

SUPPLEMENTARY INFORMATION

Electroreduction of Nitrates, Nitrites and Gaseous Nitrogen Oxides: A Potential Source of Ammonia in Dinitrogen Reduction (NRR) Studies

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EXPERIMENTAL METHODS

Materials

Bismuth(III) nitrate pentahydrate (99.99% trace metals basis), potassium sulphate (Ph. Eur.), sulphuric acid (Ph. Eur), sodium nitrite (Ph. Eur), sulphanilamide (Ph. Eur), N-1-naphthylethylenediamine dihydrochloride ($\geq 98\%$), vanadium (III) chloride (97%), Nafion dispersion in a mixture of lower aliphatic alcohols and water (5 wt.%) and Nafion 324 membrane were purchased from *Sigma-Aldrich*. Potassium nitrate (Ph. Eur), ethylene glycol (analysis grade) and ammonium chloride (analysis grade) were purchased from *Merck*. Copper metal was purchased from *Ajax Finechem*. Vulcan XC-72R carbon black support and 20 wt.% Au/Vulcan XC-72R (hereinafter Au/C; nominal average Au particle size ca 4 nm) were purchased from *Fuel Cell Store*. Nitric acid (analytical reagent grade), hydrochloric acid (37%) and ethanol (absolute) were purchased from *Univar*. Argon (ultra high purity grade, 99.999%) and dinitrogen (ultra high purity grade, 99.999%) were purchased from *BOC*. Glassy carbon electrode (3 mm diameter, MF-2012) was purchased from *BAS*. All solutions were prepared using high purity deionised water ($18.2\text{ M}\Omega\text{ cm}$ at $24 \pm 1\text{ }^{\circ}\text{C}$) from a *Sartorius Arium Comfort I* purification system equipped with a *SARTOPORE 2 150* filter; the same grade of water was used for all experimental procedures.

Synthesis of Bi powder

Air-saturated ethylene glycol (15 mL) was added to bismuth(III) nitrate pentahydrate (720 mg, 1.5 mmol) and the solid was dissolved by sonication (*Cole-Parmer* 08890-06 70 W ultrasonic bath) for 15 min in a closed glass vial; the resulting clear solution was transferred to a 25 mL Teflon-lined autoclave, which was placed into a furnace pre-heated to $180\text{ }^{\circ}\text{C}$ and kept at this temperature for 16 h. Upon cooling to ambient temperature naturally, the synthesised black powder was collected by centrifugation and washed with excess ethanol (ca 200 mL), dried under vacuum (ca 2 mbar) for 2 h and then immediately used for electrocatalytic tests.

Physical Characterisation

X-ray Diffraction. XRD analysis was performed using a *Bruker D8 Advance Eco* instrument with a Co K_{α} radiation source ($\lambda = 0.17903\text{ nm}$). The XRD patterns were recorded in a 2θ range between

15° and 100° with a step size of 0.02° and a time per step of 2 s. Powder samples were mildly ground with an agate mortar and pestle and pressed into a quartz slide support for analysis.

Transmission Electron Microscopy. TEM analysis was carried out using a *Tecnai T20* microscope equipped with a LaB₆ electron source operating at 200 kV. Prior to analysis, powder samples were dispersed in ethanol and then drop cast onto Cu grids coated with holey carbon films.

Electrochemical procedures

In order to avoid any contamination by ammonia and other N-containing sources, all components of the electrochemical and laboratory apparatus were copiously washed with water and kept in a large volume of water inside a preliminary cleaned and closed vessel before being used.

Electrode preparation. To prepare material inks for the deposition onto electrode surface, Bi powder (3 mg) and Vulcan XC-72R (10 mg) or Au/C (13 mg) were homogeneously dispersed in a mixture of 2 mL water, 0.7 mL ethanol and 0.3 mL Nafion dispersion (5 wt.% in a mixture of lower aliphatic alcohols and water) by sonication for 30 min. Further, 6 µL of the freshly prepared material ink was drop cast onto a surface of a glassy carbon electrode that was polished with an aqueous suspension of 0.05 µm Al₂O₃ (*Cypress Systems*) on a polishing cloth. Solvents were allowed to evaporate naturally under ambient conditions over 20 min. Metal loading on the electrode surface was approximately 90 and 70 µg cm⁻² for Bi and Au/C, respectively.

General electrochemical procedures. All electrochemical experiments were carried out with a gas-tight two compartment cell in a three-electrode configuration at room temperature (23 ± 2 °C) using a *BioLogic VMP* electrochemical workstation. As a working electrode, catalyst-modified glassy carbon was used; as an auxiliary electrode, a high-surface area Pt wire was used; Ag|AgCl|KCl_{sat.} (*CHI*) was used as a reference electrode. Potentials were recalculated to the reversible hydrogen electrode (RHE) scale using the Nernst equation: $E \text{ (V vs. RHE)} = E \text{ (V vs. Ag|AgCl|KCl}_{\text{sat.}}) + 0.197 \text{ V} + (0.059 \text{ V} \times \text{pH})$, where pH = 3.5 in all cases herein. pH of the electrolyte solutions was checked in the beginning and at the end of the electrochemical experiments (pH meter *Metrohm 744*) and it remained unchanged except the experiments with dissolved NO₂ gas (Figure S5); in the latter case, the potentials are reported vs. Ag|AgCl|KCl_{sat.} reference. To avoid mixing of the electrolyte solutions between the working and auxiliary compartments, a reinforced Nafion 324 membrane was used. Prior to use, the membrane was boiled in 5 wt.% H₂O₂ and 0.5 M H₂SO₄

solution for 1 h in each solution and then washed with water; no measurable amounts of ammonia were released by the membrane in any of the experiments, and no significant adsorption of NH_4^+ present at micromolar concentrations in 0.5 M K_2SO_4 solutions into the membrane occurred either. The initial volume of the electrolyte solution in both working and auxiliary compartments was 15 mL. The solution in the working chamber was continuously agitated using a Teflon-lined magnetic stirrer at 1200 rpm during all measurements.

Electrocatalytic experiments. Electrochemical measurements were carried out using aqueous 0.5 M K_2SO_4 electrolyte solutions without (for the NRR and control tests) or with intentionally added NO_x . Aliquots of the electrolyte solutions (0.50 mL) from the working electrode chamber were withdrawn for the detection of NH_3 after each voltammetric and chronoamperometric test.

To study the reduction of nitrate and nitrite, KNO_3 (1.5 mg, 15 μmol) or NaNO_2 (1.0 mg, 15 μmol) was dissolved in aqueous 0.5 M K_2SO_4 to make 1 mM KNO_3 or 1 mM NaNO_2 solutions, respectively.

Pre-saturation of the working electrolyte solutions with N_2 or Ar was provided by purging the gas through for 30 min with a flow rate of 20 mL min^{-1} prior to experiments. Prior to entering the electrochemical setup, gasses were passed through moisture- and O_2 -scavenging columns (*Agilent, BMT-2 for moisture and BOT-2 for O_2*) and then through saturators (25 mL of 0.05 M H_2SO_4 and then 25 mL of H_2O); as demonstrated in Figure S2, this was sufficient to exclude any adventitious NH_3 and/or NH_3 formation through the reduction of adventitious NO_x . For the NRR and nitrate/nitrite reduction tests, the required gas was also continuously purged through the solution during electrochemical measurements at a flow rate of 100 mL min^{-1} for the NRR tests (the flow was directed to hit the electrode ^{S1}) or 20 mL min^{-1} for the $\text{NO}_2^-/\text{NO}_3^-$ reduction (the gas inlet was located away from the working and reference electrodes, as in a normal electrochemical experiment).

The procedures for gas supply during the gaseous NO_x reduction studies were as follows. Due to the limited availability and very high price of pure NO and NO_2 , these gasses were synthesised herein via a reaction between copper metal and nitric acid. The reaction was carried out in a sealed triple-neck round bottom flask installed into the gas supply line prior to the electrochemical cell (Figure S4a). Before the experiment, Cu powder (1 or 0.03 mmol) was loaded into the flask, and the whole setup in Figure S4a was filled with Ar by flowing this gas through (5 mL min^{-1}) for at least 30 min. After stopping the Ar gas flow, 0.75 (for 1 mmol Cu) or 0.10 mL (for 0.03 mmol Cu) of 5.3 HNO_3 or

0.25 mL of 16 M HNO₃ (for 1 mmol Cu) was injected through a septum to produce either NO or NO₂ gas (Figure S4b-c).^{S2} The reaction rate was dependent on the HNO₃ concentration; specifically, complete consumption of Cu was achieved after ca 30 min for 5.3 M (NO is the dominant product) and after not more than 1 min for 16 M HNO₃ (NO₂ formation is preferred). Upon complete consumption of the metal powder, the NO_x gas was delivered to the working electrolyte solution by continuously flowing the Ar carrier gas at a rate of 5 mL min⁻¹ until electrochemical measurements were finished. Cyclic voltammetric analysis was performed after purging NO_x in Ar through the electrolyte solution for 30 min; chronoamperometric measurements were started as soon as NO_x in Ar gas reached the electrolyte solution. Concentration of dissolved NO_x was determined by quantification of NO₂⁻ and NO₃⁻ produced through the oxidation of the nitrogen oxides by O₂ and/or disproportionation of NO₂. Aliquots (0.50 mL) for this analysis were withdrawn from the electrolyte solution after 30 min of purging the NO_x in Ar gas mixture with no electrodes present in the cell; dissolved NO_x were oxidised by either air oxygen or 100% O₂ in a sealed vial that was intensively shaken for 5 min (Vortex 3, IKA) before being analysed; no difference between the results obtained with air or O₂ were found.

NH₃ quantification. The Berthelot spectrophotometric method was used for the determination of the amount of NH₃ produced during experiments in the electrolyte solution. In a typical procedure, 500 µL of a sample withdrawn from the working compartment was added to a 1.5 mL Axygen microtube and then mixed with 400 µL of the solution of 5 wt.% salicylic acid and 5 wt.% trisodium citrate in 1 M NaOH. Further, 100 µL of 0.05 M NaClO_(aq.) and 30 µL of 1 wt.% sodium nitroferricyanide in water were added to the tube. The resulting solution was incubated in the dark for 2 h at ambient temperature. Finally, the derivatised solution was transferred into a polystyrol/polystyrene 10 mm cuvette (Sarstedt), and an absorption spectrum was recorded in a 500–1000 nm range using a Cary UV–vis spectrophotometer. The absorption (*A*) vs. ammonium concentration ([NH₄⁺]) calibration curves were constructed using standard NH₄Cl solutions in 0.5 M K₂SO₄ (measured pH 3.5). The calibration plot was nearly perfectly linear (*R*² = 1.00) yielding relationships $A = 0.011 [\text{NH}_4^+] (\mu\text{M}) + 0.028$.

Presence of NO₂, but not NO, in the analysed solutions caused significant interference with the Berthelot derivatisation procedure. This was demonstrated by undertaking blank control

experiments where NO in Ar or NO₂ in Ar gas mixtures were purged through 0.5 M K₂SO₄ with no electrodes present in the cell (Figure S6). Additional absorption produced by NO₂ (Figure S6b) was subtracted from the absorption measured during the electrocatalytic NO₂ reduction tests.

NO₂⁻/NO₃⁻ quantification. The Greiss spectrophotometric method was used for the determination of the concentrations of NO₂⁻ and NO₃⁻ formed upon oxidation/disproportionation of dissolved gaseous NO_x. There are two Griess reagents for NO₂⁻ detection: diazotising reagent and coupling reagent. Diazotising reagent was obtained by adding 1 mL concentrated HCl (36%) and 0.1 g sulphanilamide (SULF) in volumetric flask and filled up to 10 mL with H₂O. Coupling reagent was prepared by dissolving 0.01 g of N-1-naphthylethylenediamine dihydrochloride (NED) in 10 mL H₂O. For quantifying the amount of NO₃⁻, 0.02 wt.% vanadium(III) chloride in 6 M HCl solution was added on top of the solution used for the NO₂⁻ detection to reduce any NO₃⁻ in the solution to NO₂⁻, which is then reacted with Griess reagents. All Griess reagents and vanadium(III) chloride solution were kept in refrigerator (ca 4 °C) in the dark. For the detection of NO₂⁻, 0.50 mL of a sample (diluted as needed) withdrawn from the working electrode compartment was added to a 1.5 mL Axygen microtube and then mixed with 0.50 mL of 0.1 M HCl. Further, 25 µL SULF and 25 µL NED were added to the tube resulting in pink colouration of the solution, which was incubated for 20 min at ambient temperature and then used for the UV-Vis analysis immediately. For the NO₃⁻ detection, 50 µL of 0.02 wt.% vanadium(III) chloride in 6 M HCl was added to the solution used for the quantification of NO₂⁻, the mixture was incubated at 60 °C on a water bath for 25 min and cooled down to the ambient temperature. Absorption spectra of the derivatised solutions were recorded in a 400–800 nm range using polystyrol/polystyrene 10 mm cuvettes and a Cary UV-vis spectrophotometer. The absorption (*A*) vs. nitrite concentration ([NO₂⁻]) calibration curves were constructed using standard NaNO₂ and KNO₃ solutions in 0.5 M K₂SO₄ (measured pH 3.5). The calibration plots were nearly perfectly linear (*R*² = 0.99) yielding relationships *A* = 0.016 [NO₂⁻] (µM) + 0.019 for NO₂⁻ and *A* = 0.014 [NO₂⁻] (µM) + 0.020 (*R*² = 0.99) for total NO₂⁻+NO₃⁻.

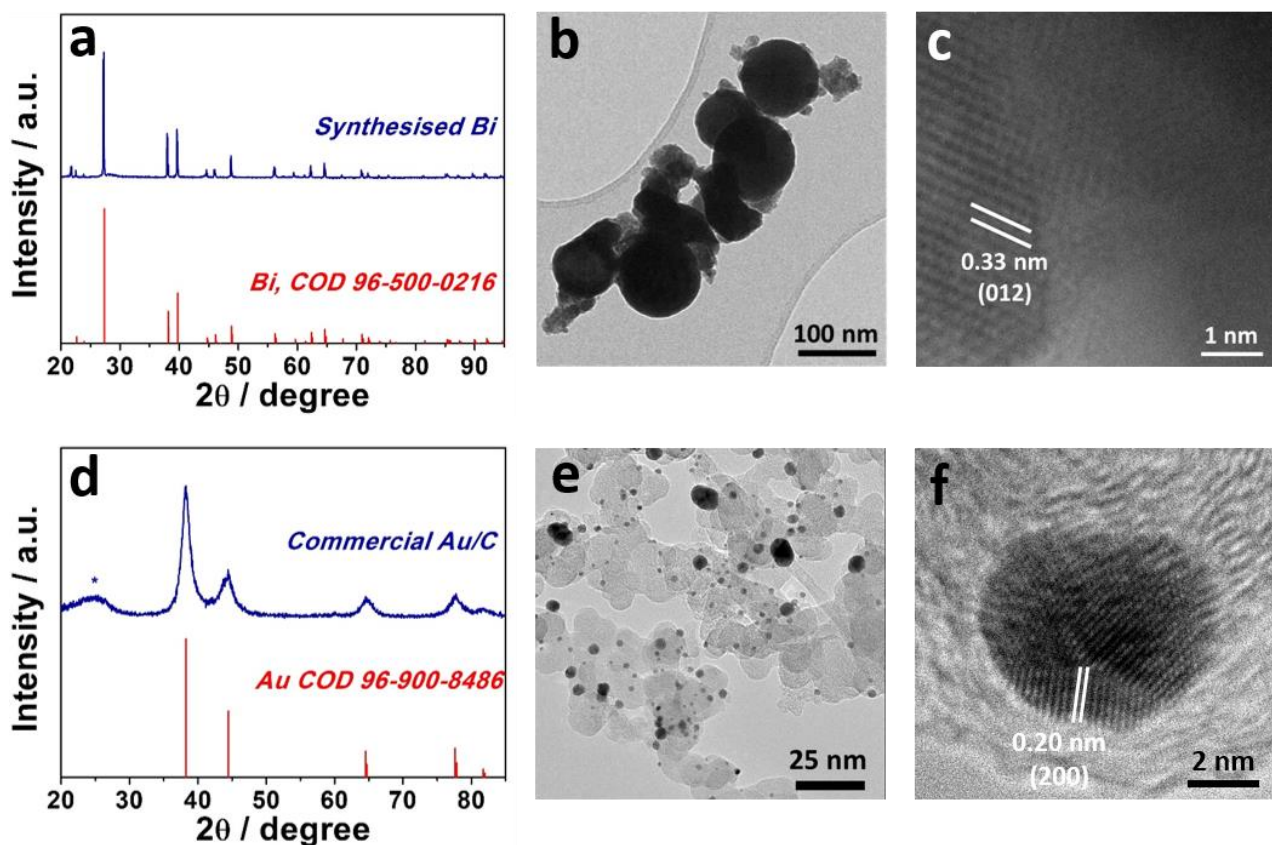


Figure S1. Characterisation of (a-c) bismuth powder and (d-f) Au/C. (a, d) X-ray diffraction patterns (*blue*) along with tabulated positions and relative intensities of reflections for metallic Bi and Au (*red*) (* denotes a 002 peak from the Vulcan XC72R carbon support). (b, e) Lower and (c, f) higher magnification transmission electron micrographs. According to the X-ray diffraction and transmission electron microscopic analysis, the synthesised bismuth powder contained crystallites of an average size $d_{\text{XRD}} \approx 66$ nm, aggregated into particles with a size ranging from 50 to 250 nm. For Au/C, d_{XRD} was 3.9 nm and the average linear particle size was 4 ± 2 nm.

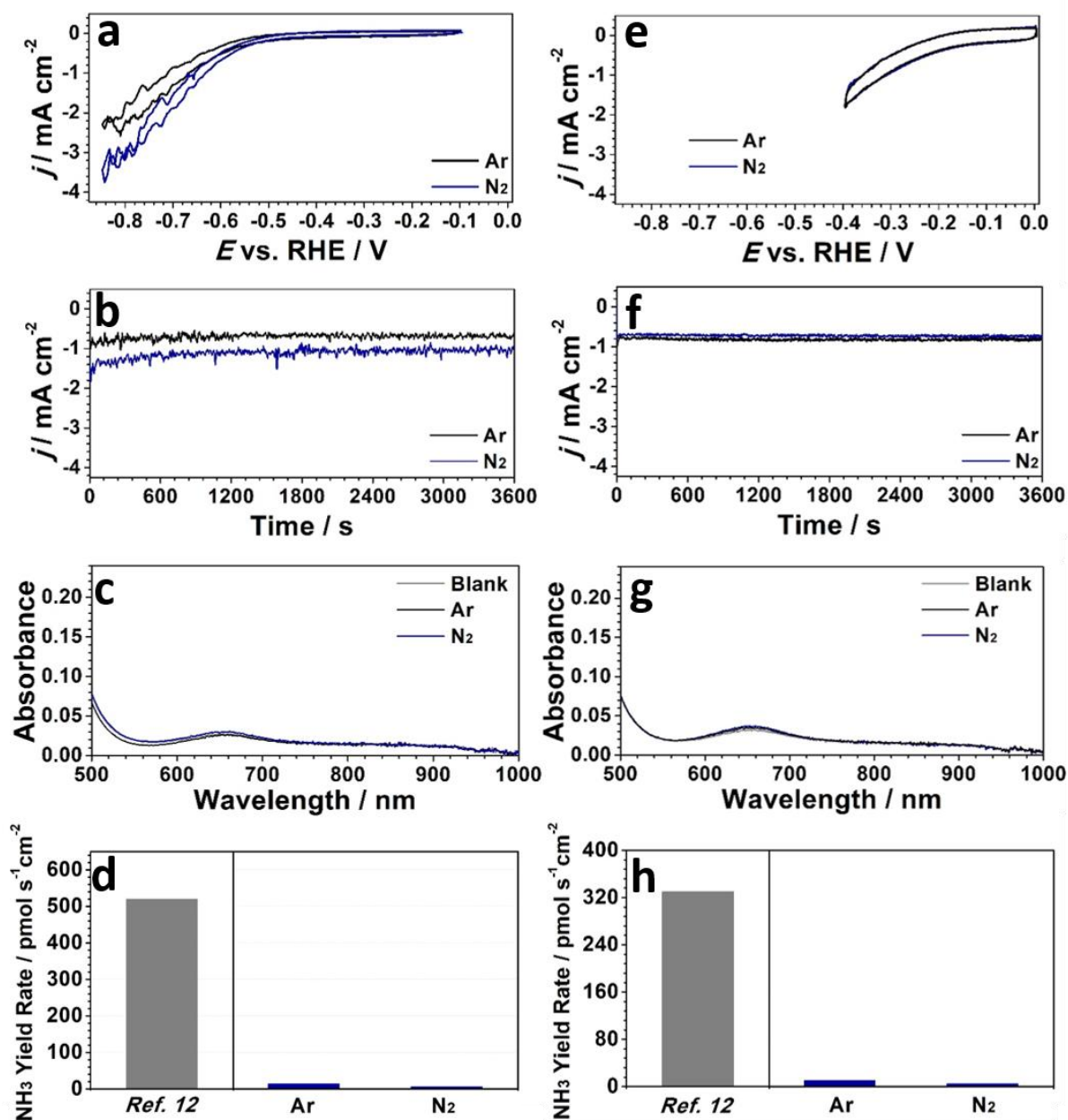


Figure S2. Tests of the NRR electrocatalytic activity of (a-d) bismuth powder and (e-h) Au/C in 0.5 M K₂SO₄ (pH 3.5). (a, e) Cyclic voltammograms at a scan rate of (a) 0.01 and (e) 0.05 V s⁻¹, and (b, f) chronoamperograms at (b) -0.65 V and (f) -0.30 V vs. RHE in Ar- (black) and N₂-saturated (blue) electrolyte solutions. (c, g) Spectrophotometric detection of ammonia using Berthelot method after chronoamperometric tests shown in panels b and f compared to the blank untreated solution (grey). (d, h) Comparison of the NH₃ formation rate reported in the literature^{S3} (Ref.¹² in the main text) and as measured in our laboratory.

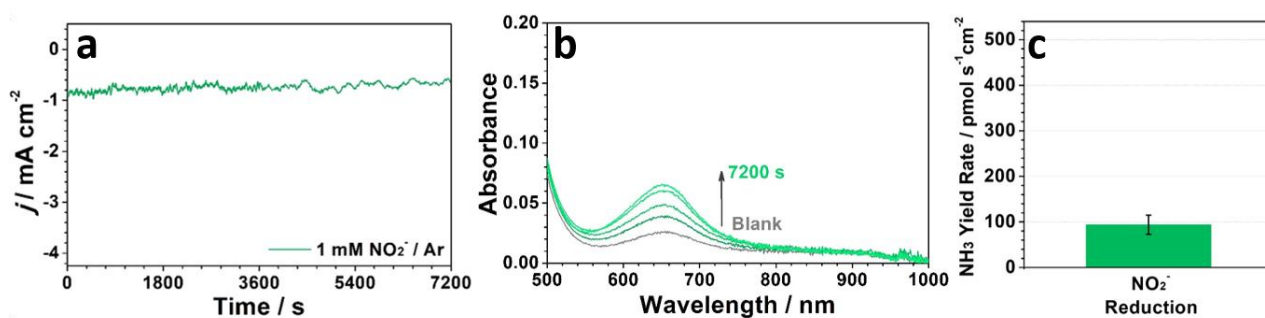


Figure S3. Tests of the electrocatalytic activity of bismuth powder for the reduction of 1 mM NaNO_2 to ammonia in Ar-saturated 0.5 M K_2SO_4 . (a) Chronoamperogram at -0.65 V vs. RHE. (b) The Berthelot spectrophotometric analysis of ammonia produced after 1800, 3600, 5400 and 7200 s (*light green*) compared to the control blank spectrum (*grey*). (c) Average \pm one standard deviation of the NH_3 formation rate measured over 7200 s experiments with three independently prepared bismuth samples.

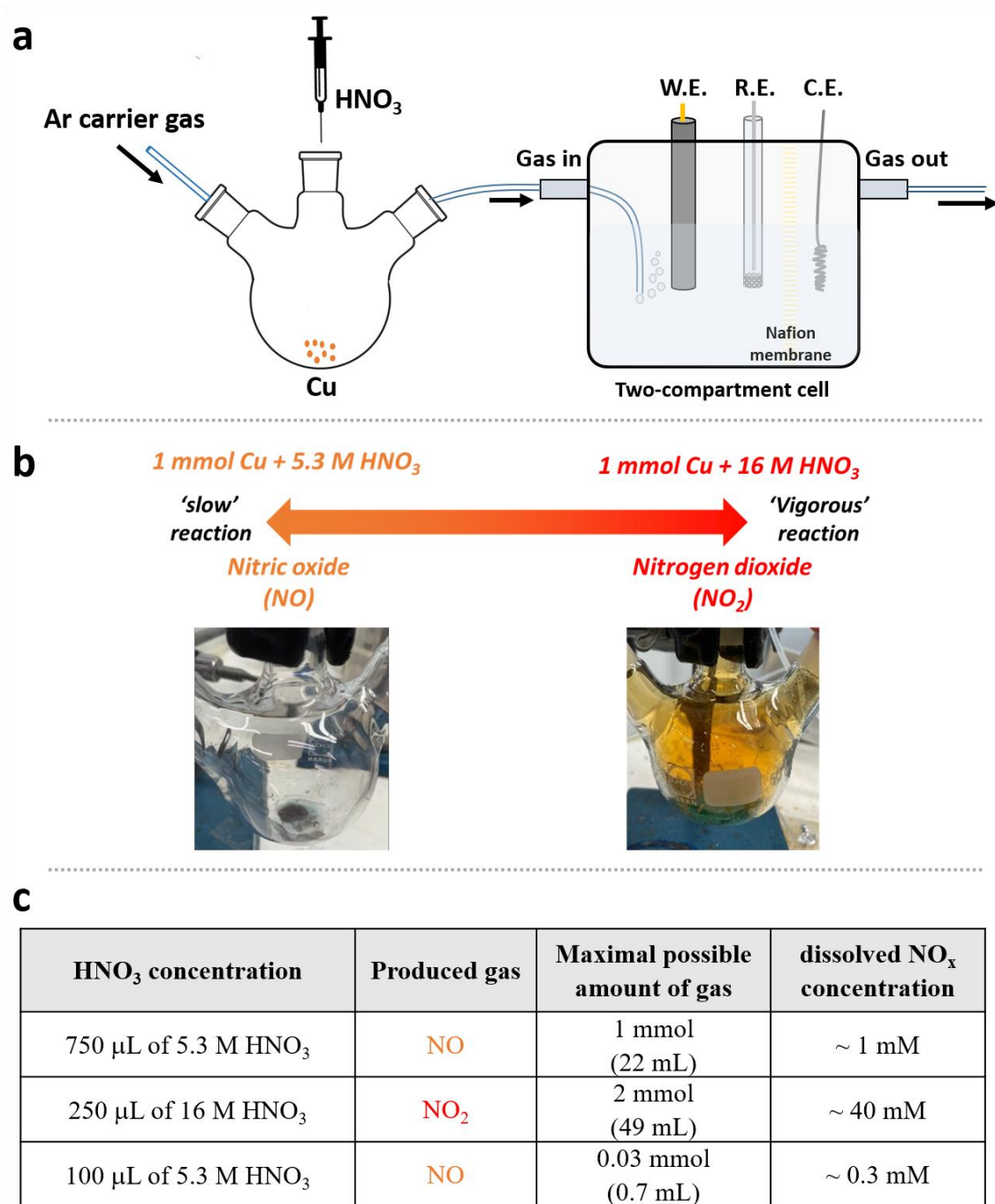


Figure S4. Preparation of gaseous NO_x. (a) Schematic diagram of the experimental setup. (b) Photographs of NO_x gasses produced with different concentrations of HNO₃. (c) Summary of the employed synthesis conditions and corresponding gaseous NO_x products.

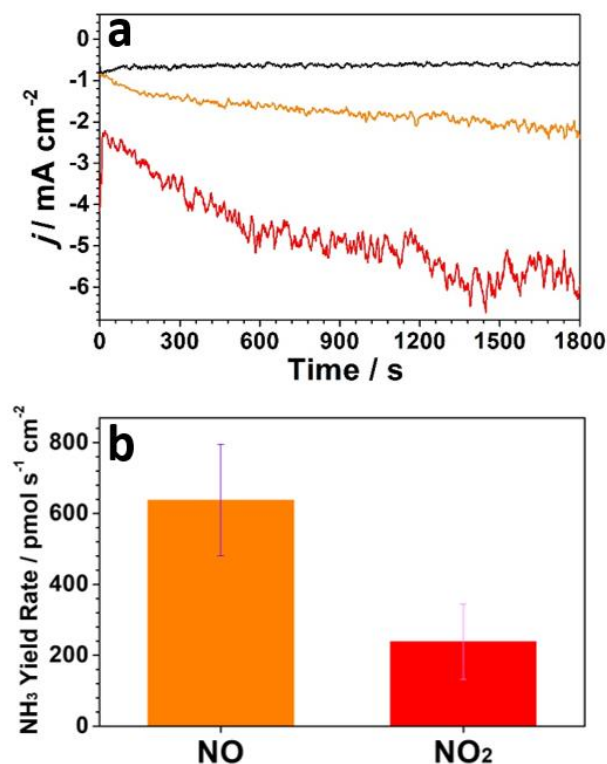


Figure S5. Electroreduction of gaseous NO_x synthesised under different conditions using Bi-modified glassy carbon electrode and 0.5 M K₂SO₄ aqueous electrolyte solution (initial pH 3.5). NO_x were synthesised under conditions favouring the formation of NO (*orange*) and NO₂ (*red*); data obtained in pure Ar flow are shown as *black* curve. For the NO reduction, the initial pH of 3.5 was maintained throughout the experiments; however, this was not the case for the tests with NO₂, where significant acidification to pH 2.5 occurred, most probably due to the disproportionation of the dissolved gas to HNO₂ and HNO₃. (a) Chronoamperograms at -1.05 V vs. Ag|AgCl|KCl_{sat}. (corresponding to -0.65 V vs. RHE at pH 3.5). (b) NH₃ formation rates presented as an average \pm one standard deviation for tests with three independent Bi samples; note that the rate for NO₂ is corrected to account for the interference of this gas with the Berthelot method (Figure S6).

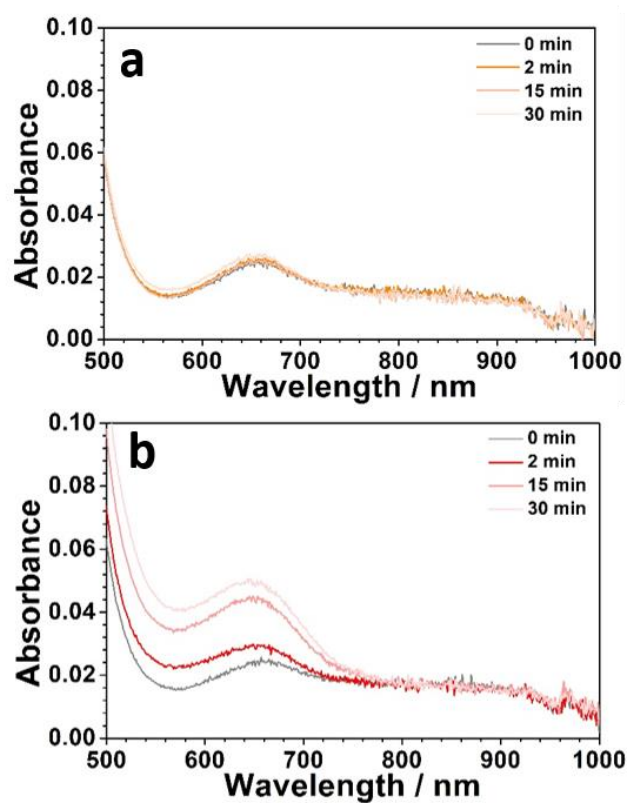


Figure S6. Spectrophotometric Berthelot analysis of 0.5 M K₂SO₄ (initial pH 3.5) solutions purged with (a) NO or (b) NO₂ in Ar at 5 ml min⁻¹ for 0 (grey), 2, 15 and 30 min (coloured curves).

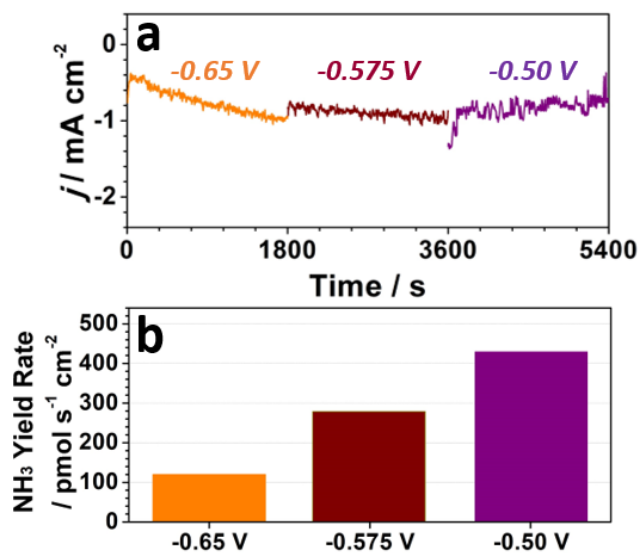


Figure S7. Electroreduction of a lower amount of gaseous NO dissolved in 0.5 M K_2SO_4 aqueous electrolyte solution (pH 3.5) using a Bi-modified glassy carbon electrode. (a) Consecutive chronoamperograms at -0.65 (orange), -0.575 (wine) and -0.50 V vs. RHE (purple). (b) Comparison of the NH_3 formation rates at different potentials.

SUPPLEMENTARY REFERENCES

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