

Supporting information

1D/2D Interface Engineering of CoPc-C₃N₄ heterostructure for boosting nitrogen reduction reaction to NH₃

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EXPERIMENTAL SECTION

Synthesis of CoPc-C₃N₄ heterostructure:

All analytical grade reagents were obtained to perform the experiments.

Synthesis of Cobalt Phthalocyanine (CoPc): 8.8 mmol of phthalonitrile, 2.2 mmol of cobalt acetate and 20 mg of ammonium molybdate as catalyst were added to ethylene glycol (48 ml) and agitated for few minutes. Then the solution was transferred to Teflon lined autoclave (reactor capacity 60 ml) and then placed in a heating oven for 12 hours at 180°C. After natural cooling to ambient temperature, the precipitate was collected and washed with mild hot 1 N HCl, ethanol and mild hot water for several times to wash away the unreacted residual reagents. Finally, the blue colored precipitate was dried in an oven for 14 hours at 60°C and collected for further use. [1]

Preparation of C₃N₄ nanosheets: The C₃N₄ was prepared by annealing urea at 500 °C in presence of air for 4 h at a heating rate of 5°C min⁻¹. The synthesized C₃N₄ compound was grounded and converted into powder form with fine texture, and then the powder is further

subjected to liquid exfoliation by periodic ultrasonication treatment in ethanol medium for 72 h (30 mins alternate cycle was followed), in order to obtain C_3N_4 nanosheets.

CoPc– C_3N_4 heterostructure synthesis: Equal amount(s) of C_3N_4 and CoPc (50 mg each) were pre-mixed and added to 100 ml ethanol. The solution was subjected to 10 h of constant stirring, and the resultant material was collected via centrifugation and washed with deionized water for 3 times. Then the residue was oven dried for 12–14 hours for complete drying of the catalyst. In this way CoPc- C_3N_4 heterostructure was prepared.

Characterizations Technique: X-ray diffraction (XRD) analysis of the catalyst was done using the Bruker D-8 advanced Eco X-ray powder diffractometer. In this study, monochromatic Cu- K_α radiation (wavelength = 0.15404 nm) was used and the X-ray tube voltage and current were maintained at 40 kV and 25 mA respectively. X-ray photoelectron spectroscopy (XPS) study was done using an OMICRON-0571 framework. The morphological characterization was done by using the high-resolution transmission electron microscope (FEG-TEM, JEOL-JEM 2100F). Specific surface area was determined by BET measurements (Quantachrome instrument), degassing was done using helium gas for a period of 4 hours at a temperature of 120 °C, and the isotherm study was done using nitrogen gas. The UV-visible absorbance spectroscopy analysis was studied by Shimadzu UV-3600 Plus Spectrophotometer. All electrochemical nitrogen reduction analysis was done by CHI 760E instrument; the glassy carbon electrode (GCE) played the role of working electrode with an effective area of 0.07 cm^2 . The Ion chromatography measurements were done using ECO IC Metrohm Instrument, cationic column: Metrosep C6 – 150/4.0, eluent flow rate: 0.9 ml/min, and the eluent consists of 1.7 mmol/L nitric acid.

Electrochemical analysis

The electrochemical nitrogen reduction reaction (NRR) was executed in 0.1 M HCl electrolyte solution by purging of ultra-high pure nitrogen gas (N₂) (99.999 %). Before starting the experiment, N₂ gas was purged for 30 minutes.

All potentials were converted from Ag/AgCl (saturated in 3.5 M KCl) to the standard hydrogen electrode using the following relation: $E \text{ (vs RHE)} = E \text{ (vs Ag/AgCl)} + 0.198 \text{ V} + (0.059 \text{ V} \times \text{pH})$. Nafion 117 membrane (thickness 0.007 in, CAS No.: 31175-20-9, Product No.: 274674, Sigma Aldrich Co. Ltd.) was used to separate the two chambers of H-type cell (70 ml, cathodic analyte volume). Nafion 117 membrane was pre-treated in the following manner, at first boiling in water at 80 °C for an hour, then boiling in H₂O₂ aqueous solution at 80 °C for an hour, again water treatment at 80 °C for an hour, then 3 hours treated with 0.5 M H₂SO₄ at 80 °C, finally treated in water at 80 °C for 6 hours. After rinsing it few times with triple distilled water, the membrane was used.

In case of electrocatalytic recycling experiment, the following process was adapted. At first, the H-cell was disassembled after every cycle, thoroughly washed and cleaned with DI water for 3 times. During recycle experiment, for every cycle the Nafion membrane was properly cleaned with triple distilled water for 3 times before starting the experiment.

Catalytic ink preparation

Catalyst ink was prepared by mixing of 1mg of synthesized CoPc-C₃N₄, 10 μL (5 wt. %) nafion 117 solution (Sigma Aldrich), and 100 μL of 2-propanol (Merck). Then, the ink was sonicated for few seconds and then vortexed for 2 minutes to get a homogeneous mixture solution. Finally, 10 μL of the ink solution was coated on the glassy carbon electrode, and dried in vacuum oven at 60 °C for 4 hours. Hence, the total loading of the catalyst is 0.09 mg on the working electrode surface.

Determination of ammonium concentration

By using indophenol blue method, the amount of ammonia produced by electrochemical NRR was quantified using a UV-Visible spectrophotometer. At first, 2 ml of colorant solution (1 M sodium hydroxide solution containing 5 wt% trisodium citrate dihydrate and 5 wt% salicylic acid), 1 ml of oxidant (0.05 M sodium hypochlorite solution (4% w/v available chlorine)) and 0.2 ml of catalyst solution (1.01g (3.34 mmol) sodium nitroprusside dihydrate) were added to 2 ml solution taken from the electrochemical cell after NRR.

After incubation for two hours at room temperature, the solution was analyzed spectrophotometrically. The absorption spectrum showed maximum absorbance at 655 nm. The calibration was done using standard ammonium chloride (99.998% purity, Merck Co., Ltd.) solution (of varying concentration, (0.0, 0.2, 0.4, 0.6, 0.8, 1.0 $\mu\text{g mL}^{-1}$) with the fixed concentration of HCl as used in the NRR experiments, the plot of concentration and absorbance were measured. From the **Figure S5**, the fitting curve ($y = 0.2877x + 0.0248$; $R^2 = 0.998$) revealed an optimized linear correlation between absorbance and concentration of ammonia, after three repeated calibrations.

Calculation of the Ammonia yield rate and Faradaic efficiency:

The rate of ammonia produced after electrolysis was calculated by the given formula,

$$R_{\text{NH}_3} = \frac{C_{\text{NH}_3} \times V}{t \times m} \quad (1)$$

Where ' C_{NH_3} ' is concentration of ammonia produced, ' V ' is volume of electrolyte, ' t ' is time taken to complete the electrocatalysis reaction and ' m ' is mass of the catalyst.

The Faradaic efficiency for NRR, are calculated by the following formula,

$$\text{FE}_{\text{NRR}} (\%) = \frac{(3 \times F \times C_{\text{NH}_3} \times V)}{M \times Q} \times 100\% \quad (2)$$

Where 'F' is the Faraday constant (96,485 C/mol), ' C_{NH_3} ' is concentration of ammonia produced, 'V' is volume of the electrolyte, 'M' is the molecular mass of ammonia, 'Q' is the total charge passed through the electrode during NRR experiment.

Determination of Hydrazine (N_2H_4) concentration

The amount of hydrazine produced via electrochemical NRR was determined through the Watt and Chrisp method using UV-Visible spectrometer. At first, the colored solution was prepared by adding 5.99 g of para-(dimethylamino) benzaldehyde (98% purity, Merck Co. Ltd.) into 30 ml HCl (concentrated) (35%, Merck Co. Ltd.) and 300 ml of absolute ethanol (Merck Co. Ltd.). Then 1 ml of the electrolyte after NRR experiment was taken and added with 4 ml of colored solution, and then after stirring for 10 minutes, kept at the standing condition for further 5 minutes in a dark room at room temperature, then the absorbance spectrum of the solution was measured using UV-Vis spectrophotometer, the maximum absorbance was quantified at 455 nm. The calibration plot was made in the following way: at first, a series of varying concentrations of hydrazine-mono hydrate as standard solutions (0.0, 0.1, 0.3, 0.5, 0.9, 1.1 $\mu\text{g mL}^{-1}$) were made in 0.1 M HCl. Then the volume was adjusted to 1 ml using 0.1 M HCl. Then 1 ml of as prepared hydrazine-hydrate solution were added to 4 ml of colored solution and stirred at room temperature for 10 mins, then after stirring, the solution was kept in dark room at room temperature for 10 mins; then UV-Visible spectroscopy was done and the maximum absorbance was measured at 455 nm. The plot of concentration and absorbance curves (**Figure S7**) yielded a fitting plot ($y = 1.4101x + 0.1325$; $R^2 = 0.9992$) that showed a virtuous linear relationship between the concentration of hydrazine-mono hydrate and absorbance, after three independent calibrations were done then it was reported for estimation of hydrazine.

Determination of NO_x Contaminants

The amount of NO_x produced via electrochemical NRR was determined using UV-vis spectrophotometer using N-(1-naphthyl)-ethylenediamine dihydrochloride (98% purity Merck Co. Ltd.) The colorant solution was prepared by dissolution of 0.5 g of sulfanilic acid (98% purity Merck Co. Ltd.) in 90 ml of millipore water and 5 ml acetic acid, followed by the addition of 5 mg of N-(1-naphthyl)-ethylenediamine dihydrochloride and then making the solution to 100 ml. Then, 1 ml of electrolyte was added to 4 ml of coloring solution. Then the solution was incubated for 15 minutes, and then an ultraviolet-visible spectrophotometer was utilized to obtain the absorption spectrum. The calibration plots (concentration-absorbance curves) were made using sodium nitrite solution (99% purity, Merck Co. Ltd.) with a series of concentrations in 0.1 M HCl (solvent). The plot of absorption versus concentration (**Figure S15**), generates a fitting plot ($y = 0.2581x + 0.0078$; $R^2 = 0.9996$), it showed a linear relationship of absorbance and concentration of NO_x. We conclude from (**Figure S16**), the UV-Vis absorption spectra of 0.1 M HCl background and ¹⁴N₂ ultra-high purity grade (99.999% purity) purged in electrolyte, that NO_x was not present in the feeding gas. Hence it is confirmed that ammonia is formed by reduction of feeding ¹⁴N₂ gas.

Isotope tracing experiment

Prior to NMR sample preparation, 70 mL of cathodic electrolyte was converted to ~2 mL by distillation at ~100-105 °C after the electroreduction process. The isotope tracing experiment was done by using ¹⁵N₂ (98 atom% ¹⁵N Sigma-Aldrich Co.) as the reactant gas to validate the origin of ammonia formation. The ¹⁵N₂ gas was purged into the electrocatalytic system, followed by electrolysis at -0.2V (vs RHE) for 4 hours, the formed ¹⁵NH₄⁺ was determined by ¹H nuclear magnetic resonance (Bruker 400 MHz, USA) with 160 scans and duration of 10 minutes. D₂O (99.99%, Sigma Aldrich Co.Ltd.) was used as the internal standard solution, the

ratio of electrolyte and internal standard solution was about 0.3 ml : 0.1 ml. Similarly, the determination of $^{14}\text{NH}_4^+$ was done using $^{14}\text{N}_2$ (99.999% ultra-high grade purity) as the reactant gas. The standard reference reaction was carried out by purging argon (Ar) gas into the system.

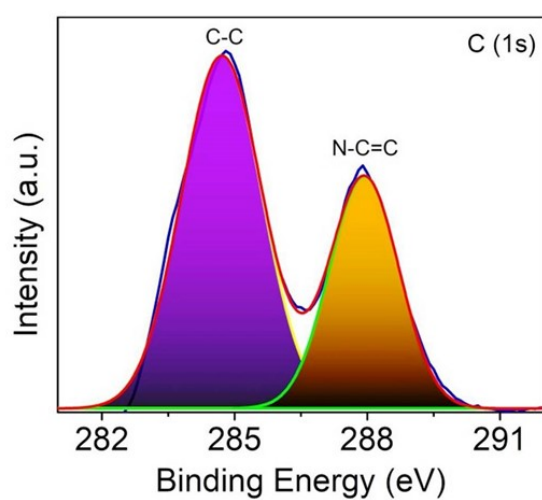


Figure S1: High resolution XPS scan of C (1s) in CoPc-C₃N₄ system.

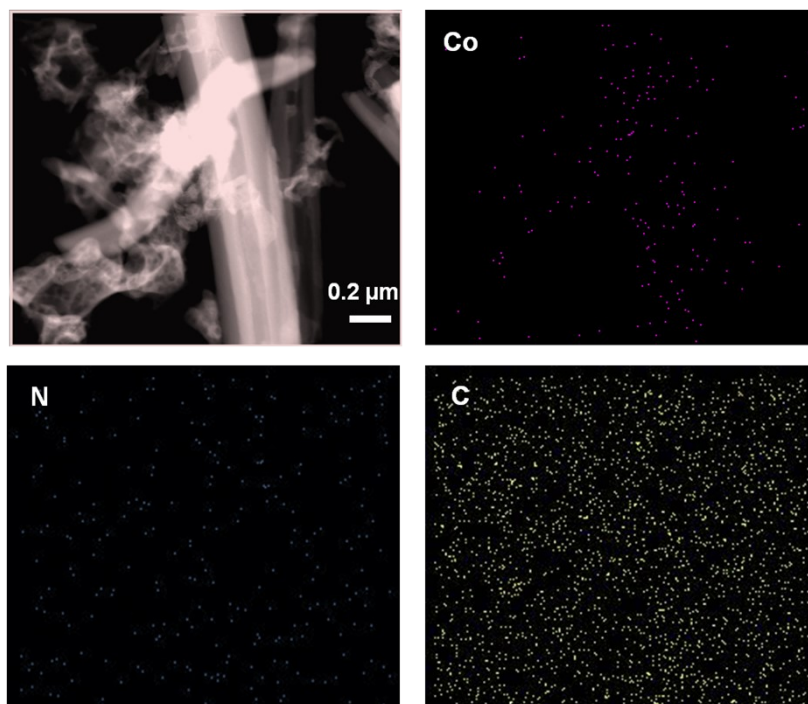


Figure S2: HAADF-STEM image with elemental mappings of CoPc-C₃N₄ heterostructure system.

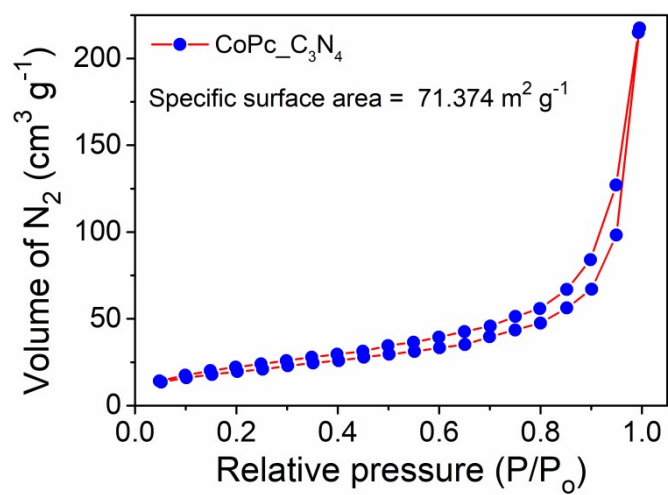


Figure S3: N₂ adsorption-desorption isotherm curve of CoPc-C₃N₄.

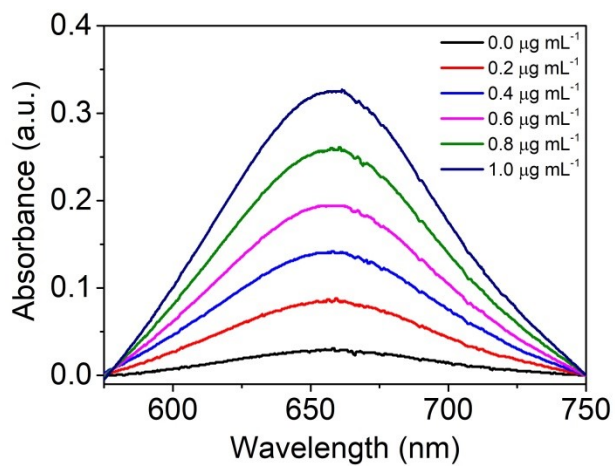


Figure S4: UV-Vis absorbance spectra for different concentrations of NH_4^+ ions.

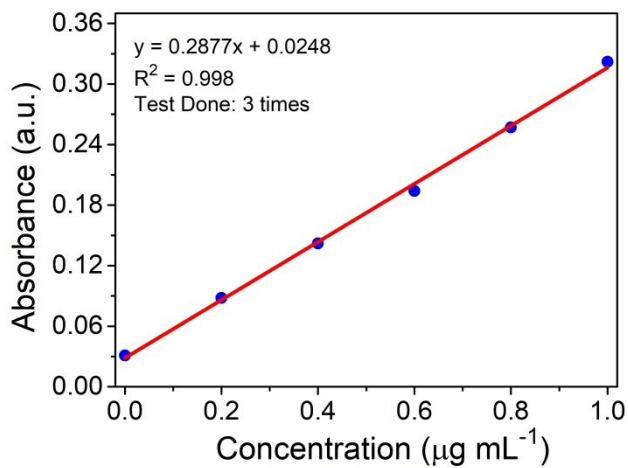


Figure S5: Standard calibration curve for quantitative estimation of NH_4^+ ions by UV-Vis absorption method.

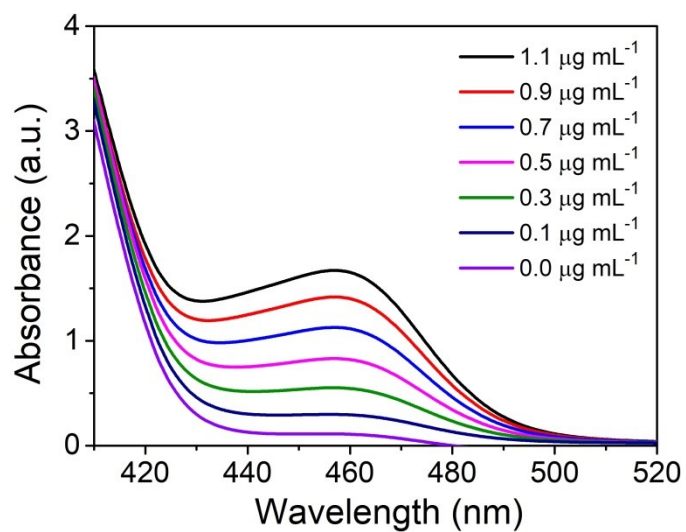


Figure S6: UV-Vis absorption spectra for different concentrations of N_2H_4 .

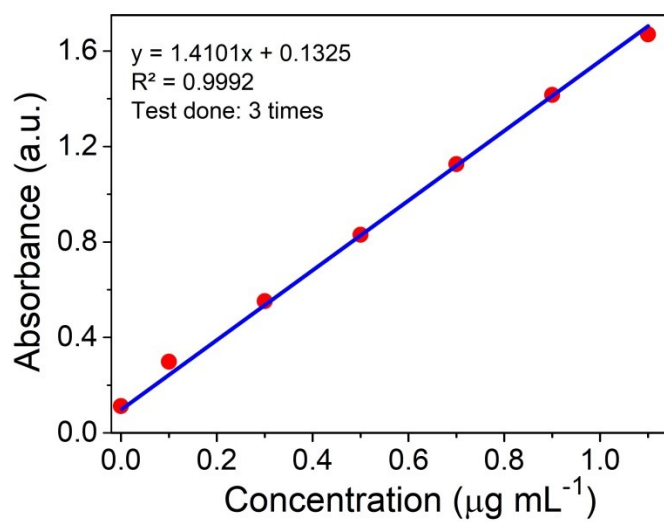


Figure S7: Standard calibration curve used for quantitative estimation of N_2H_4 concentration.

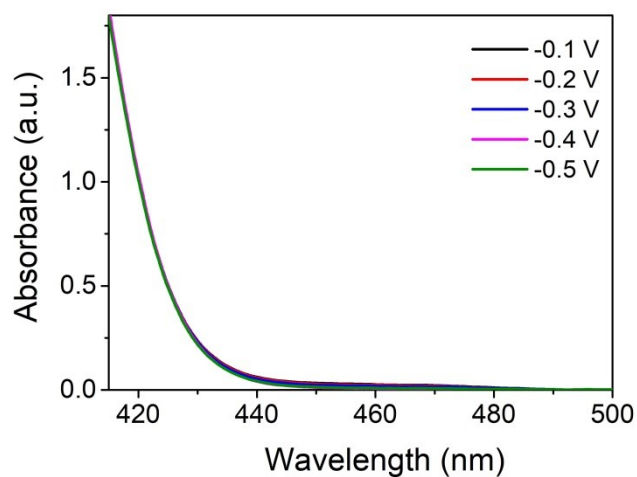


Figure S8: UV-Vis absorption spectra for quantitative determination of N_2H_4 at different potentials.

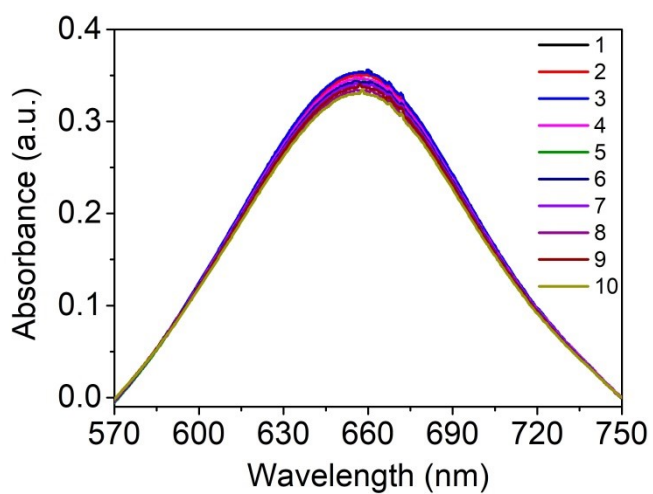


Figure S9: UV-Vis absorption spectra of the electrolytes during indophenol blue tests at -0.2 V vs RHE after 2 hours of electrolysis at different cycles.

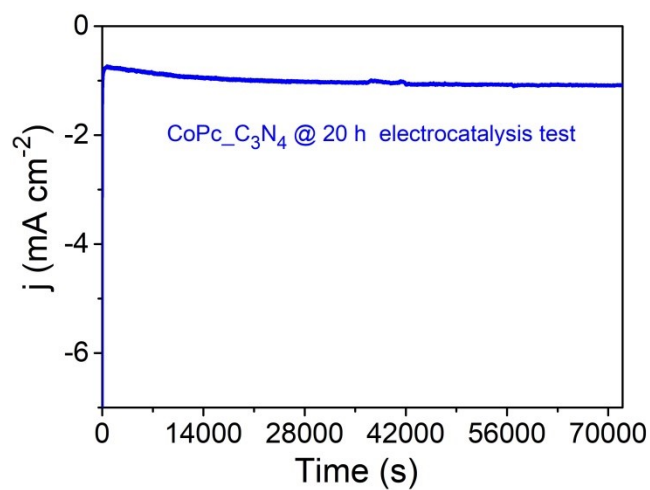


Fig S10: 20 h durability test for CoPc-C₃N₄ for NRR at -0.2 V vs RHE.

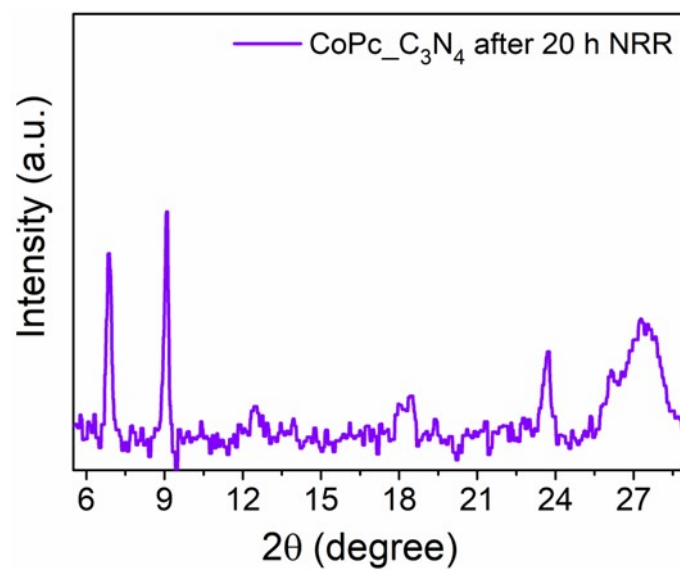


Fig S11: PXRD pattern of CoPc-C₃N₄ after 20 h NRR.

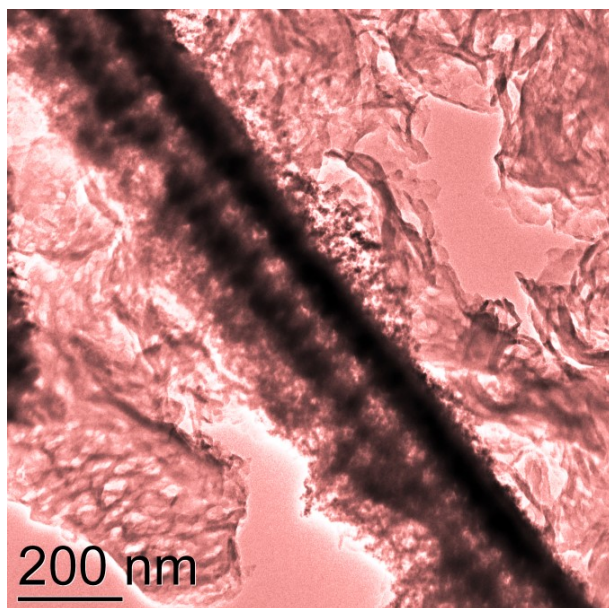


Fig S12: FEGTEM image of CoPc-C₃N₄ after 20 h NRR.

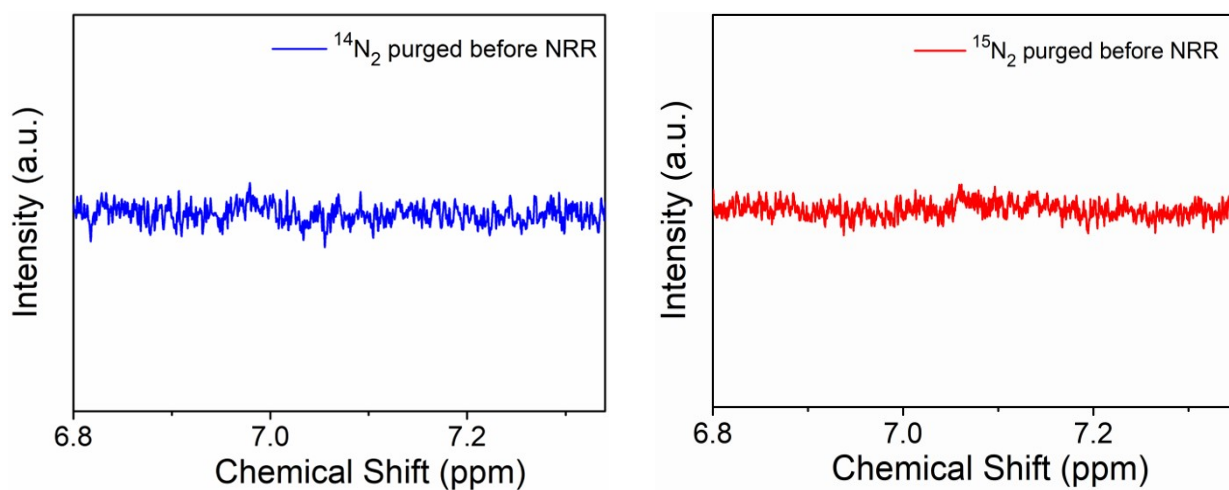


Figure S13: ¹H NMR spectrum of ¹⁴N₂ (left, blue trace) and ¹⁵N₂ (right, red trace) gas purged electrolyte before nitrogen reduction reaction.

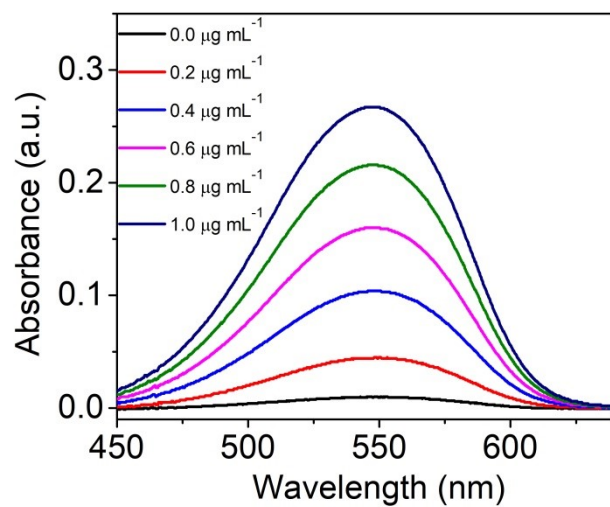


Figure S14: UV-Vis absorption spectra for various NO_x concentrations.

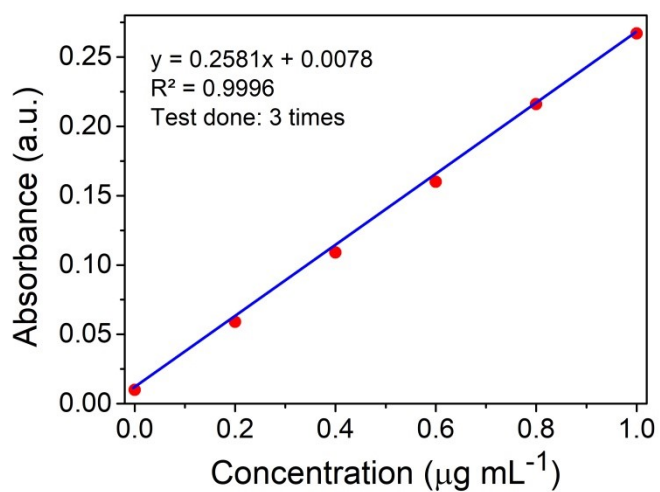


Figure S15: Standard calibration curve used for quantitative estimation of NO_x concentration.

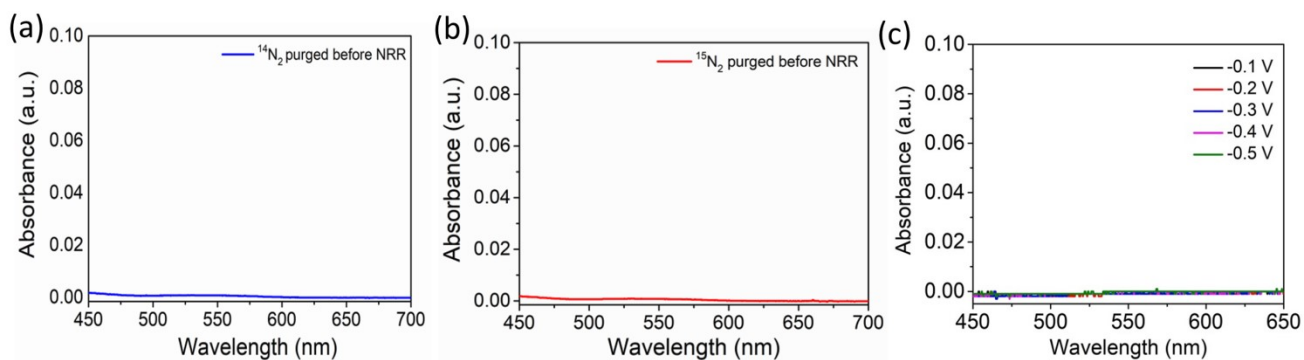


Figure S16: UV-vis absorption spectra for NO_x quantification (a) electrolyte after continuously purging ¹⁴N₂ gas for 30 minutes, (b) electrolyte after continuously purging ¹⁵N₂ gas for 30 minutes, (c) at various potentials after electrolysis.

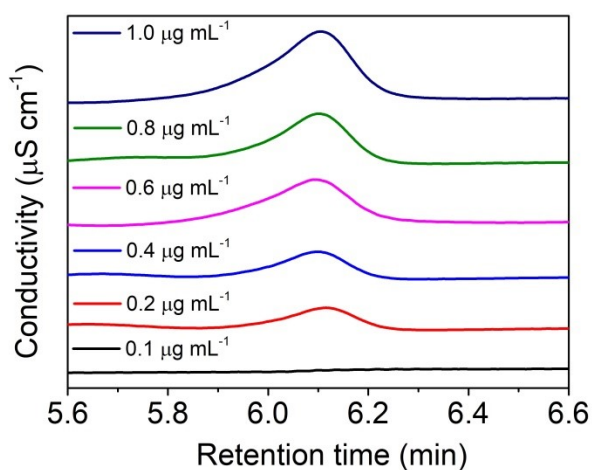


Figure S17: Ion chromatography (IC) measurement for different concentrations of NH₄⁺ ions.

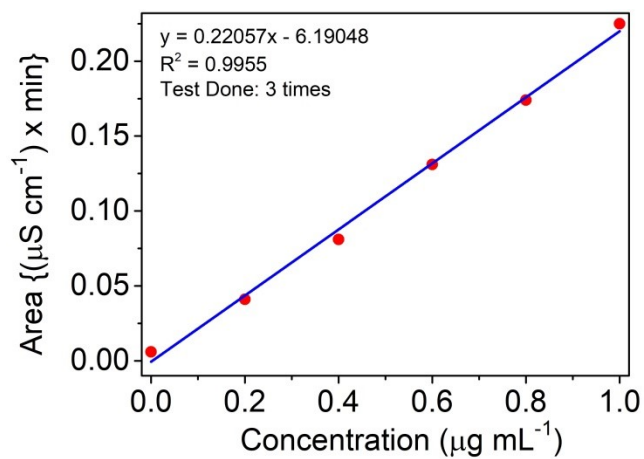


Figure S18: Standard calibration curve for quantitative determination of NH_4^+ ions by IC method.

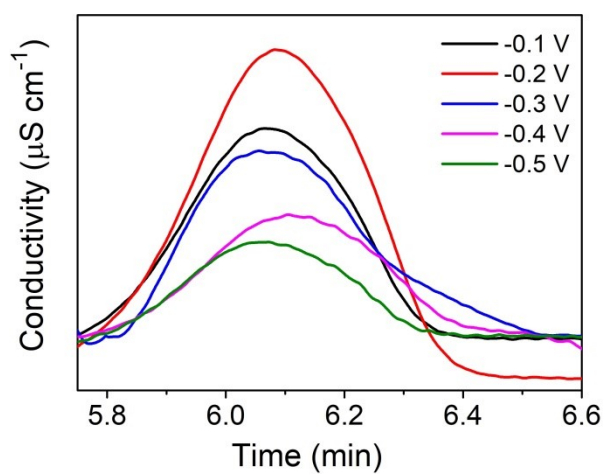


Figure S19: Ion chromatography (IC) measurement for electrolytes at different potentials.

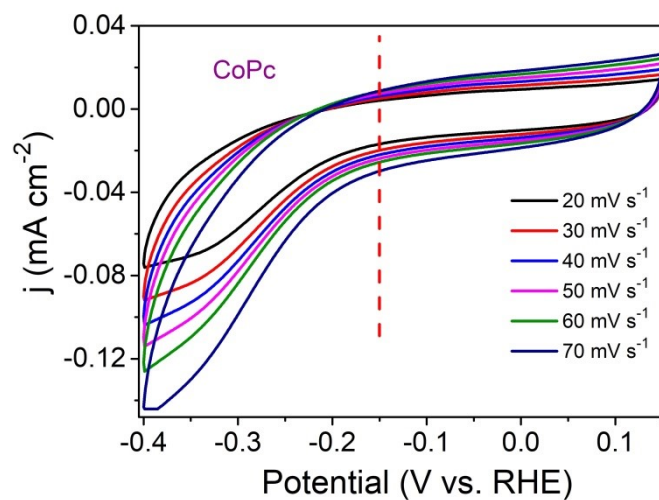


Figure S20: Cyclic voltammetry of CoPc at various scan rates.

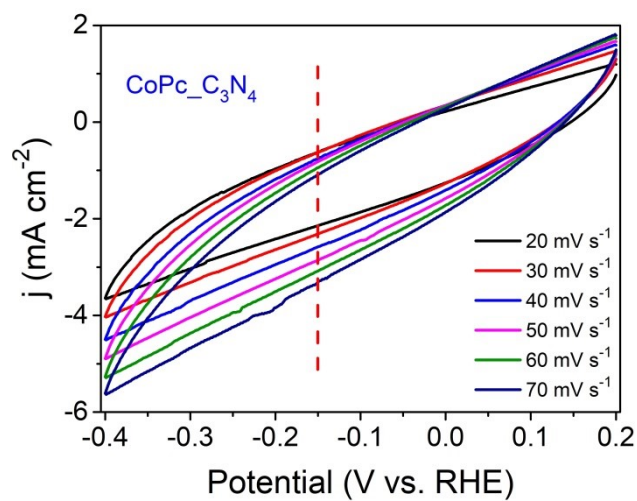


Figure S21: Cyclic voltammetry of CoPc-C₃N₄ 1D/2D heterostructure at various scan rates.

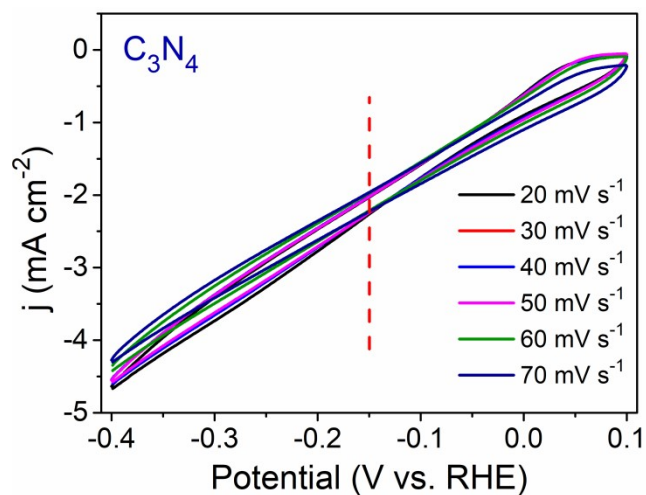


Figure S22: Cyclic voltammetry curve of C_3N_4 at various scan rates.

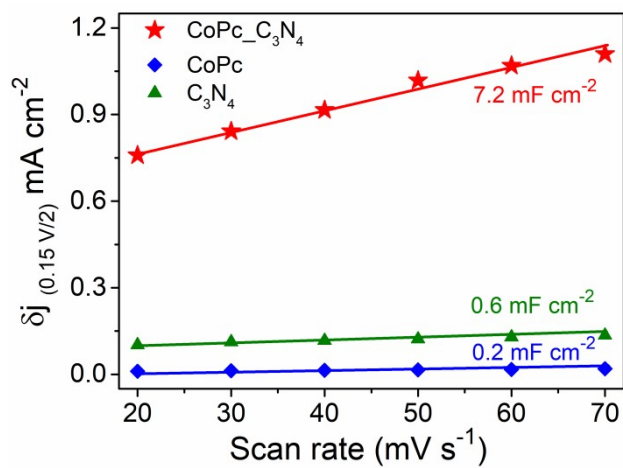


Figure S23: Plot of current density differences ($\delta j/2$) versus scan rate at -0.15 V vs. RHE so as to estimate the C_{dl} values of CoPc, C_3N_4 , and CoPc- C_3N_4 .

Calculation of the electrochemical active surface area (ECSA) of the working electrode

By dividing the measured C_{dl} by the capacitance of the generally used specific capacitance for the catalytic system over a unit surface area, the electrochemically surface area (ECSA) was computed, and specific capacitance (C_s) value is taken as $40 \mu\text{F}/\text{cm}^2$. [2, 3]

We have calculated the electrochemical active surface area (ECSA):

$$\text{ECSA} = R_f \times S$$

Where R_f stands for roughness factor of the working electrode:

$$R_f = (C_{dl} \div C_s) = (C_{dl} \div 40)$$

S represents the geometric surface area of the electrode (glassy carbon electrode) and the diameter (d) of the glassy carbon electrode is 3 mm,

$$\text{The Area of the working electrode} = \pi \times (d/2)^2 = 0.07 \text{ cm}^2$$

Calculation:

For CoPc,

$$C_{dl} = 0.2 \text{ mF cm}^{-2}, \text{ so } R_f = \{ (0.2 \times 1000) \div 40 \} = 5$$

$$\text{ECSA [CoPc]} = 5 \times 0.07 = 0.35 \text{ cm}^2$$

For C_3N_4 ,

$$C_{dl} = 0.6 \text{ mF cm}^{-2}, \text{ so } R_f = \{ (0.6 \times 1000) \div 40 \} = 15$$

$$\text{ECSA [C}_3\text{N}_4] = 15 \times 0.07 = 1.05 \text{ cm}^2$$

For CoPc- C_3N_4 ,

$$C_{dl} = 7.2 \text{ mF cm}^{-2}, \text{ so } R_f = \{ (7.2 \times 1000) \div 40 \} = 180$$

$$\text{ECSA [CoPc-C}_3\text{N}_4] = 180 \times 0.07 = 12.6 \text{ cm}^2$$

Therefore, the calculation suggests that the ECSA of CoPc- C_3N_4 is almost 36 times, and 12 times as compared to CoPc, and C_3N_4 respectively.

Table 1: NRR performance for different catalysts embedded on carbon-based substrate

Catalyst	Electrolyte	Potential (V vs RHE)	NH₃ Yield	FE	References
Au ₁ Co ₁ @GO	0.5 M K ₂ SO ₄	− 0.2 V	36.82 μg h ^{−1} mg ^{−1} _{cat}	22.03 %	[4]
SnO ₂ /RGO	0.1 M Na ₂ SO ₄	− 0.5 V	25.60 μg h ^{−1} mg ^{−1} _{cat}	7.1 %	[5]
TA-RGO	0.5 M LiClO ₄	− 0.75 V	17.02 μg h ^{−1} mg ^{−1} _{cat}	4.83 %	[6]
NiO/G	0.1 M Na ₂ SO ₄	− 0.7 V	18.6 μg h ^{−1} mg ^{−1} _{cat}	7.8 %	[7]
CoO-QD/RGO	0.1 M Na ₂ SO ₄	− 0.6 V	21.5 μg h ^{−1} mg ^{−1} _{cat}	8.3 %	[8]
FePc/O-MWCNT	0.1 M HCl	− 0.3 V	36 μg h ^{−1} mg ^{−1} _{cat}	9.73 %	[9]
Mo ₂ C/C	0.5 M Li ₂ SO ₄	− 0.3 V	11.3 μg h ^{−1} mg ^{−1} _{cat}	7.8 %	[10]
CoPc	0.1 M HCl	−0.3 V	107.9 μg h ^{−1} mg ^{−1} _{cat}	27.7 %	[1]
FePc/C	0.1 M Na ₂ SO ₄	− 0.3 V	10.25 μg h ^{−1} mg ^{−1} _{cat}	10.50%	[11]
NiPc/RGO	0.1 M HCl	− 0.2 V	23.9 μg h ^{−1} mg ^{−1} _{cat}	18.8 %	[12]
MoS ₂ /C ₃ N ₄	0.1 M Na ₂ SO ₄	−0.5 V	19.86 μg h ^{−1} mg ^{−1} _{cat}	6.87 %	[13]
MoS ₂ /C ₃ N ₄	0.1 M LiClO ₄	−0.3 V	18.5 μg h ^{−1} mg ^{−1}	17.8 %	[14]
2D C ₃ N ₄ (N vacancy)	0.1 M HCl	−0.3 V	17.85 μg h ^{−1} mg ^{−1} _{cat}	10.96 %	[15]
CoPc–C₃N₄	0.1 M HCl	−0.2 V	423.8 μg h^{−1} mg^{−1}_{cat}	33%	This work

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