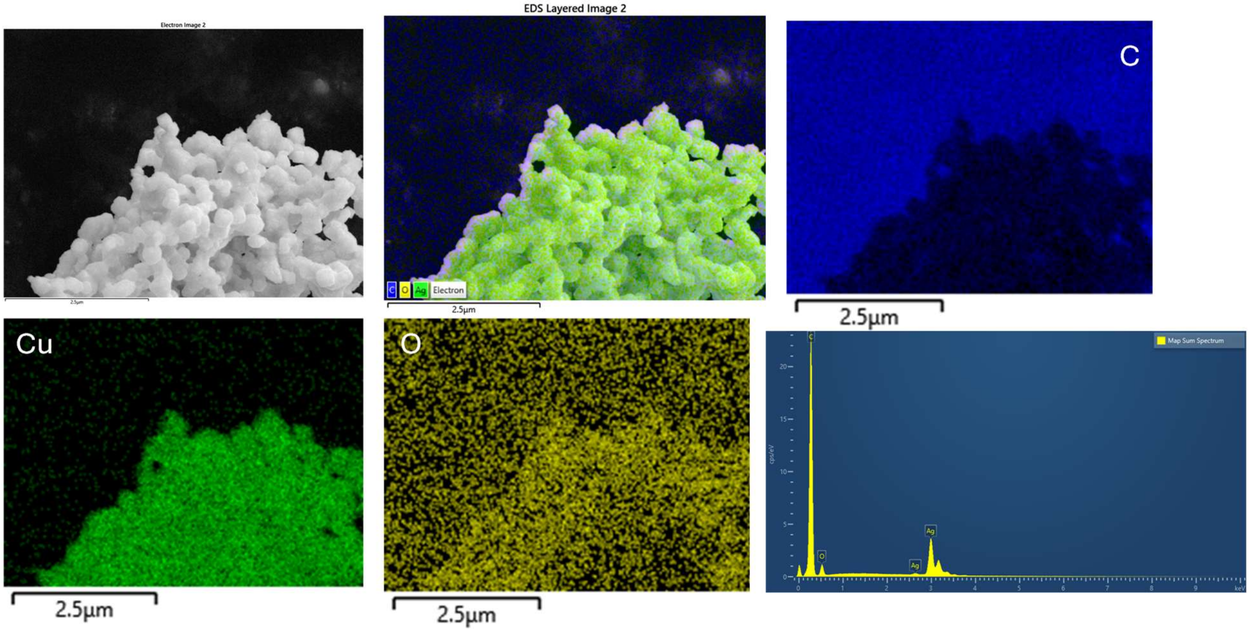


Figure S7: EDS elemental mapping of AgO NPs.

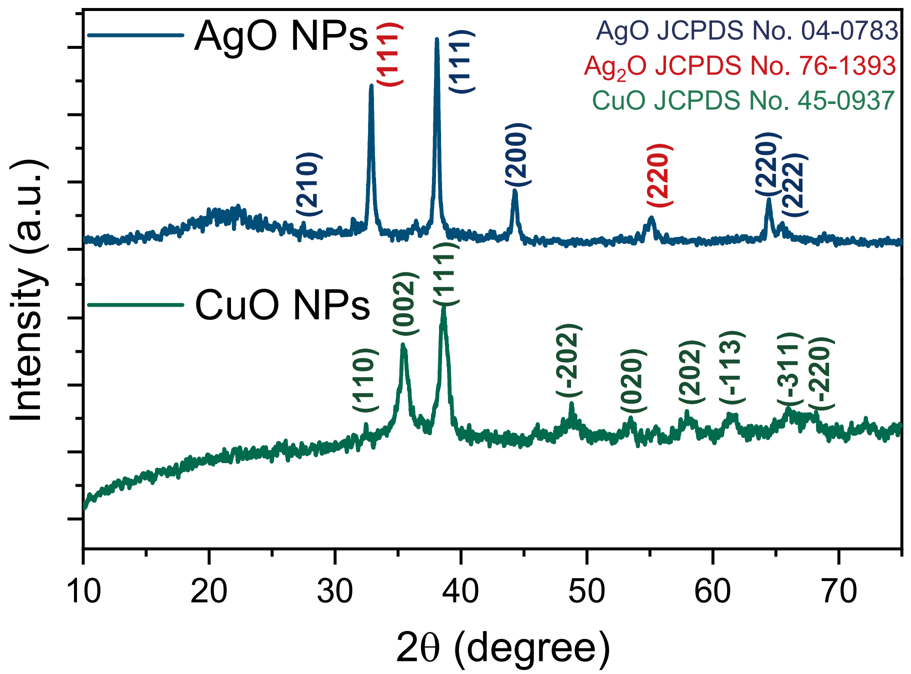


Figure S8: XRD spectra of CuO and AgO NPs.

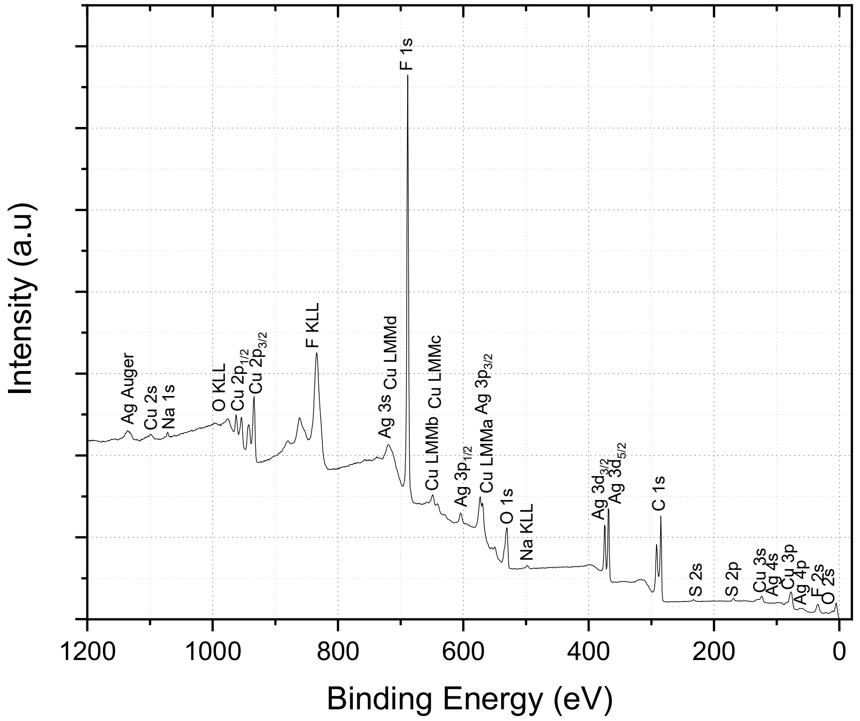


Figure S9: XPS survey spectra of CuO/AgO-coated gas diffusion layer.

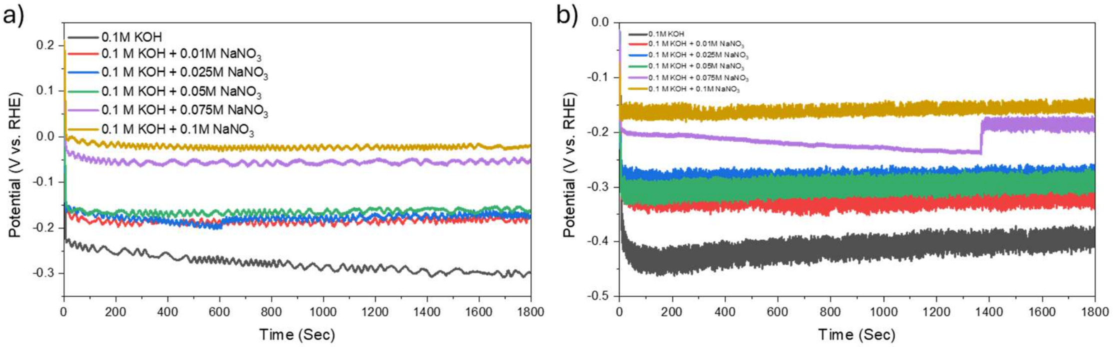


Figure S10: CP of CuO/AgO at various nitrate concentrations.

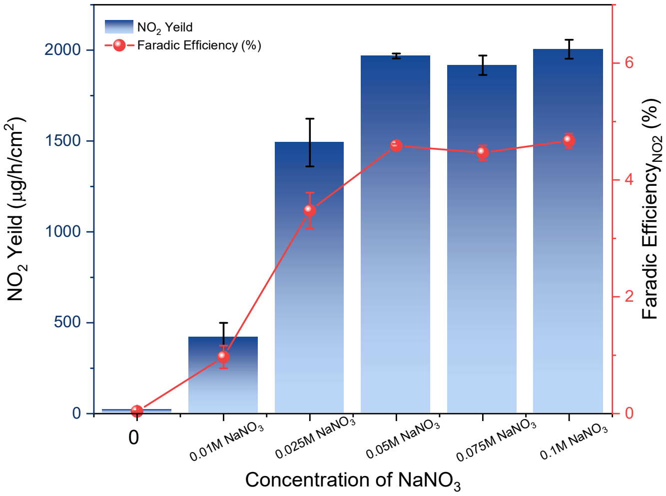


Figure S11: NO_2 quantification corresponding to Figure S10 and its Faradic efficiency.

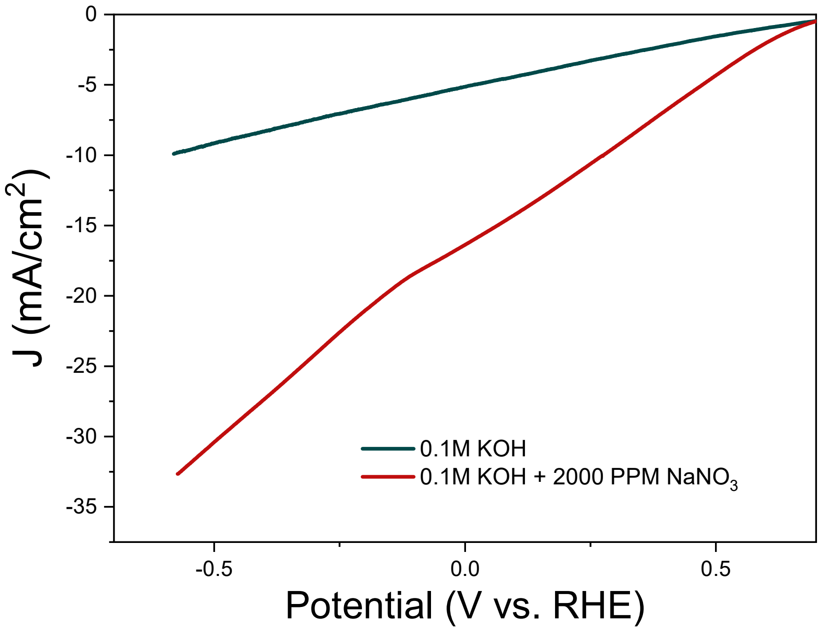


Figure S12: LSV of CuO/AgO at 0.1M KOH + 2000 PPM $NaNO_3$.

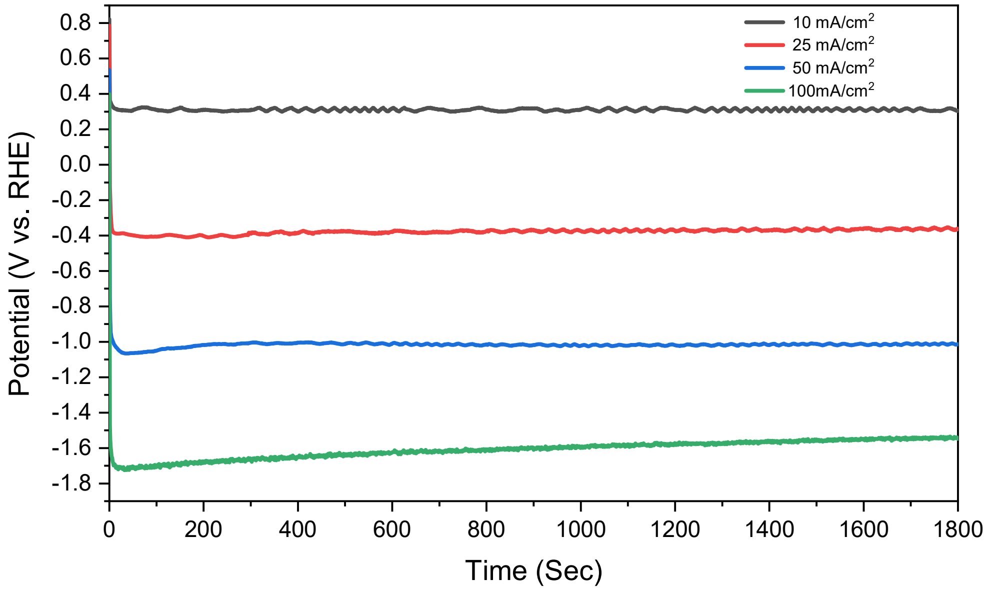


Figure S13: CP of CuO/AgO at 2000 PPM NO_3 concentration at various applied potentials.

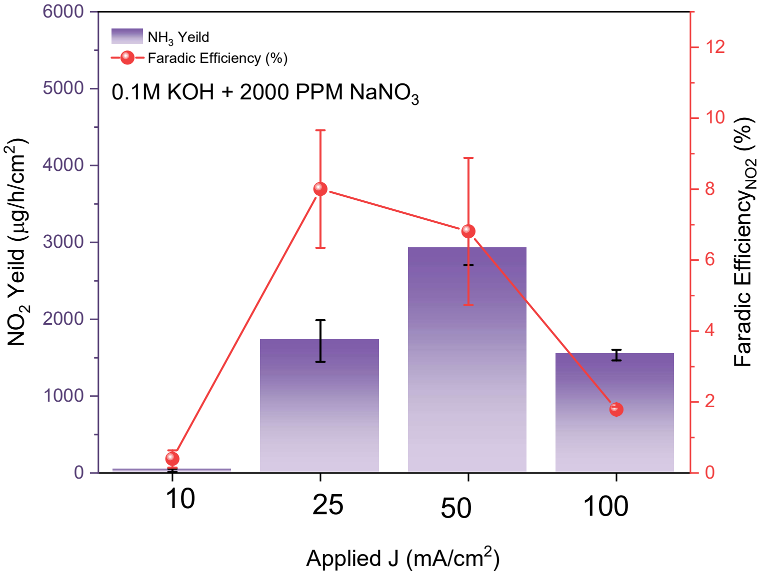


Figure S14: NO_2 quantification corresponding to Figure S13 and its Faradic efficiency.

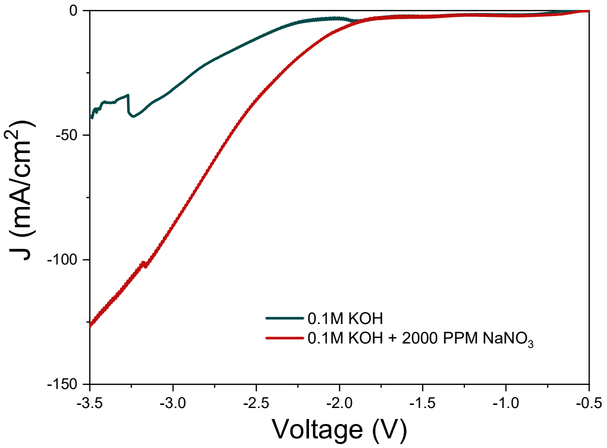


Figure S15: LSV of CuO/AgO at 0.1M KOH + 2000 PPM NO_3 concentration in 1cm^2 electrolyzer.

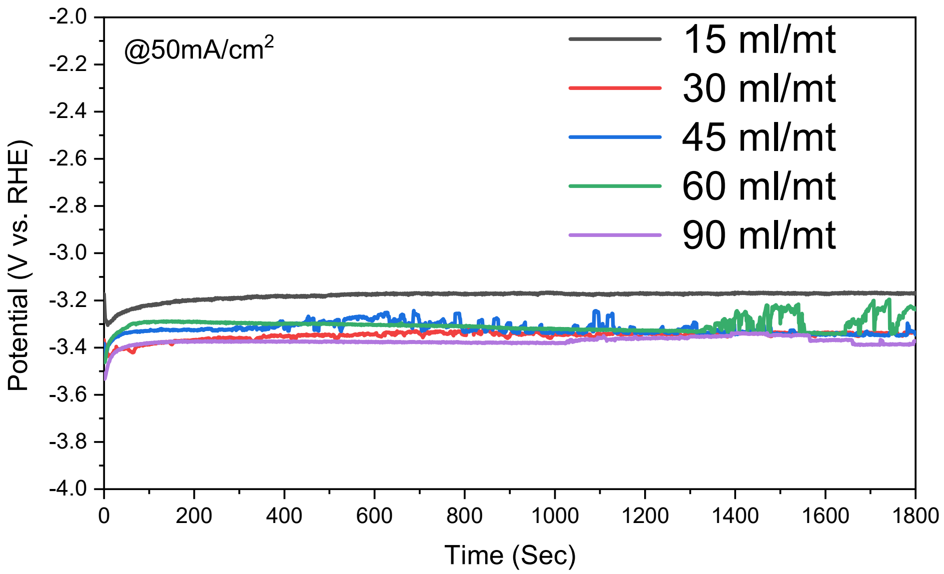


Figure S16: CP at 50mA/cm^2 of CuO/AgO at 0.1M KOH + 2000 PPM NO_3 concentration at various flow rate.

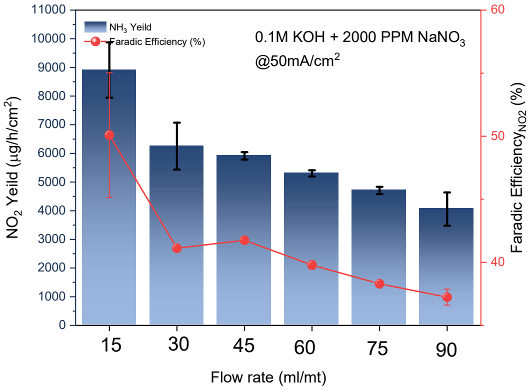


Figure S17: NO_2 quantification corresponding to Figure S16 and its Faradic efficiency.

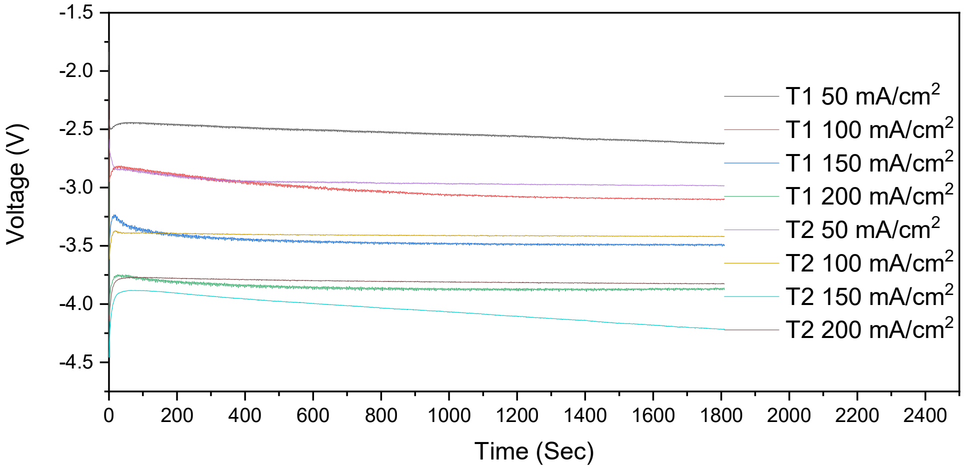


Figure S18: CP at various potentials for CuO/AgO at 0.1M KOH + 2000 PPM NO_3 concentration at a flow rate of 15 ml/mt.

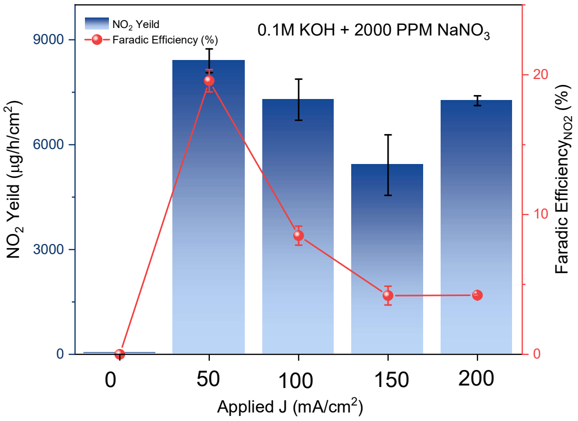


Figure S19: NO_2 quantification corresponding to Figure S18 and its Faradic efficiency.

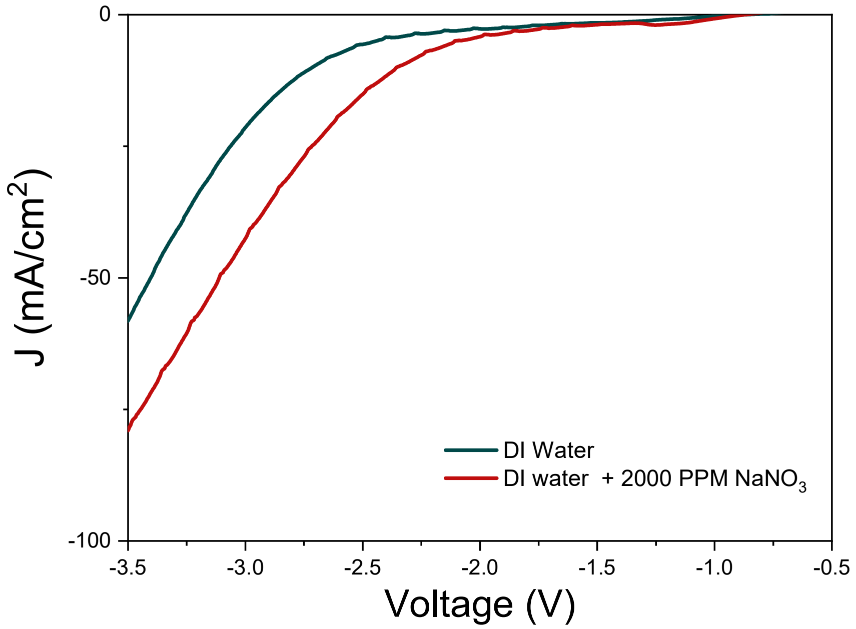


Figure S20: LSV of CuO/AgO at DI Water + 2000 PPM NO_3 concentration in 1cm^2 electrolyzer.

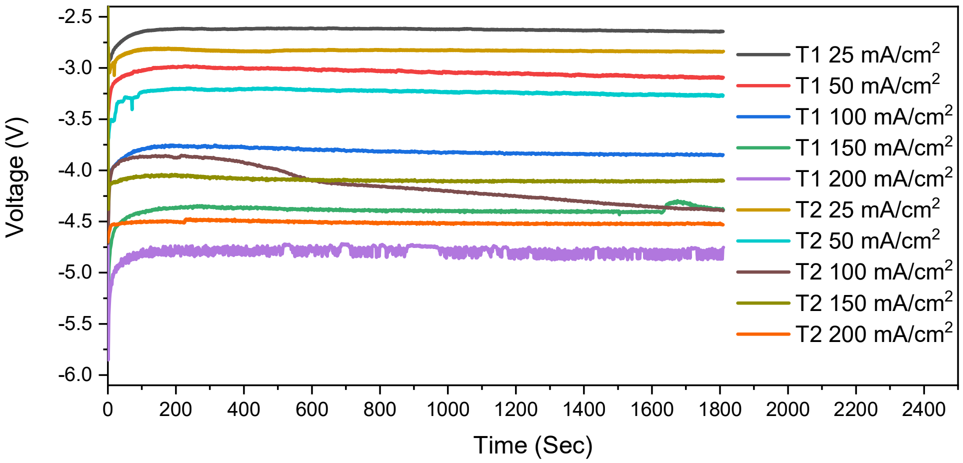


Figure S21: CP of CuO/AgO at DI water + 2000 PPM NO_3 concentration at various applied potentials.

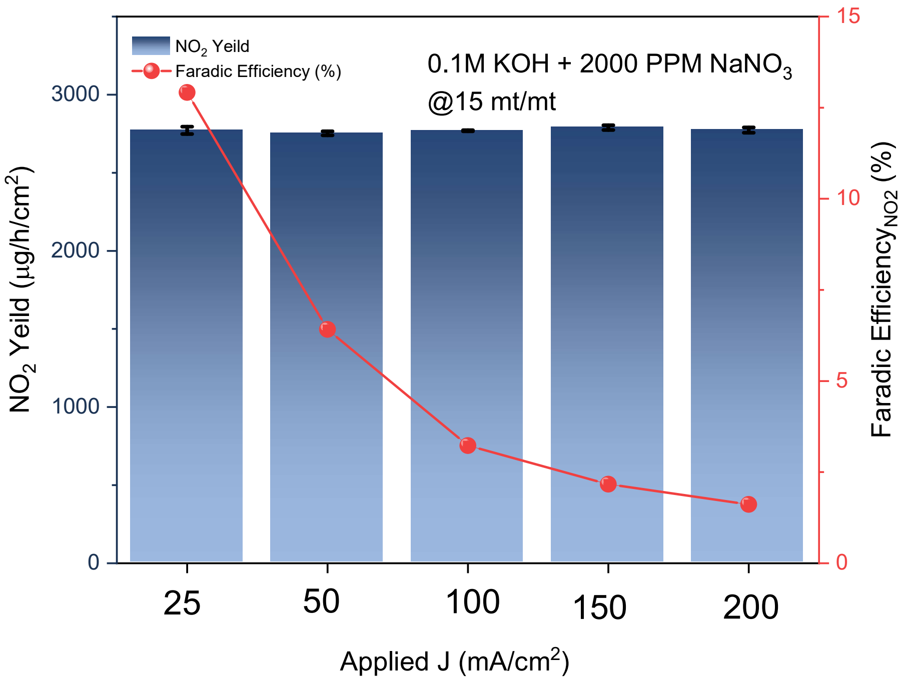


Figure S22: NO_2 quantification corresponding to Figure S21 and its Faradic efficiency.

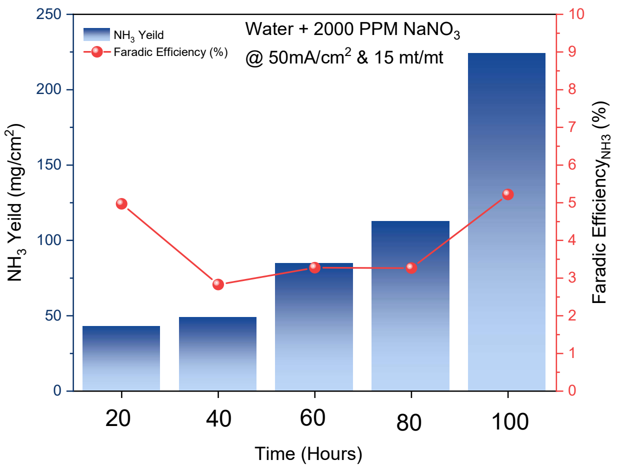


Figure S23: NO_2 quantification corresponding to Figure 3b and its Faradic efficiency.

Stacked Electrolyzer development:

A custom-made electrolyzer was built with two stacks, each having an active area of 25 cm². The end plates were custom cut using a CO_2 laser cutter from 8 mm thick acrylic sheets. Additionally, the back contact and liquid flow channels were created using nickel sheets cut with a sand jet cutter. A schematic illustration of the setup is given in image S24.

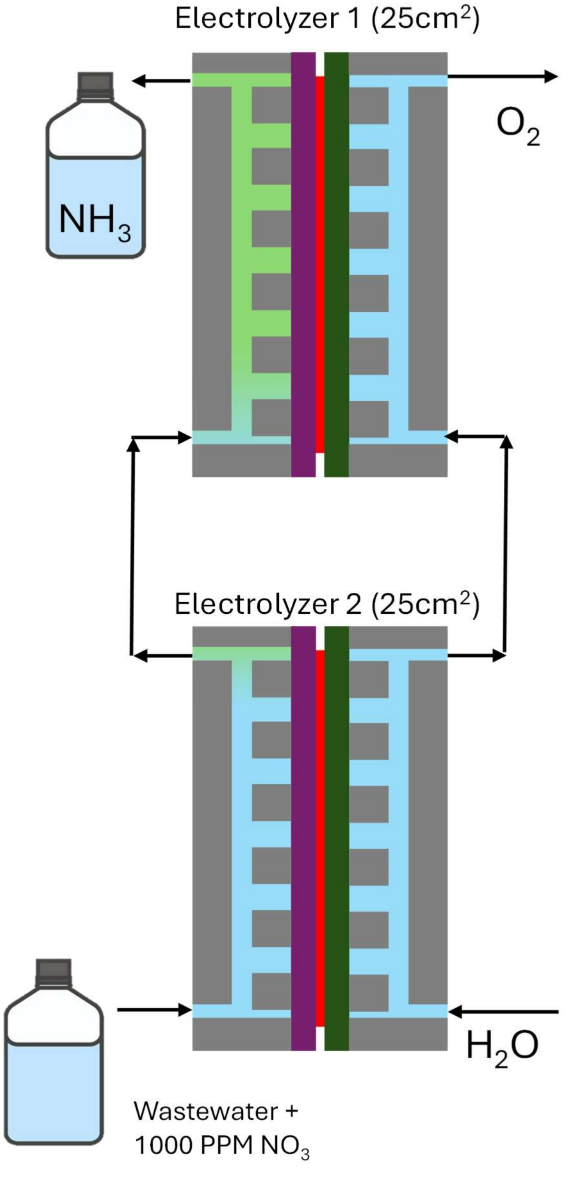


Figure S24: Stacked electrolyzer development and setup.

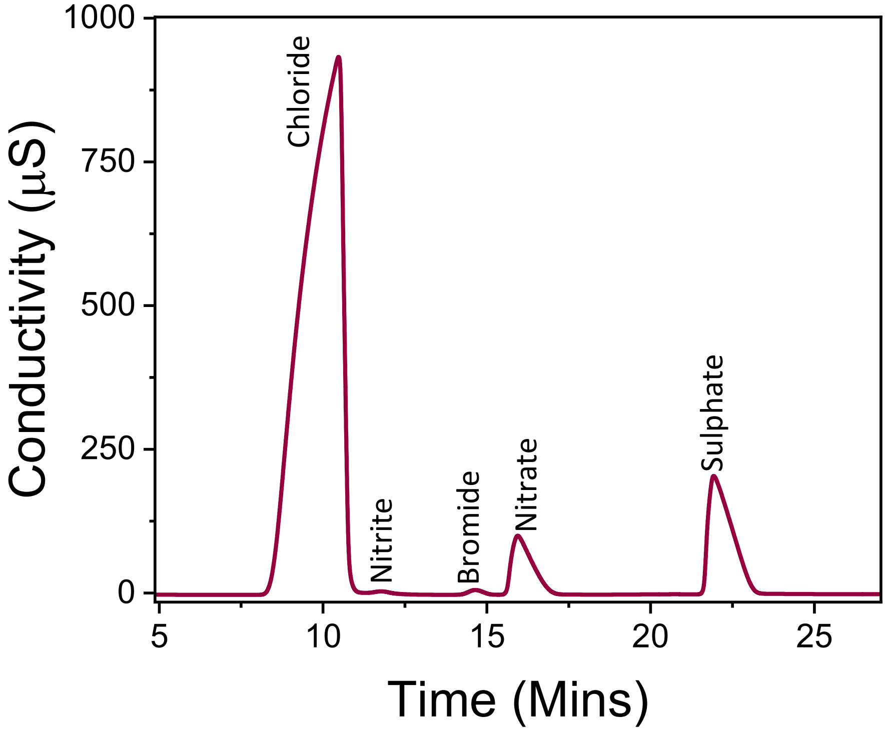


Figure S25: Ion chromatography results of real wastewater sample

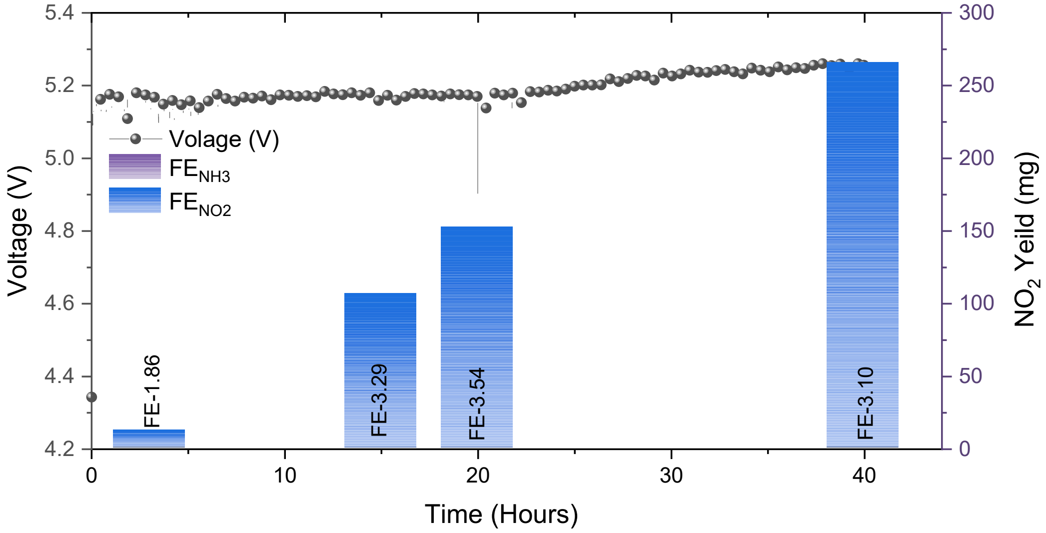


Figure S26: NO_2 quantification and its corresponding FE_{NO2} related to Figure 3c.

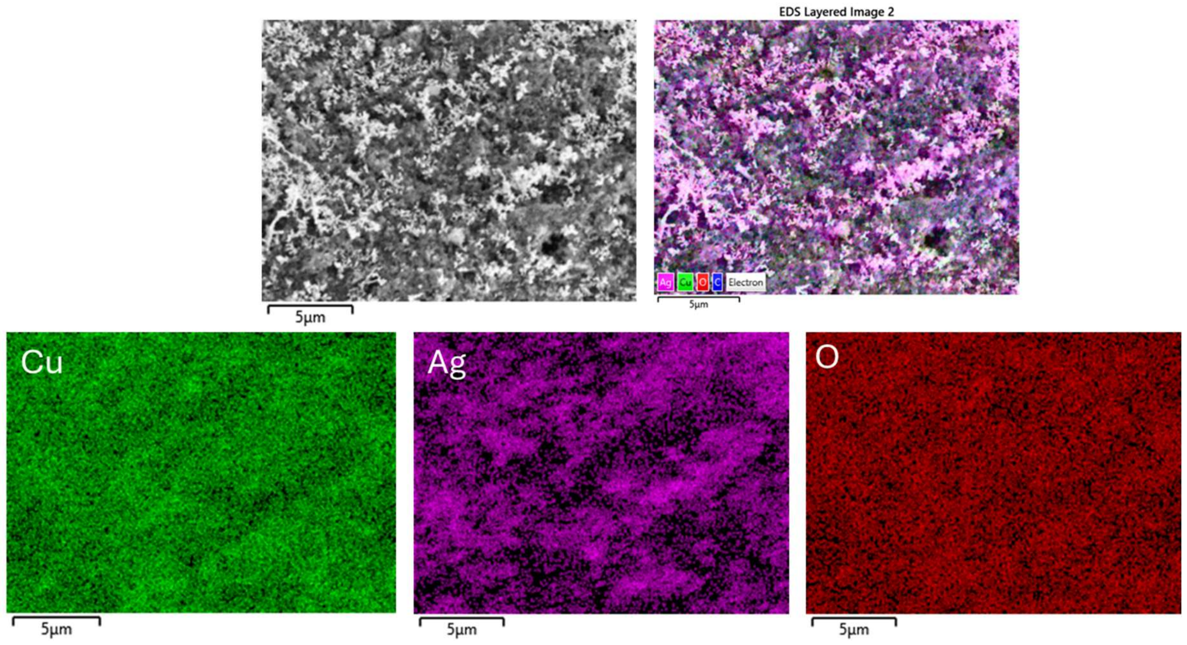


Figure S27: Post CP FESEM images and EDS mapping of CuO/AgO NPs catalyst.

Sample	Cu @ 217.89 nm	Cu @ 224.7 nm	Ag @ 243.78 nm	Ag @ 328.07nm
Standard - 0 PPM	61.04	99.26	7.64	27.17
Standard - 1 PPM	3299.83	7201.9	135.5	48323.18
Standard - 10 PPM	32157.48	70179.79	1279.18	473085.14
Standard - 25 PPM	79350.26	174338.96	3186.78	1151332.62
Standard - 100 PPM	309148.47	669123.29	12449.21	4172040.43
CuO/AgO after 100hrs	**173.79**	**342.89**	**8.6**	**414.07**

Table S1: ICP results of CuO/AgO.

Catalyst	***Electrolyte***	***Cell type***	***FE***	***Ref***
CuO/AgO	***Real industrial wastewater***	***Stacked electrolyzer***	***37 %***	***This work***
Cu-PTCDA	*PBS +* KNO_3	*H-Cell*	*85.9 %*	*5*
Fe_2O_3	*NaOH+*$NaNO_3$	*H-Cell*	*91.5 %*	*6*
Fe single atom catalyst	K_2SO_4 *+* KNO_3	*Flow cell*	*75 %*	*7*
CuP	*PBS +* $NaNO_2$	*H-Cell*	*62.9 %*	*8*
$CuO\text{-}Co_3O_4$	Na_2SO_4 *+* $NaNO_3$	*Electrolyzer*	*79.8%*	*9*

Table S2: Comparative analysis on the NO3RR performance with existing reports.

Techno-Economic analysis (TEA):

TEA includes the cost of the electrolyzer, the cost of the electricity, the maintenance cost, the balance of the plant cost, the water cost, and the ammonia extraction cost.

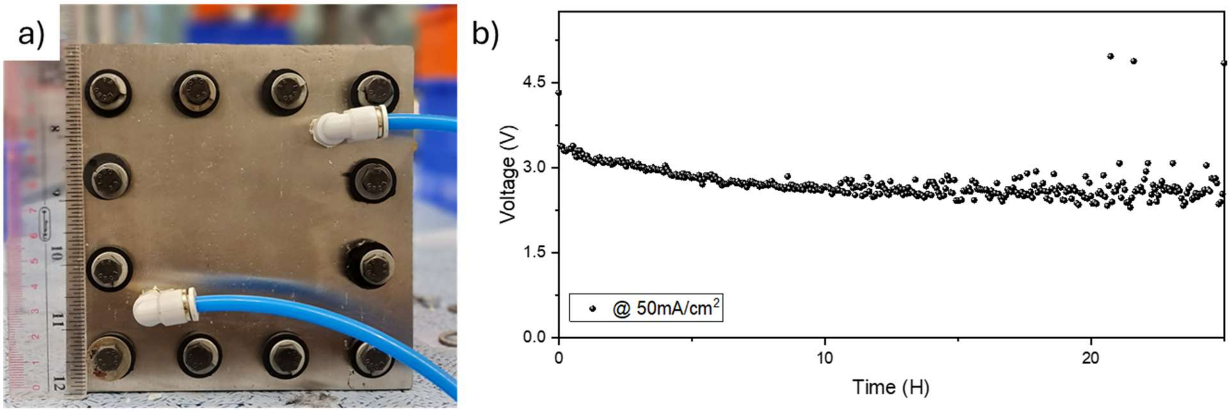


Figure S28: a) Digital image of 50cm^2 electrolyzer and b) CP at the applied current of 2.5 A (50 mA/cm^2) for the period of 25 hours at the NO3 concentration of 1000 PPM in industrial wastewater (average current is 2.73 V).

Electrolyzer cost:

The cost of the electrolyzer was calculated for the applied current density of 50 mA/cm^2 with FE_{NH3} of 32% (obtained from ammonia quantification of Figure S27) for the volume of 1000 kg/day for 350 days.

Power Requirement Calculation:

$$Total\ Current = Production\ volume\ \times\ Duration\ \times molecualr\ wegith\ of\ NH_3 \times\ no. of\ electron\ required\ for\ the\ reaciton\ \times\ F\ \times \frac{1}{FE_{NH3}}$$

$$= 1000000\frac{g}{day}\ \times \frac{day}{24*3600\ S} \times \frac{1}{17.031\frac{g}{mol}} \times 8e^- \times \frac{96485\ C}{mol} \times \frac{1}{0.32} = 1639252\ A$$

Total power required can be calculated using P = V×I,

$$Total\ power\ requirement = 2.73\ V \times\ 1639252\ A = 4.47\ MW$$

$$Total\ Electrolzyer\ area = \frac{1639252\ A}{0.05\ A/cm^2} = 3278\ m^2$$

Electrolyzer cost:

From the recent literature, the cost of a 1 m^2 electrolyzer was estimated to be \$4321.23 from literature.[11-13]

$$= \frac{\$4321.23}{m^2} \times\ 3278m^2 = \$\ 40.47/kg$$

Balance of plant cost:

Balance of plant cost was calculated as 25% of total electrolyzer cost, and it was estimated to be \$0.518/Kg$_{NH3}$

$$\text{BOP} = 40.47\ \frac{\$}{kg_{NH}} \times\ 25\% = \$\ 10.12/kg_{NH3}$$

Operational Expenditure

Electricity cost:

The cost of renewable electricity is ~\$0.03/kW, and it was estimated that \$0.9792 \$/kg$_{NH3}$ to be as follows.

$$=\ 4.47\ MW\ \times \frac{1000\ kW}{1\ MW} \times\ 24h\ \times \frac{\$0.03}{kW} \times \frac{1}{1000\ \frac{kg}{day}}$$

$$= 3.22\ \$/kg_{NH3}$$

Maintenance cost:

Maintenance cost was estimated as 2.5% of the total electrolyzer cost.

$$= \$40.47\ \times\ \frac{2.5\%}{Year}$$

$$= \$\ 1.01/kg_{NH}$$

Water cost was eliminated in this calculation since the system is entirely planned to run with industrial wastewater. Air Stripping cost is estimated with the same parameters mentioned in the previous literature and found to be \$0.138/kg$_{NH3}$. The overall cost of sustainable ammonia production from Industrial nitrate recovery approach is ~ \$ 55/kg.

Reference:

1. Sullivan, K. T.; Wu, C.; Piekiel, N. W.; Gaskell, K.; Zachariah, M. R. Synthesis and Reactivity of Nano-Ag2O as an Oxidizer for Energetic Systems Yielding Antimicrobial Products. *Combust. Flame* **2013**, *160* (2), 438–446. https://doi.org/10.1016/j.combustflame.2012.09.011.
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