Supplementary Information (SI) for Dalton Transactions.

Supporting Information

Synergistic $CoFe_2O_4$ Spinel–Cobalt Phthalocyanine–Carbon Nanotube Hybrid Catalyst for Highly Selective Electrochemical Nitrate-to-Ammonia Conversion

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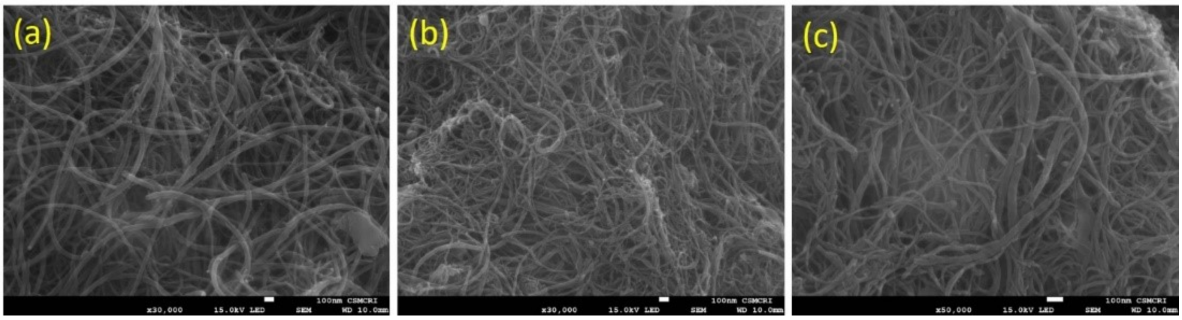

Figure S1. FESEM images of the different $CoFe_2O_4$/CoPc/CNT samples prepared by varying ($Co(NO_3)_2 \cdot 6H_2O$: $FeSO_4 \cdot 7H_2O$ (a) Co:Fe = 1:1, (b) Co:Fe = 1:0.5 and (c) Co:Fe = 1:0.25 keeping other reaction parameters constant.

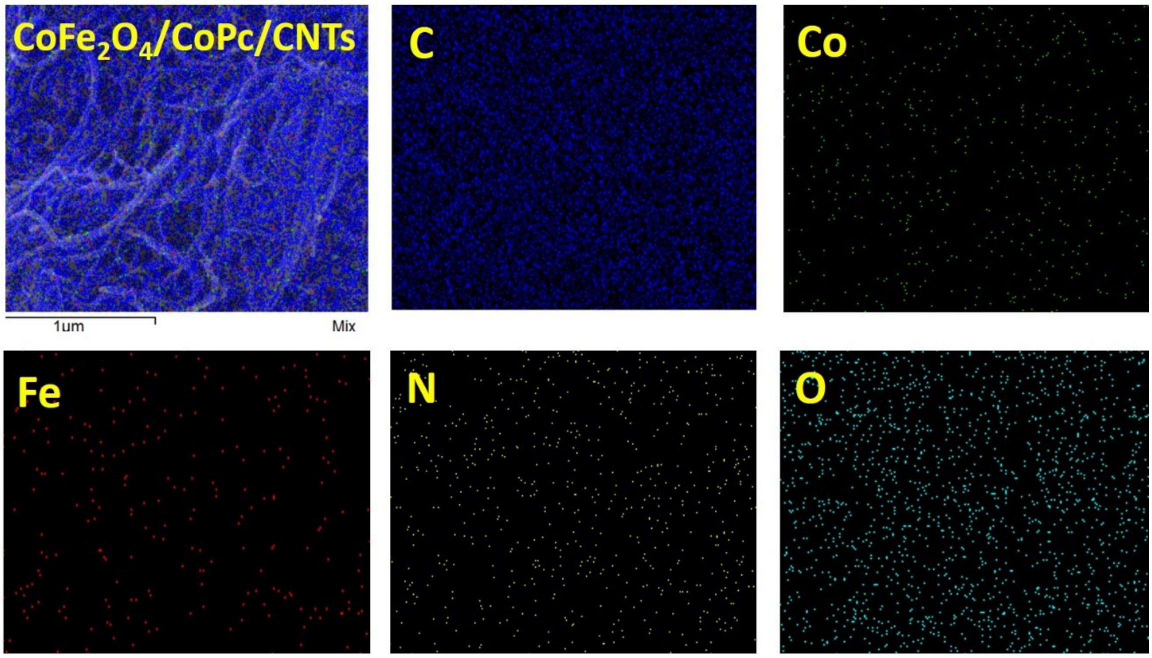

Figure S2. Elemental mappings of the CoFe$_2$O$_4$/CoPc/CNT samples prepared by using 1 mmole (Co(NO$_3$)$_2$·6H$_2$O and 0.125 mmole FeSO$_4$·7H$_2$O keeping other reaction parameters constant. Insets display the overlapped elements or the individual element as mentioned.

Table S1: Table of weight loss (%) during TGA for the different samples

(Molar ratio)	Initial Weight loss (%)	Weight loss due of CoPc at first segment (%)	Weight loss due of CoPc at Second segment (%)	Weight loss due to CoPc (%)
Co:Fe=1:0.125	4.7	7.5	4.4	12.48
Co:Fe=1:0.25	2.3	5.7	3.3	9.21
Co:Fe=1:0.5	1.9	2.7	5.4	8.26
Co:Fe=1:1	10.4	12.4	2.9	17.1

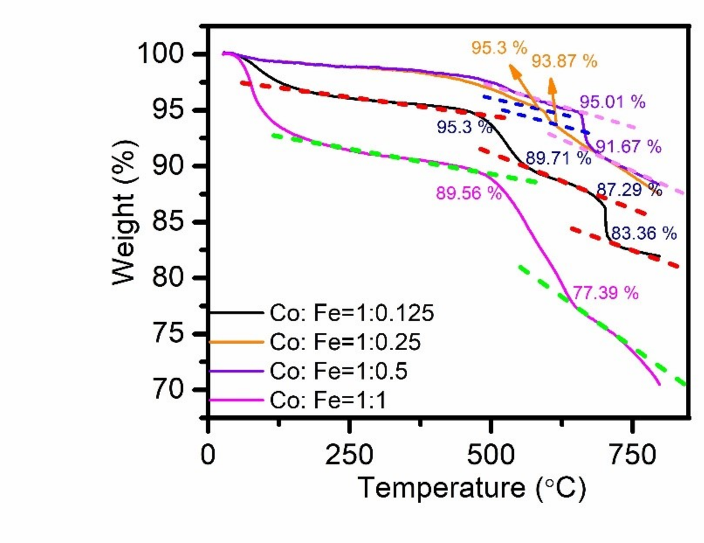

Figure S3. TGA plots of the catalyst, $CoFe_2O_4$/CoPc/CNT synthesised using different molar ratio (Co:Fe=1:1, 1:0.5, 1:0.25 and 1:0.125)

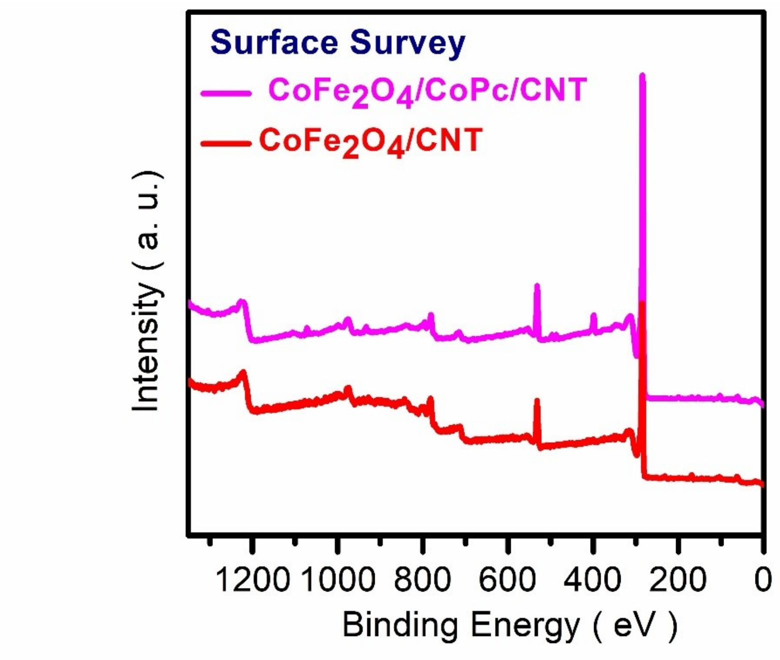

Figure S4. XPS survey spectrum of $CoFe_2O_4$/CoPc/CNT and $CoFe_2O_4$/CNT synthesized using 1 mmole $Co(NO_3)_2 \cdot 6H_2O$ and 0.125 mmole $FeSO_4 \cdot 7H_2O$ with and without H_2Pc keeping other reaction parameters fixed.

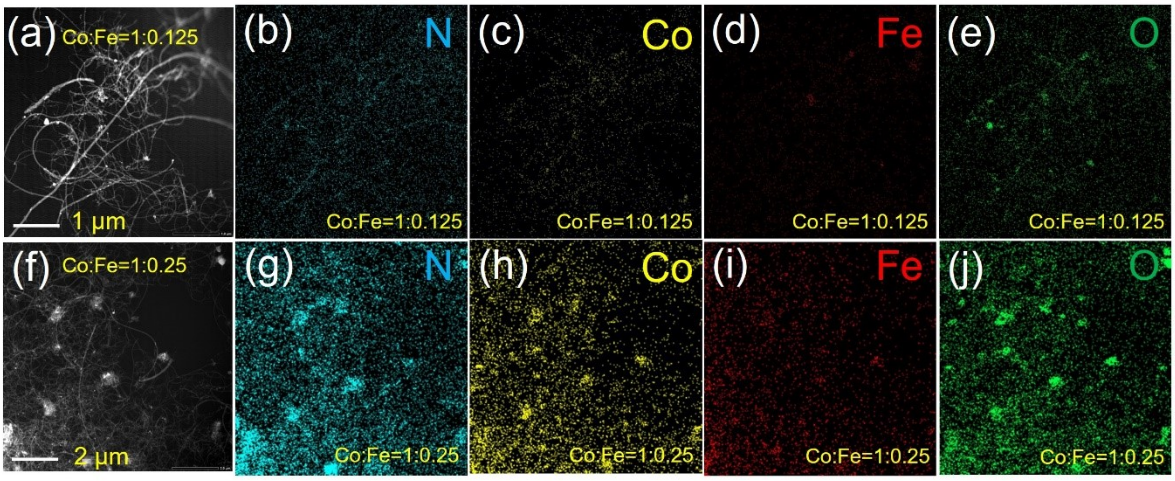

Figure S5. STEM image and corresponding EDS elemental mapping of different elemenets obtained from samples $CoFe_2O_4$/CoPc/CNT synthesized using Co:Fe = 1:0.125 and Co:Fe = 1:0.25, respectively.

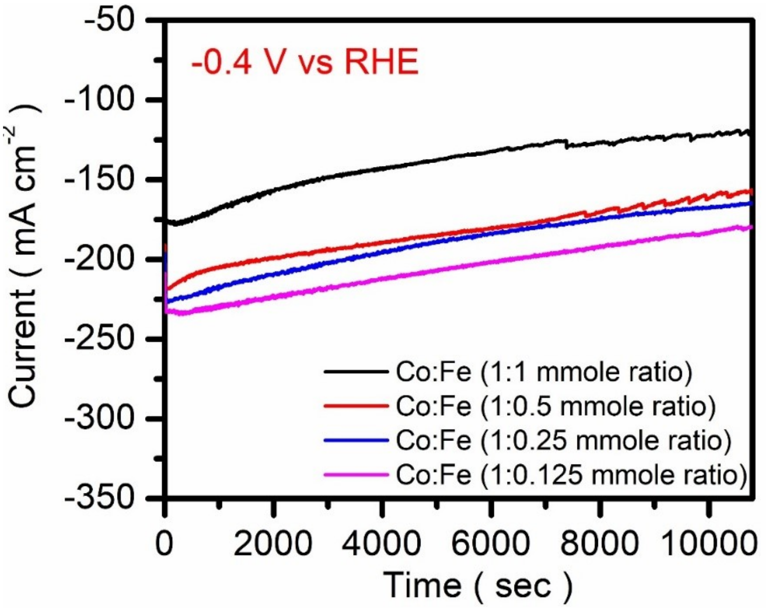

Figure S6. Chronoamperometry plots of the different $CoFe_2O_4$/CoPc/CNT samples prepared by varying ($Co(NO_3)_2 \cdot 6H_2O$ (1 mmole): $FeSO_4 \cdot 7H_2O$ (1 to 0.125 mmole) mole ratio as mentioned keeping other reaction parameters constant) at -0.4 V vs RHE for 3 h.

Table S2: Table of the Rs, Rp and CPE of different samples synthesised using different molar ratio (Co:Fe=1:1, 1:0.5, 1:0.25 and 1:0.125)

(Molar ratio)	Rs (Ω)	Rp (Ω)	CPE (Ω)
Co:Fe=1:1	22.8	23.1	12.2
Co:Fe=1:0.5	19.6	9.78	8.69
Co:Fe=1:0.25	19.3	7.27	6.38
Co:Fe=1:0.125	14.1	7.16	3.24

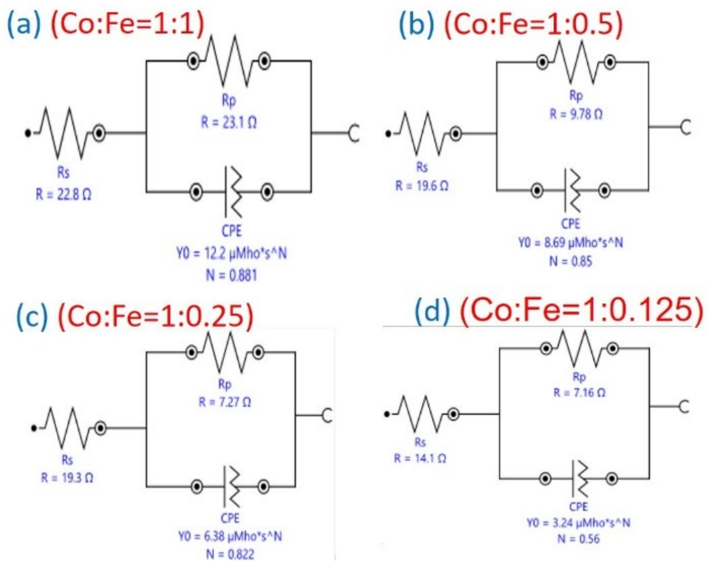

Figure S7. (a-d) Equivalent Circuit diagram of the catalyst, $CoFe_2O_4$/CoPc/CNT synthesised using the molar ratio Co:Fe=1:1, 1:0.5, 1:0.25 and 1:0.125.

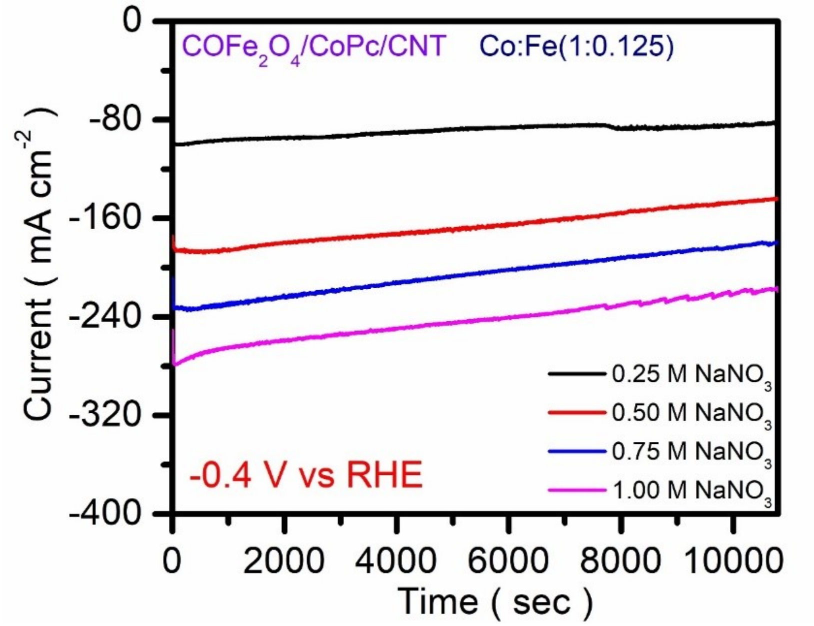

Figure S8. Chronoamperometry plots of the optimized $CoFe_2O_4$/CoPc/CNT catalyst variation performed using various $NaNO_3$ concentration at -0.4 V vs RHE for 3 h.

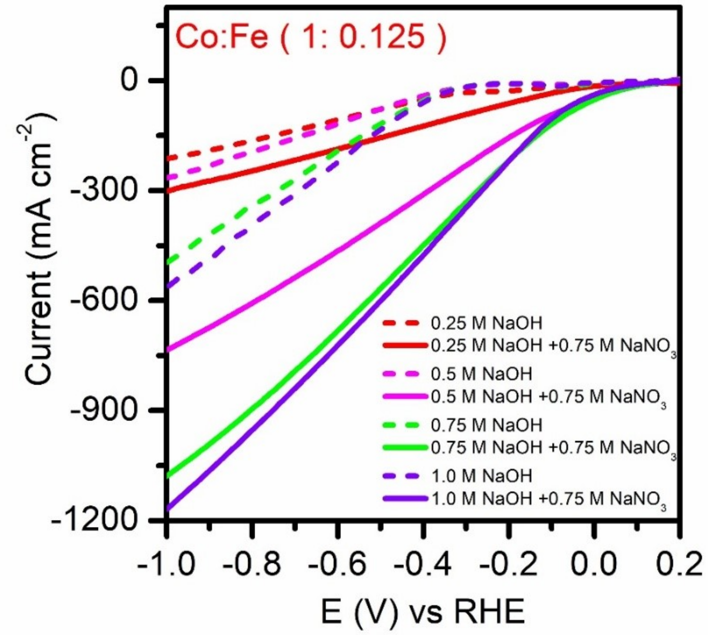

Figure S9. LSVs plots of the optimized catalyst, $CoFe_2O_4$/CoPc/CNT with molar ratio (Co:Fe=1:0.125) in different electrolyte concentration (0.25 M , 0.5 M, 0.75 M and 1.0 M) NaOH.

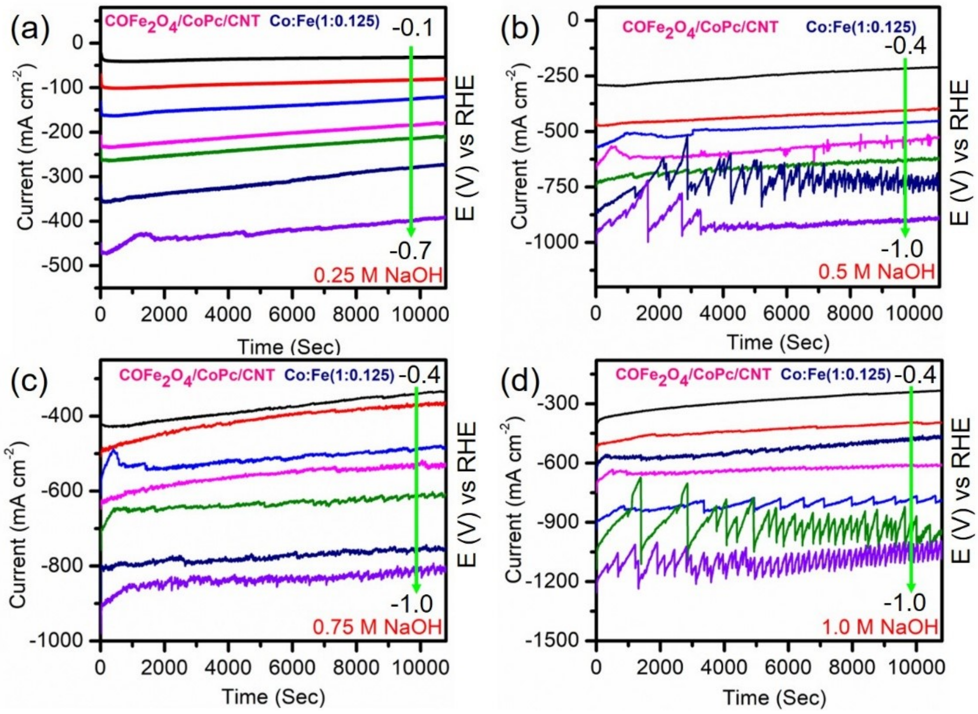

Figure S10. (a-d) Chronoamperometry plots of the optimized $CoFe_2O_4$/CoPc/CNT catalyst at different cathodic potential (V vs RHE) by varying the electrolyte concentration (0.25 M, 0.5 M, 0.75 M and 1.0 M) NaOH.

Detection of NH_3

To quantify NH_3 produced during the electrochemical nitrate reduction, the electrolyte collected after chronoamperometric measurements was diluted 20-fold. The indophenol blue method was employed for NH_3 determination. Specifically, 1 mL of the diluted electrolyte was mixed with 17 mL of distilled water, 0.5 mL of phenolic solution (5% phenol in ethanol), 0.5 mL of 0.1 M sodium nitroprusside [$Na_2[Fe(CN)_5NO]$], and 1 mL of NaClO solution (prepared using a 4:1 molar ratio of alkaline solution to NaClO). The mixture was kept in the dark for 30 minutes to allow the formation of an intense blue color. The resulting solution was further diluted 10-fold, and its absorbance was recorded at 655 nm. Calibration was performed with standard NH_4Cl solutions as shown in Figure S6, which showed good linearity. The absorbance at 655 nm was then used to quantify the NH_3 concentration in the electrolyte after chronoamperometric studies.

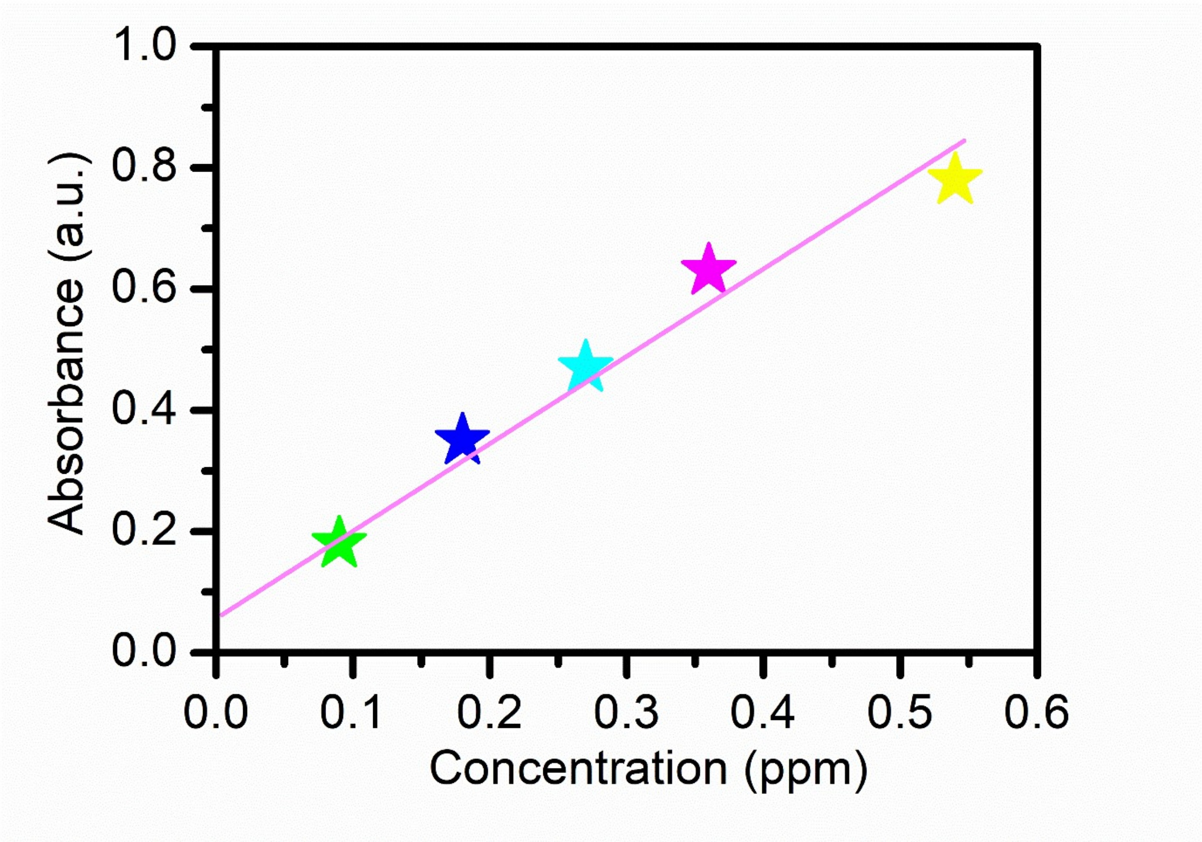

Figure S11. Linear relationship of absorbance of the Indo-phenol complex with NH_3 concentration at 655 nm.

Determination of NO_2^-

To quantify nitrite (NO_2^-) as a by-product during the electrochemical nitrate reduction, the electrolyte collected after chronoamperometric measurements was diluted 50-fold. Nitrite concentration was determined using the Griess test combined with UV–Vis spectroscopy. The Griess reagent was prepared by dissolving 0.1 g of N-(1-naphthyl)ethylenediamine dihydrochloride, 1.0 g of sulfanilamide, and 2.94 mL of H_3PO_4 in 50 mL of deionized water. For the measurement, 1 mL of the diluted electrolyte was mixed with 1 mL of Griess reagent and 2 mL of deionized water at room temperature, and the mixture was allowed to stand for 20 minutes to develop a pink color. The absorbance was recorded at 540 nm and compared with reference standards to determine the nitrite concentration. Calibration plot is shown in Figure S7.

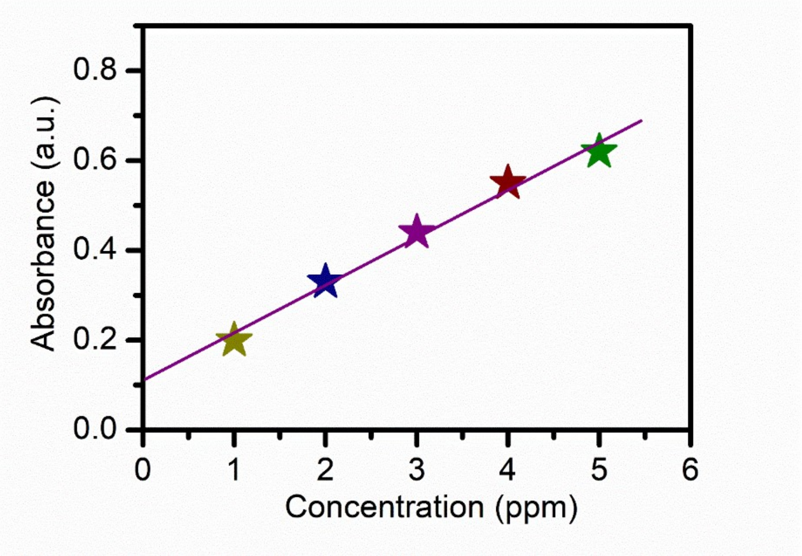

Figure S12. Linear relationship of absorbance of the azo dye complex with nitrite concentration at 540 nm.

Calculation of the FE for NH_3

$$Faradaic\ Efficiency\ \% = \frac{Ammonia\ produced\ per\ total\ charge\ passed}{Total\ charge\ passed} \text{x}100\%$$

$$Faradaic\ Efficiency\ \% = (8 \times [NH_3] \times V \times N_A) \times 100\ \% / (M_{NH3} \times A \times t \times C)$$

$$\text{Yield of } NH_3 = (8 \times [NH_3]) \times V / (M_{NH3}).$$

Where, $[NH_3]$ is concentration of ammonia, V is volume of electrolyte solution, N_A is Avogadro number, M_{NH3} is malar mass of ammonia, A is current, t is total time of electrolysis and C is coulomb.

Calculation of FE for Nitrite

$$Faradaic\ Efficiency\ \% = \frac{Nitrite\ produced\ per\ total\ charge\ passed}{Total\ charge\ passed} \text{x}100\%$$

$$Faradaic\ Efficiency\ \% = (2 \times [NO_2^-] \times V \times N_A) \times 100\ \% / (M_{NH3} \times A \times t \times C)$$

$$\text{Yield of } NO_2^- = (2 \times [NO_2^-] \times V) / (M_{NaNO2}).$$

Where $[NO_2^-]$ is the concentration of nitrite