

Supporting information for

Electrocatalytic Reduction of Nitrate by *in-situ*
Generated Cobalt Nanoparticles

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General considerations

All anaerobic experiments, including non-aqueous electrochemical measurements, were performed under an argon environment using standard Schlenk techniques. UV-Visible spectra were recorded using an Agilent Cary 60 UV-Visible spectrometer. Mass spectra were recorded using positive electrospray ionization on a Thermo Electron Corp MAT-95XP spectrometer. NMR spectra were obtained in various deuterated solvents at 25 °C on a Varian Inova-400 spectrometer (^1H : 400.11 MHz). Proton chemical shifts are reported in ppm *versus* solvent protic impurity and referenced to SiMe_4 . Solution pH was measured using a Mettler Toledo pH meter at 25 °C. Deionized water was used for all aqueous experiment or measurements. Ammonia, hydroxylamine, and nitrite were analyzed using literature procedures.¹⁻³

The ligand $^{\text{H}}\text{N}_4^4$ ($^{\text{H}}\text{N}_4 = 3,7\text{-diazadiazapentacyclooctaphane}$ or pyridinophane)⁵ and the complex $[\text{Co}(^{\text{H}}\text{N}_4)\text{Cl}_2]^{+4}$ were prepared according to literature procedures with slight modifications. All other reagents were purchased from commercial vendors and used as received.

Electrochemical Methods

Electrochemical measurements were recorded using a CHI 600D electrochemical analyzer (CH instruments). Cyclic voltammetry experiments were carried out in an argon purged, air-tight, single compartment cell. Controlled-potential electrolysis (CPE) experiments were carried out in a two-compartment cell. Glassy carbon electrode (3 mm diameter, CH instruments) was used as working electrode for cyclic voltammetry, flexible graphite (Grafoil®) used for CPE. Platinum wire (Alfa Aesar, 99.99 %) was used as auxiliary electrode. Ag/AgCl (CH instruments, 1 M KCl, -0.006 V vs. SCE) was used as reference electrode in aqueous solution.

Synthesis of [Co(^HN4)Cl₂]Cl

The pyridinophane ligand ^HN4 and [Co(^HN4)Cl₂]Cl were synthesized using literature procedures with slight modifications.^{4, 5} The ligand ^HN4 (200 mg, 0.83 mmol) was dissolved in a small volume of ethanol (10 mL). A 7 ml ethanolic solution of Co(OAc)₂·4H₂O (147 mg, 0.83 mmol) was added to this solution and the reaction stirred for 30 min. Concentrated HCl (12.1 M) was added to the reaction mixture while air was bubbled through the solution, oxidizing Co(II) to Co(III). A purple-colored precipitate was formed, which was washed with dilute HCl in ethanol (~1 M). The crystalline product was obtained by diffusing diethyl ether into a concentrated ethanolic solution of [Co(^HN4)Cl₂]⁺ (144 mg, 43%). The ¹H NMR spectrum of [Co(^HN4)Cl₂]⁺ in D₂O shows four resonances between 0 and 10 ppm, as expected for a diamagnetic Co(III) complex (**Figure S2**). It is noteworthy that the protons of the methylene groups attached to pyridine are inequivalent indicating that the ligand is folded to create a *cis*-divacant coordination environment at cobalt. There is no change in the UV-vis spectrum of an aqueous solution of the complex over the period of two weeks (**Figure S6**).

¹H NMR (400 MHz, D₂O): δ 7.93 (t, *J* = 7.6 Hz, py 4-H, 1H); 7.49 (d, *J* = 7.9 Hz, py 3,5-H, 2H); 5.19 (d, *J* = 17.6 Hz, CH₂, 2H); 4.58 (d, *J* = 15.1 Hz, CH₂, 2H). UV/Vis λ_{max} (MeCN)/nm 415 (267 M⁻¹cm⁻¹) (**Figure S1**).

X-Ray Photoelectron Spectroscopy (XPS)

X-Ray photoelectron spectra (XPS) spectra were recorded for flexible graphite (Grafoil®) electrodes following CPE in the presence of [Co(^HN4)Cl₂]Cl and CoCl₂. Spectra were recorded using a Physical Electronics PHI Versaprobe II XPS with a hemispherical energy analyzer and a monochromatic aluminum K_α X-ray source (1486.6 eV). The XPS spectra were collected with X-ray power of 25 W at 15 kV and a 200 micron beam size. Metallic Au, Ag and Cu were used for

instrument calibration. The PHI dual charge compensation system was used at all measurements. The ultimate Versaprobe II instrumental resolution was determined to be better than 0.125 eV using the Fermi edge of the valence band for metallic silver. XPS spectra with an energy step of 0.1 eV were recorded using *SmartSoft-XPS* v2.6.3 at pass energies of 46.95 eV for N 1s, 23.5 eV for C and O 1s, 93.9 eV for Cl 2p and, Co 2p. All peaks were referenced to the 1s graphitic carbon peak (284.4 eV) in highly oriented pyrolytic graphite (HOPG). Spectra were processed with PHI *MultiPack* v9.0 software. Peaks were fitted using GL line shapes, i.e., a combination of Gaussians and Lorentzians with 10-50% Lorentzian content. Shirley background was used for curve-fitting. The sample for XPS was placed on the sample platform using double-sided Scotch tape. Spectral reproducibility over three sample regions showed the reliability of the data.

X-ray photoelectron spectroscopy (XPS) of the Grafoil working electrode following 1 h CPE with $[\text{Co}(\text{H}_2\text{N}_4)\text{Cl}_2]\text{Cl}$ provides insight into the nature of the surface-adsorbed species. Most notably, high resolution XPS exhibits Co 2p and N 1s peaks that are absent for a fresh electrode (**Figure 4**). While the binding energies for the $2p_{3/2}$ and $2p_{1/2}$ doublet (781.1 eV and 796.8 eV respectively) in the Co 2p spectrum are consistent with Co(III),⁶ this is likely the result of aerobic oxidation of the surface-adsorbed cobalt species during sample preparation. XPS of CoCl_2 is obtained similarly (**Figure S7**).

Scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS)

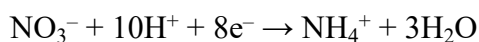
Scanning electron microscopy (SEM) images were collected on an FEI Quanta 600F environmental SEM and a Zeiss Auriga focused-ion beam (FIB) in the SEM mode, both at a beam energy of 30 kV with a spot size of 3 μm .

The atomic percentages of cobalt in the deposition were determined using a scanning electron microscope (SEM) interfaced with energy-dispersive X-ray spectroscopy (EDS) with an FEI

Quanta 600F Environmental SEM operating at 30 kV with a spot size of 3 μm interfaced with an Oxford Aztec EDS detector. Multiple samples were investigated, and multiple sections were sampled at low magnification. The atomic ratio of cobalt in the deposition was found to be reproducible in all cases.

Faradaic Efficiency Calculations

Nitrate requires 8 electrons to be reduced to the ammonium ion.



The ammonium produced by controlled potential electrolysis (CPE) of a 0.1 M Na_2SO_4 solution in the presence of 20 mM NaNO_3 substrate was quantified using the indophenol method.¹ The Faradaic efficiency was calculated according to:

$$\text{FE} = \frac{(ne^-)F(\text{mol NH}_3)}{Q} \quad (1)$$

where ne^- is the number of electrons, F is the Faraday constant, mol NH_3 is the moles of ammonia produced in CPE, and Q is the charge consumption for the conversion.

The amount of ammonium produced by controlled potential electrolysis (CPE) using $[\text{Co}(\text{H}^{\text{N}}\text{4})\text{Cl}_2]^+$, and CoCl_2 and Grafoil® as working electrode at -1.31 V vs. SCE was determined. Colorimetric quantification by the indophenol method shows the formation of 0.019 mmol of ammonium with $[\text{Co}(\text{H}^{\text{N}}\text{4})\text{Cl}_2]^+$ after 1 hour of CPE. No ammonium is produced in a control experiment under identical conditions but without $[\text{Co}(\text{H}^{\text{N}}\text{4})\text{Cl}_2]^+$. According to equation 1, the Faradaic efficiency for ammonium formation is 68 ± 5 %. Similar quantification yielded 0.037 mmol ammonium for CoCl_2 catalyst after 2 hours of CPE (**Figure S10**). The Faradaic efficiency for ammonium formation is 63 ± 5 % using CoCl_2 . No hydroxylamine or nitrite is observed.

During the CPE experiment with $[\text{Co}(\text{H}_4\text{N})\text{Cl}_2]^+$, the color of the solution changes from pale purple to yellow brown, which indicates the decomposition of the complex. There is no spectral change in the absence of any reductive potential, suggesting the complex has good thermal stability in solution (**Figure S6**).

The nitrate reduction activity of the deposited Co nanoparticles was determined in a separate experiment. A 1 mM $[\text{Co}(\text{H}_4\text{N})\text{Cl}_2]\text{Cl}$ solution (0.1 M Na_2SO_4 , no NaNO_3) was subject to CPE at -1.31 V vs. SCE for 1 h. The electrode was thoroughly rinsed with water and immersed in a fresh electrolyte solution (0.1 M Na_2SO_4 , 20 mM NaNO_3), but without any cobalt complex. Product quantification after 2 h CPE at -1.31 V vs. SCE (**Figure S13**) shows 0.0702 mmol of ammonium, with a Faradaic efficiency of 90 %. In addition, the formation of H_2 was also observed (8.5 % Faradaic efficiency). Therefore, the Faradaic efficiency is lowered by charge consumption associated with the decomposition of $[\text{Co}(\text{H}_4\text{N})\text{Cl}_2]^+$.

Supporting Figures and Tables

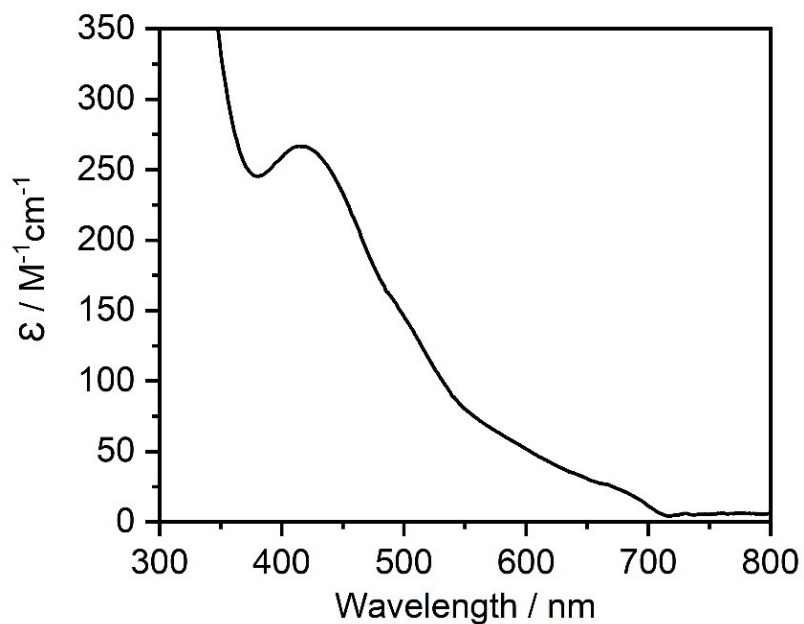


Figure S1. UV-Vis spectrum of $[Co(HN4)Cl_2]Cl$.

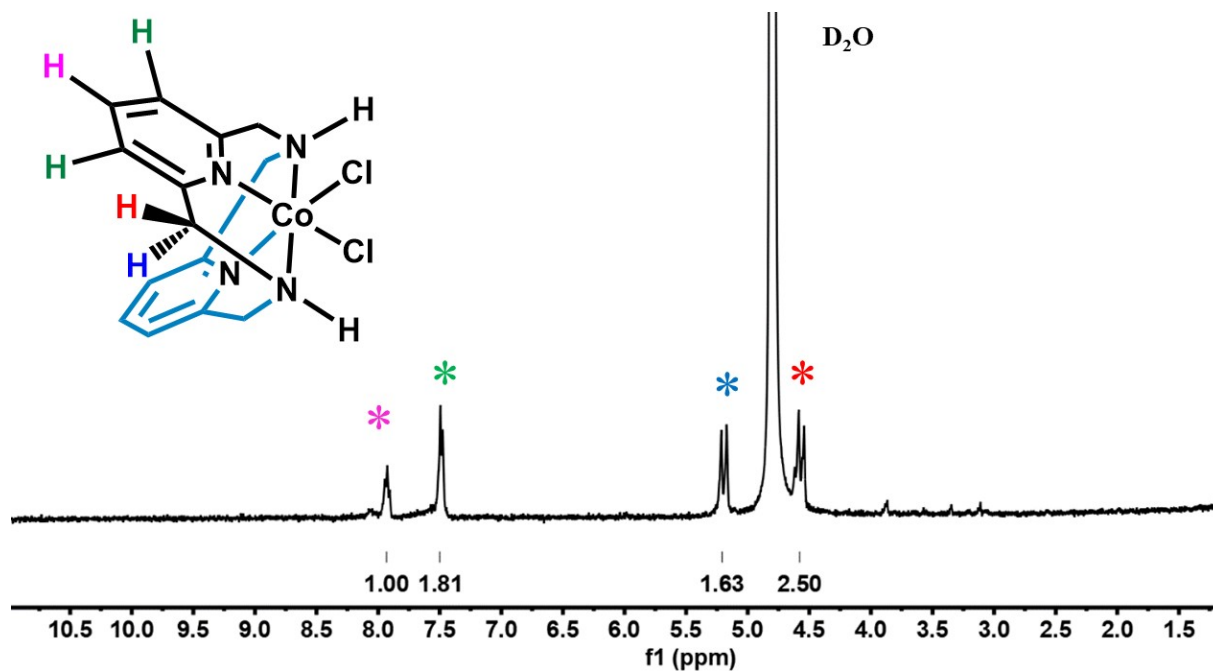


Figure S2. 1H NMR spectrum of $[Co(HN4)Cl_2]Cl$ in D_2O .

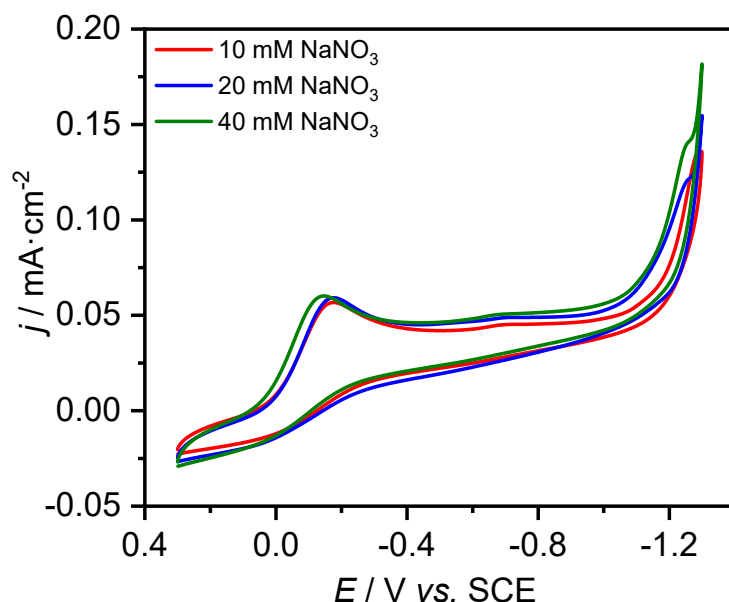


Figure S3. Cyclic voltammograms of 1 mM $[\text{Co}(\text{H}_2\text{N})_4\text{Cl}_2]\text{Cl}$ in 0.1 M Na_2SO_4 solution, pH 6.0 with variable concentrations of NaNO_3 , Glassy carbon working electrode, scan rate 100 mV/s. Current enhancement increases with increasing nitrate concentration. Electrode is polished between experiments.

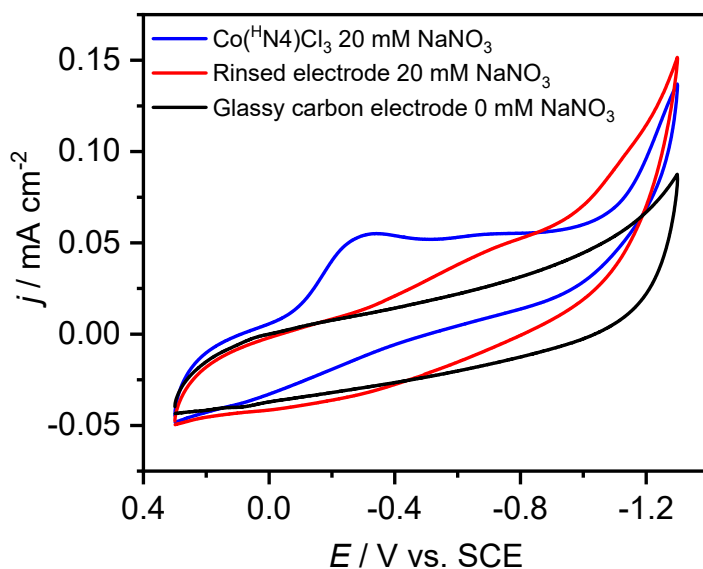


Figure S4. Cyclic voltammograms of a glassy carbon electrode in absence of NaNO_3 (black), in presence of 1 mM $[\text{Co}(\text{H}_2\text{N})_4\text{Cl}_2]\text{Cl}$ and 20 mM NaNO_3 (Blue), and a glassy carbon electrode that was rinsed following 20 min CPE at -1.31 V vs. SCE in the presence of 1 mM $[\text{Co}(\text{H}_2\text{N})_4\text{Cl}_2]\text{Cl}$ and 20 mM NaNO_3 and re-immersed in a 0.1 M Na_2SO_4 solution with 20 mM NaNO_3 without any catalyst (red). Conditions: 0.1 M Na_2SO_4 , pH 6.0, scan rate 0.100 V/s.

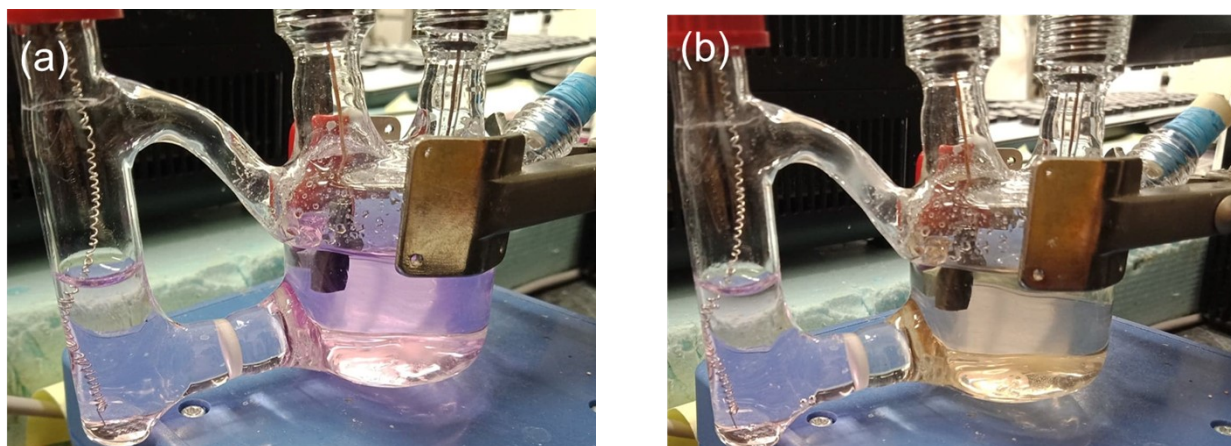


Figure S5. (a) Images of 1 mM $[\text{Co}(\text{H}_4\text{N})\text{Cl}_2]\text{Cl}$ and 20 mM NaNO_3 solution before the CPE and (b) after the CPE at -1.31 V vs. SCE for 2 h. Condition: 0.1 M Na_2SO_4 . Color changes from pale purple to yellow brown.

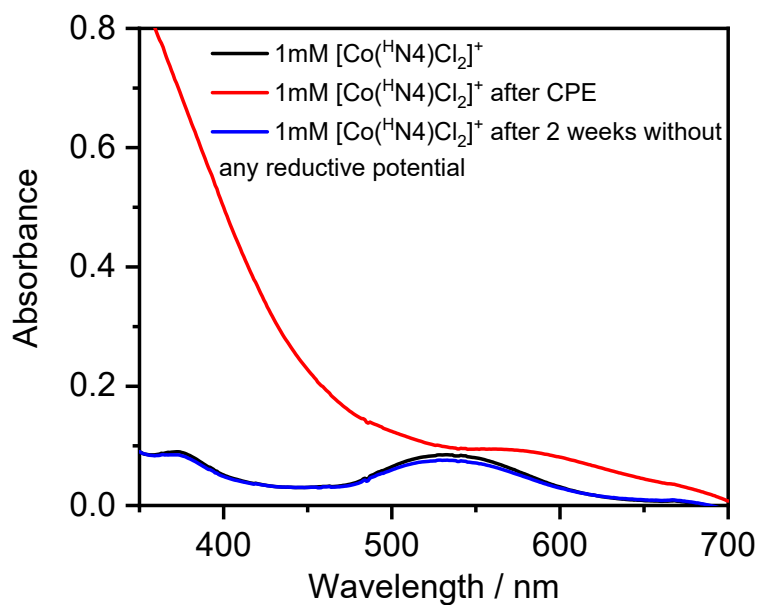


Figure S6. UV-Vis spectra of fresh 1 mM $[\text{Co}(\text{H}_4\text{N})\text{Cl}_2]\text{Cl}$ in water (black), same 1 mM $[\text{Co}(\text{H}_4\text{N})\text{Cl}_2]\text{Cl}$ solution after 2 weeks without any reductive potential (blue), and after doing 2 h CPE at -1.31 V vs. SCE with 20 mM NaNO_3 (red).

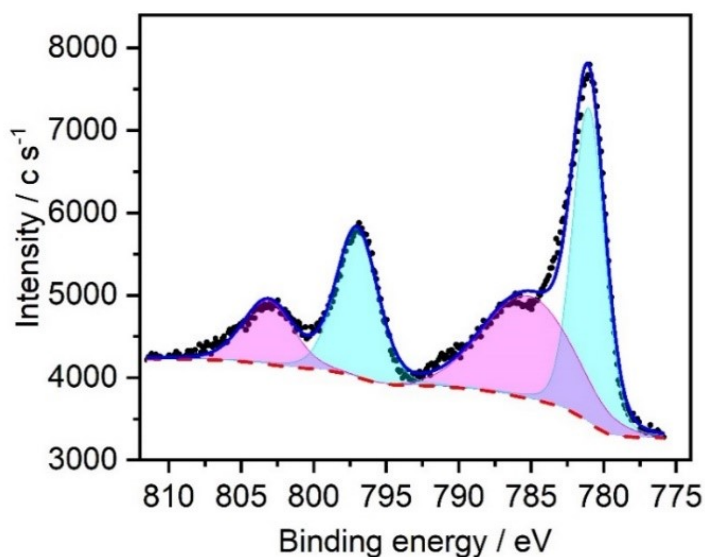


Figure S7. High-resolution Co 2p XPS spectrum of a Grafoil® electrode following 2 h CPE of 1 mM CoCl₂ at -1.31 V vs. SCE. The measured signal is in black, the overall fit manifold in blue, and the fit peaks in cyan and magenta.

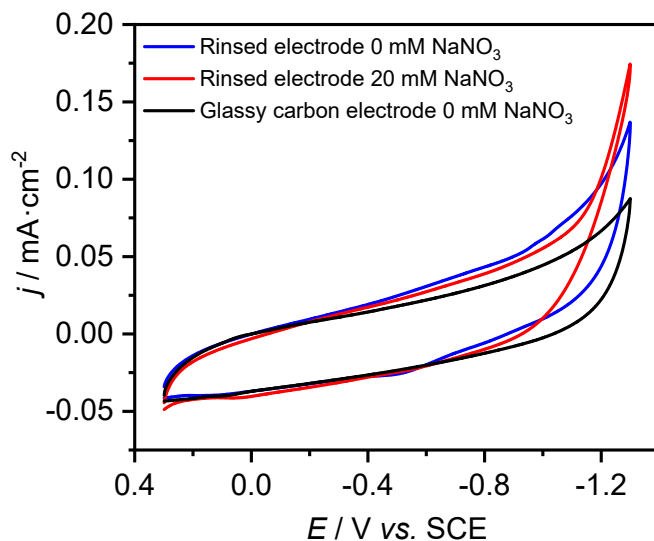


Figure S8. Cyclic voltammograms of a glassy carbon electrode in absence of NaNO₃ (black). A glassy carbon electrode that was rinsed following 20 min CPE at -1.31 V vs. SCE in the presence of 1 mM CoCl₂, and 20 mM NaNO₃ and re-immersed in a 0.1 M Na₂SO₄ solution without any NaNO₃ (blue), and with 20 mM NaNO₃ without any catalyst (red). Conditions: 0.1 M Na₂SO₄, pH 6.0, scan rate 0.100 V/s.

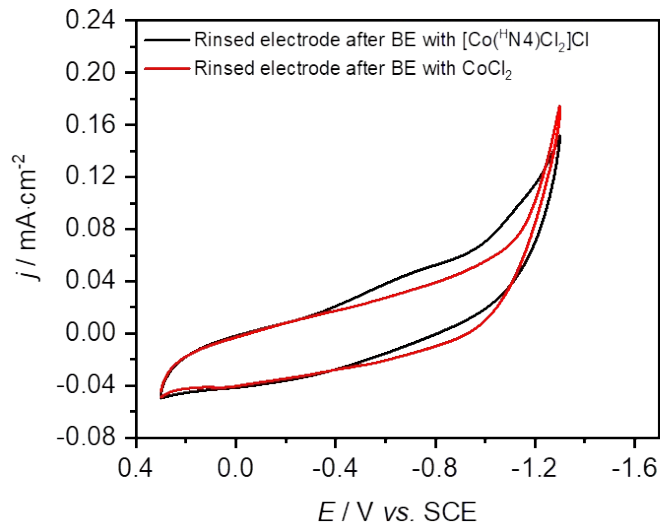


Figure S9. Cyclic voltammograms of rinsed glassy carbon electrode in presence of 20 mM NaNO_3 . A glassy carbon electrode that was rinsed following 20 min CPE at -1.31 V vs. SCE in the presence of 1 mM $[\text{Co}(\text{H}_4\text{N})\text{Cl}_2]\text{Cl}$ and 20 mM NaNO_3 , and re-immersed in a 20 mM NaNO_3 solution without any catalyst (black). A glassy carbon electrode that was rinsed following 20 mins CPE at -1.31 V vs. SCE in the presence of 1 mM CoCl_2 and 20 mM NaNO_3 , and re-immersed in a 20 mM NaNO_3 without any catalyst (red). Conditions: 0.1 M Na_2SO_4 , pH 6.0, scan rate 0.100 V/s.

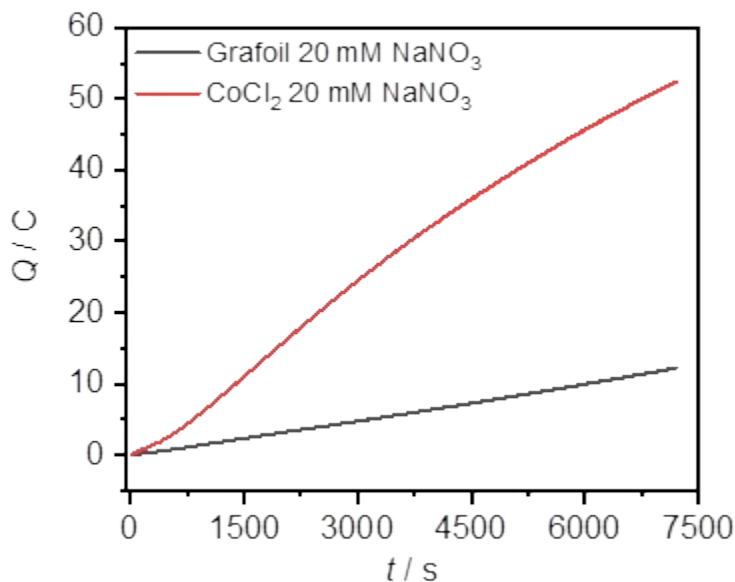


Figure S10. Charge passed during 2 h CPE at -1.31 V vs. SCE in the presence (red) and absence (black) of CoCl_2 . Initial conditions: 0.1 M Na_2SO_4 , 20 mM NaNO_3 , pH 6.0, Grafoil® working electrode.

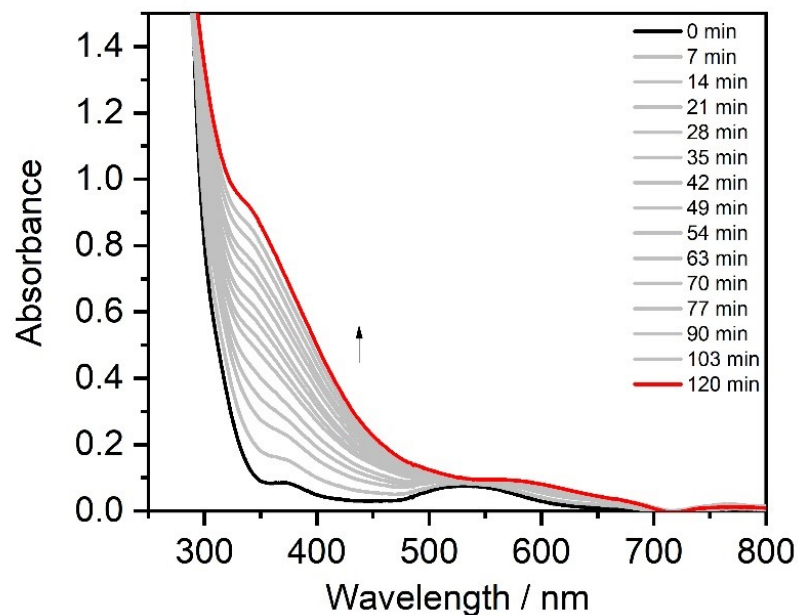


Figure S11. Evolution of the UV-vis spectrum of 1 mM $[\text{Co}(\text{HN}4)\text{Cl}_2]\text{Cl}$ during CPE with 20 mM NaNO_3 . Initial conditions: 0.1 M Na_2SO_4 , pH 6.0, Grafoil® working electrode.

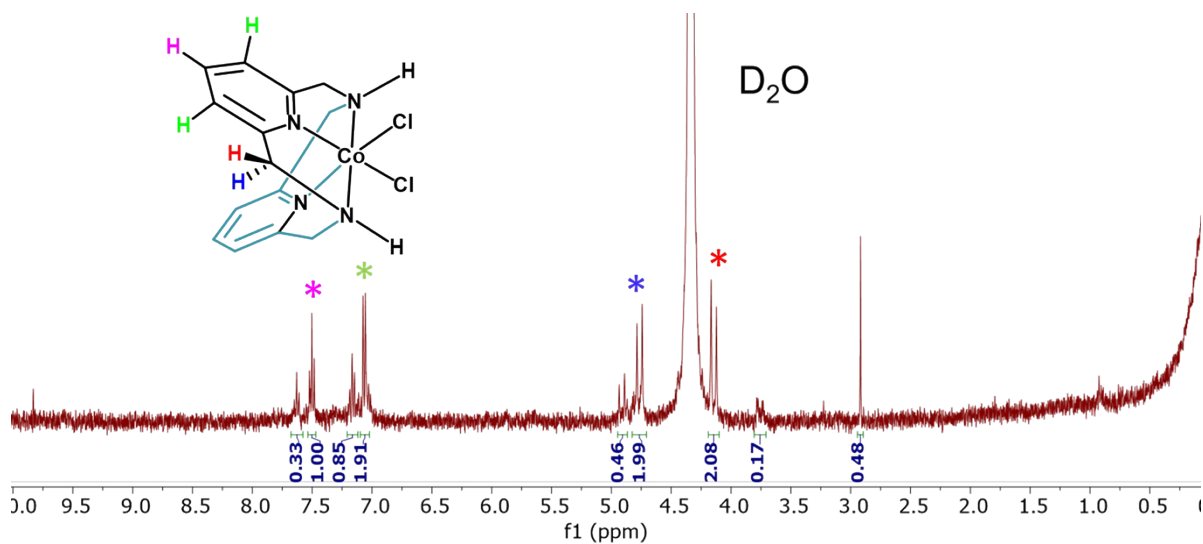


Figure S12. ^1H NMR of $[\text{Co}(\text{HN}4)\text{Cl}_2]\text{Cl}$ in D_2O after CPE at -1.31 V vs. SCE for 1 h. There is some $[\text{Co}(\text{HN}4)\text{Cl}_2]\text{Cl}$ present in the solution. The spectrum reveals signals for the pyridinophane ligand, but with loss of symmetry, likely due to functionalization and/or bond cleavage.

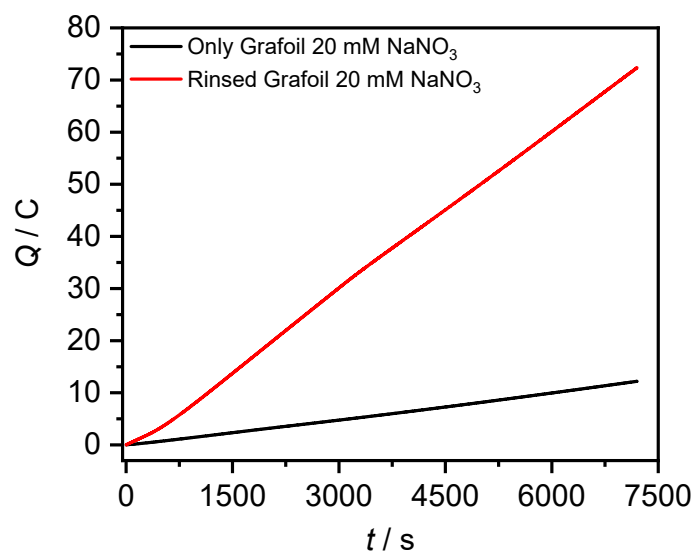


Figure S13. Charge passed during 2 h CPE at -1.31 V vs. SCE in the Co deposited electrode (red) and fresh electrode (black). Co was deposited on Grafoil electrode by doing CPE at -1.31 V vs. SCE for 1h with 1 mM of $[\text{Co}(\text{H}_4\text{N})\text{Cl}_2]\text{Cl}$, without any nitrate. Initial conditions: 0.1 M Na_2SO_4 , 20 mM NaNO_3 , pH 6.0, Grafoil® working electrode.

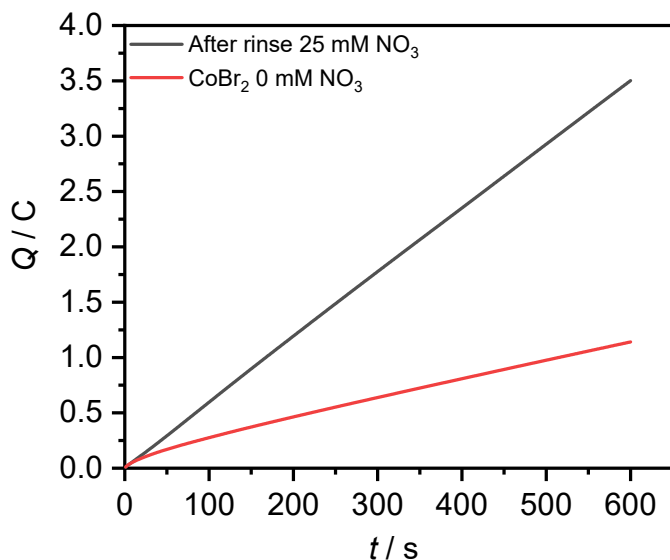


Figure S14. Charge passed during 10 min CPE at -1.31 V vs. SCE in the presence (red) and absence (black) of 1 mM CoBr_2 . Initial conditions 0.1 M Na_2SO_4 , pH 6.0 in a Grafoil® working electrode, no NaNO_3 (red); rinsed Grafoil® electrode re-immersed in a fresh Na_2SO_4 solution, pH 6.0, 20 mM NaNO_3 (black).

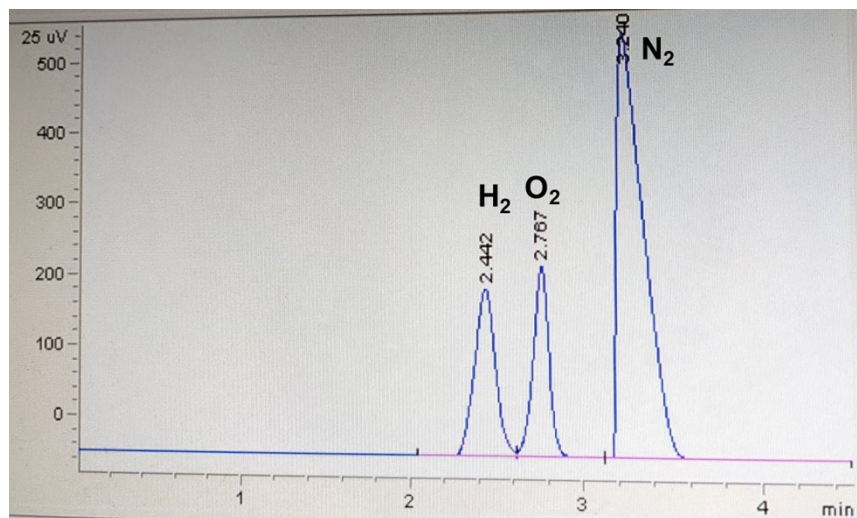


Figure S15. TCD-GC data of 500 μl of gas obtained from the headspace of the cell after CPE of 1 mM $[\text{Co}(\text{H}_2\text{N}_4)\text{Cl}_2]\text{Cl}$ and 20 mM NaNO_3 at -1.31 V vs. SCE for 2h. Condition: 0.1 M Na_2SO_4 . The area of integration for H_2 gas is 1909.30. Faradaic efficiency of H_2 gas is 8.5 %.

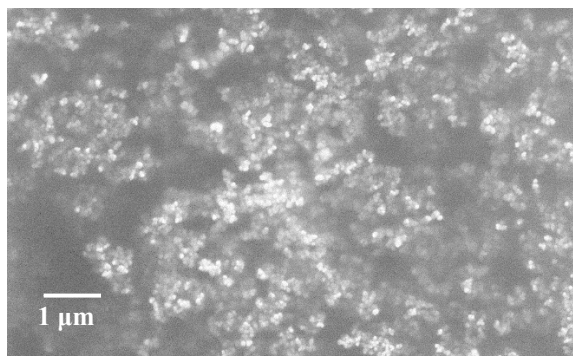
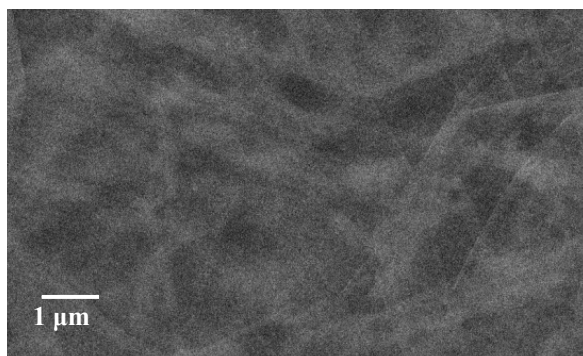


Figure S16. SEM images of new Grafoil® electrode and cobalt deposited Grafoil® electrode (following 10 min CPE at -1.31 V vs. SCE using 1 mM CoCl_2).

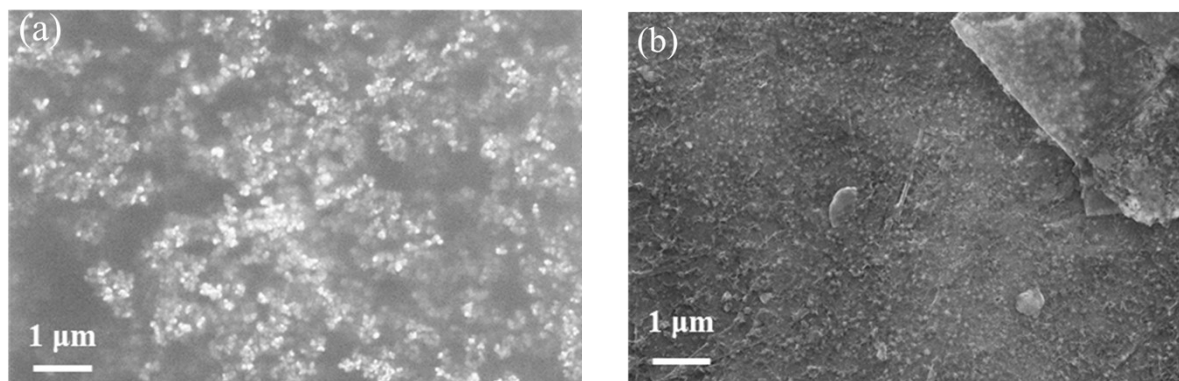


Figure S17. (a) SEM image of cobalt deposits on the Grafoil electrode after CPE at -1.31 V vs. SCE for 1 h without any nitrate; (b) SEM image of cobalt deposits on the Grafoil electrode after CPE at -1.31 V vs. SCE for 1 hour with 20 mM of nitrate. Conditions: 0.1 M Na_2SO_4 , 1 mM CoCl_2 .

Table S1: SEM-EDS atomic percentage of deposition of cobalt on Grafoil®.

Sample	C	O	N	Co	S	Na
New electrode	99.7 ± 0.1 %	0.1 ± 0.00 1 %	0.2 ± 0.001 %	0.0%	0.1 ± 0.001 %	0.0%
Electrode following CPE with CoCl_2	64.4 ± 0.2 %	33.2 ± 0.1 %	$0.1 \pm 0.02\%$	$1.3 \pm 0.1\%$	$0.3 \pm 0.02\%$	0.6 ± 0.02 %
Electrode following CPE with $[\text{Co}(\text{H}_4\text{N})\text{Cl}_2]\text{Cl}$	88.20 ± 0.2 %	7.73 ± 0.1 %	$1.48 \pm 0.1\%$	2.50 ± 0.1 %	-	-

Table S2: Relative surface atom concentration of Grafoil® electrodes after 1 h CPE as determined by XPS.

Sample	C	O	N	Co	Cl
CPE with $[\text{Co}(\text{H}_4\text{N})\text{Cl}_2]\text{Cl}$	94.0±1%	-	2.7±0.1%	3.2±0.1%	0.1±0.001%
CPE with CoCl_2	56.9±1%	30.4±1%	0.5±0.02%	11.9±0.2%	0.3±0.01%

Table S3: Faradaic efficiency of ammonium production for CPE of 20 mM NaNO_3 with 1 mM $[\text{Co}(\text{H}_4\text{N})\text{Cl}_2]\text{Cl}$ and 1 mM CoCl_2 .

Trial	$[\text{Co}(\text{H}_4\text{N})\text{Cl}_2]\text{Cl}$	CoCl_2
1	65 %	63 %
2	69 %	56 %
3	74 %	68 %
4	63 %	67 %
5	69 %	61 %

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