Electronic Supplementary Information

Experimental section

Materials: Graphite powder (20-80 mesh) was purchased from Alfa Aesar. Potassium permanganate (KMnO₄), sulphuric acid (H₂SO₄), hydrochloric acid (HCl), hydrogen peroxide (H₂O₂), ethylene glycol (C₂H₆O₂), Iron acetate (Fe(CH₃COO)₂), Cobalt acetate (Co(CH₃COO)₂), hydrazine hydrate (N₂H₄.H₂O), Para-(dimethylamino) benzaldehyde (C₉H₁₁NO), Ammonium standard solution (1000 ppm), and sodium nitroferricyanide (III) dihydrate (Na₂Fe(CN)₅NO·2H₂O) were purchased from Sigma Aldrich Australia. Sodium hypochlorite (NaClO), sodium hydroxide (NaOH), sodium salicylate(C₇H₅O₃Na), sodium sulfate (Na₂SO₄), and isopropanol (C₃H₈O) were purchased from Chem-supply Australia. Carbon paper (Toray carbon), and Nafion (211) were bought from Fuel cell store. Milli-Q water was used in all experiments.

Preparation of CoFe₂O₄/rGO: Graphite oxide (GO) was developed from graphite powder by modified Hummer’s method.¹ Synthesized GO was subjected to liquid exfoliation by ultrasonication for 2 h and the non-oxidized layers were separated by centrifugation at 1000 rpm to get graphene oxide dispersed in the ethylene glycol (1 mg mL⁻¹). 20 mL of this dispersion was incorporated with the cobalt acetate (25 mM) and iron acetate (50 mM) at 60 °C for 2h. Later, this solution was transferred to the 45 mL autoclave for solvothermal self-assembly of CoFe₂O₄ nanoclusters on graphene at 210 °C for 20h. The resulted product was washed with ethanol, water and dried under vacuum. A similar procedure was used for the synthesis of rGO (without CoFe), Co₃O₄/rGO (without Fe) and Fe₃O₄/rGO (without Co).

Electrode preparation for NRR:

To prepare CoFe₂O₄/rGO/CFP, a catalyst ink was prepared by the ultrasonic-assisted dispersion of 10 mg of active material in a mixture of solvent (200 µL H₂O: 750 µL IPA) with Nafion (50...
µL) as a binder material. An appropriate amount of catalyst ink was drop cast on a carbon fiber paper (1×1 cm²) and dried in ambient air to act as a working electrode for NRR evaluations (mass loading of 1 mg cm⁻²).

**Characterizations:** Crystalline structure of the material was analyzed by X-ray diffraction (XRD, Malvern Panalytical Empyrean-II X-ray diffractometer) with Co-Kα radiation (λ=1.789 Å). High angle annular dark field (HAADF) – scanning transmission electron microscopy (STEM) images and energy-dispersive X-ray spectroscopy (EDS) mapping were obtained by using JEOL JEM-F200 Multi-Purpose FEG-S/TEM instrument. X-ray photoelectron spectroscopy (XPS) analysis was conducted using the Thermo ESCALAB 250i X-ray photoelectron spectrometer equipped with a monochromatic Al Kα X-ray source (hv=1486.68 eV). UV-vis spectroscopy was carried out on Varian Cary 100 Scan double-beam UV/Vis spectrophotometer. Raman spectra were recorded using a Renishaw inVia 2 Raman spectrometer with a 532 nm laser. Fourier transform infrared spectroscopy (FTIR) was conducted on Thermo Fischer Nicolet iS10 FTIR (IR4). Inductively coupled plasma optical emission spectroscopy (ICP-OES) was conducted on PerkinElmer Optima. Brunauer–Emmett–Teller (BET) surface area was determined by Micromeritics Tristar II Plus 2.02.

**Electrochemical NRR evaluation:**

The electrochemical measurements were carried out with an electrochemical workstation (CHI 760D) in a H-type double compartment cell. Ag/AgCl and Pt electrodes were used as reference and counter electrodes, respectively. The potentials reported in this work were converted to reversible hydrogen electrode (RHE) scale via calibration with the following equation: E (vs. RHE) = E (vs. Ag/AgCl) + 0.222 V + 0.059 × pH. For electrochemical NRR evaluation, chrono-
Amperometry tests were conducted in N$_2$-saturated 0.1 M Na$_2$SO$_4$ solution (electrolyte was purged with N$_2$ for 30 min before the measurement).

**Nafion membrane pretreatment:**
The membrane was treated with ultrapure water for 1 h and treated with H$_2$O$_2$ (5%) aqueous solution at 80 °C for another 1 h, respectively. And then, the membrane was treated with 0.5 M H$_2$SO$_4$ for 3 h at 80 °C and finally in water for 6 h.

**Quantification of NH$_3$:**
After chrono-amperometry tests (CA), ammonia quantification was done by Indophenol blue method. In a typical experiment, 2 mL of the electrolyte was collected from cathode chamber and mixed with 2 mL of coloring solution (5 wt% each of salicylic acid and sodium citrate in 1 M NaOH), 1 mL of oxidizing solution (0.05M NaClO), and 0.2 mL of 1 wt% catalyst (Sodium nitroferricyanide) solution, successively. The resulted solution was incubated for 2 h for stable color development and analyzed by UV spectrophotometer at 655 nm. Respective calibration curves were plotted by standard NH$_3$ solution of different concentrations that shows good linear relation of absorption with NH$_3$ concentration in three independent calibrations.

**Quantification of N$_2$H$_4$:**
The amount of N$_2$H$_4$ produced during this process was estimated by the method of Watt and Chrisp. A mixture of 5.99 g C$_9$H$_{11}$NO, 30 mL HCl, and 300 mL ethanol was used as a color reagent. A calibration curve was plotted by making standard solutions of N$_2$H$_4$ in different concentration. 5 mL of respective concentration was mixed with 5 mL of coloring solution and incubated for 20 min to achieve stable color. The good Linear relation was obtained between N$_2$H$_4$ concentration and absorbance in three independent calibration measurements.
Calculation of faradaic efficiency and rate of \( \text{NH}_3 \) production:

The faradaic efficiency (FE) for \( \text{N}_2 \) reduction was defined as the amount of electric charge used for synthesizing \( \text{NH}_3 \) divided the total charge passed through the electrodes during the electrolysis.\(^4\) The total amount of \( \text{NH}_3 \) produced was measured using colorimetric methods. Assuming three electrons were needed to produce one \( \text{NH}_3 \) molecule, the FE could be calculated as

\[
\text{FE} = \frac{3 \times F \times C_{\text{NH}_3} \times V}{17 \times Q}
\]

The rate of \( \text{NH}_3 \) formation was calculated as

\[
\text{Rate of } \text{NH}_3 \text{ formation} = \frac{C_{\text{NH}_3} \times V}{t \times A}
\]

Where \( F \) is the Faradays constant, \( C_{\text{NH}_3} \) is the measured ammonia concentration, \( V \) is the volume of the electrolyte, \( A \) is the geometrical surface area of electrode, \( t \) is time for electrolysis and \( Q \) is the total charge consumed during electrolysis in coulombs.

Thermodynamic equilibrium potential:

The equilibrium potentials required for NRR in neutral medium can be calculated as follow.

\( \text{N}_2(\text{gas}) + 8\text{H}_2\text{O} + 6e^- \rightarrow 2\text{NH}_4\text{OH} (\text{aq}) + 6\text{OH}^- \quad \Delta G^0 = 426.38 \text{ kJ mol}^{-1} \)

\( E^0 = -\Delta G^0/nF = -0.737 \text{ V vs SHE (Standard hydrogen electrode)} \)

So, thermodynamic potential in \( \text{N}_2 \) saturated electrolyte (1 atm) is
\[ E = E^0 - \frac{RT}{6F} \times \ln \left[ c^2(\text{NH}_4\text{OH}) \times c^6(\text{OH}^-) \right] + 0.059 \times \text{pH} \]

\[ F = \text{Faradays constant (96485 C mol}^{-1}) \]

\[ R = \text{Gas constant (8.314 J mol}^{-1} \text{ K}^{-1}) \]

\[ C (\text{OH}) = 1.58 \times 10^{-7} \text{ M} \]

\[ C (\text{NH}_4\text{OH}) = 10 \mu \text{M} \]

\[ \text{pH} = 7.2 \]

\[ T = 298.15 \text{ K} \]

\[ n (\text{number of electrons}) = 6 \]

Thermodynamic equilibrium potential for this reaction is calculated to be -0.196 V vs RHE.
Fig. S1. SEM (a) TEM (b) and HRTEM image of CoFe$_2$O$_4$/rGO.
Fig. S2. SEM (a) and TEM (b) image of rGO.
Fig. S3. HAADF-STEM image and STEM-EDS elemental mapping of (a) Fe$_3$O$_4$/rGO and (b) Co$_3$O$_4$/rGO.
Fig. S4. FTIR spectrum of (a) GO and rGO, and (b) rGO, Fe_3O_4/rGO, Co_3O_4/rGO and CoFe_2O_4/rGO.
Fig. S5. XPS survey spectrum of CoFe$_2$O$_4$/rGO.
Fig. S6. Linear sweep voltammetry of CoFe$_2$O$_4$/rGO in Ar and N$_2$ in 0.1 M Na$_2$SO$_4$. 
Fig. S7. (a) UV-vis absorption spectra of different \( \text{NH}_3 \) concentrations stained with indophenol assay for 2h. (b) calibration curve for \( \text{NH}_3 \) determination.
Fig. S8. (a) UV-vis absorption spectra of different N$_2$H$_4$ concentration. (b) calibration curve for N$_2$H$_4$ determination.
Fig. S9. (a) UV-vis absorption spectra of different control experiments stained by indophenol assay for 2h.
**Fig. S10.** (a) UV-vis absorption spectra of electrolyte after 2h of electrolysis at -0.4 V for the estimation of N$_2$H$_4$ by Watt and Chrisp method.
Fig. S11. NRR performance of Fe$_3$O$_4$/rGO. (a) Chronoamperometry curves at respective potentials in 0.1 M Na$_2$SO$_4$, (b) UV-visible colorimetric spectra at respective potentials stained by indophenol method after 2h electrolysis in N$_2$, and (c) Corresponding FE and rate of NH$_3$ production. NRR performance of Co$_3$O$_4$/rGO. (d) Chronoamperometry curves at respective potentials in 0.1 M Na$_2$SO$_4$, (e) UV-visible colorimetric spectra at respective potentials stained by indophenol method after 2h electrolysis in N$_2$, and (f) Corresponding FE and rate of NH$_3$ production.
Fig. S12. STEM (a), HRTEM (b), and (c) STEM-EDS mapping of CoFe$_2$O$_4$/rGO after NRR.
Fig. S13. Double layer capacitance measurements by cyclic voltammetric scan at various scan rate ($v$) ranging from 1- 40 mV s$^{-1}$ (a) CoFe$_2$O$_4$/rGO, (b) Fe$_3$O$_4$/rGO and (c) Co$_3$O$_4$/rGO. Calculated $R_f$ factor for all samples with respect to carbon paper (d).
Table S1: ICP analysis of CoFe$_2$O$_4$/rGO, Fe$_3$O$_4$/rGO and Co$_3$O$_4$/rGO.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Co</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%wt</td>
<td>%wt</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$/rGO</td>
<td>1.40</td>
<td>3.30</td>
</tr>
<tr>
<td>Co$_3$O$_4$/rGO</td>
<td>4.8</td>
<td>0.0</td>
</tr>
<tr>
<td>Fe$_3$O$_4$/rGO</td>
<td>0.0</td>
<td>4.9</td>
</tr>
</tbody>
</table>
Table S2: BET normalized rate of NH$_3$ production

<table>
<thead>
<tr>
<th>Sample name</th>
<th>BET surface area (m$^2$/g)</th>
<th>BET normalized rate of NH$_3$ (mol cm$^{-2}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoFe$_2$O$_4$/rGO</td>
<td>133.5</td>
<td>3.14 × 10$^{-13}$</td>
</tr>
<tr>
<td>Co$_3$O$_4$/rGO</td>
<td>140.2</td>
<td>2.13×10$^{-13}$</td>
</tr>
<tr>
<td>Fe$_3$O$_4$/rGO</td>
<td>147.8</td>
<td>1.3×10$^{-13}$</td>
</tr>
<tr>
<td>rGO</td>
<td>180.7</td>
<td>2.7×10$^{-14}$</td>
</tr>
</tbody>
</table>
Table S3: Comparison of NRR performance of CoFe/rGO with other Fe-based electrocatalysts at ambient conditions.

<table>
<thead>
<tr>
<th>S/No</th>
<th>Catalyst/Substrate</th>
<th>Electrolyte/system</th>
<th>Rate of NH\textsubscript{3} production</th>
<th>Faradaic Efficiency (%)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe/FTO</td>
<td>Ionic liquids (phosphonium based)</td>
<td>$4.7 \times 10^{-12}$ mol s\textsuperscript{-1} cm\textsuperscript{-2}</td>
<td>60 at -0.8 V vs NHE</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>$\alpha$-Fe nanorods@Fe\textsubscript{3}O\textsubscript{4}/CFP</td>
<td>Aprotic solvents-Ionic liquids</td>
<td>$2.35 \times 10^{-11}$ mol s\textsuperscript{-1} cm\textsuperscript{-2}</td>
<td>32 at -0.65 V vs NHE</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>$\gamma$-Fe\textsubscript{2}O\textsubscript{3}/CFP</td>
<td>AEM electrolyte</td>
<td>55.96 nmol h\textsuperscript{-1} mg\textsuperscript{-1}</td>
<td>0.044 at 1.6 V\textsubscript{cell}</td>
<td>7</td>
</tr>
<tr>
<td>4</td>
<td>Fe/Fe\textsubscript{3}O\textsubscript{4}</td>
<td>PBS</td>
<td>0.20 µg h\textsuperscript{-1} cm\textsuperscript{-2}</td>
<td>8.29 at -0.3 V vs RHE</td>
<td>8</td>
</tr>
<tr>
<td>5</td>
<td>Spinel Fe\textsubscript{3}O\textsubscript{4}</td>
<td>0.1 M Na\textsubscript{2}SO\textsubscript{4}</td>
<td>$5.6 \times 10^{-11}$ mol s\textsuperscript{-1} cm\textsuperscript{-2}</td>
<td>2.6 at -0.4 V vs RHE</td>
<td>9</td>
</tr>
<tr>
<td>6</td>
<td>$\beta$-FeOOH</td>
<td>0.5 M LiClO\textsubscript{4}</td>
<td>$23.32$ µg h\textsuperscript{-1} mg\textsuperscript{-1}</td>
<td>6.7 at -0.70 V vs Ag/AgCl</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>Fe-N/C</td>
<td>0.1 M KOH</td>
<td>$34.83$ µg h\textsuperscript{-1} mg\textsubscript{cat}-1</td>
<td>9.28% at -0.2 V vs RHE</td>
<td>11</td>
</tr>
<tr>
<td>8</td>
<td>Fe\textsubscript{SA}-N/C</td>
<td>0.1 M KOH</td>
<td>$7.48$ µg h\textsuperscript{-1} mg\textsubscript{cat}-1</td>
<td>56.55% at 0 V vs RHE</td>
<td>11</td>
</tr>
<tr>
<td>9</td>
<td>CoFe\textsubscript{2}O\textsubscript{4}/rGO</td>
<td>0.1 M Na\textsubscript{2}SO\textsubscript{4}</td>
<td>$4.2 \times 10^{-11}$ mol s\textsuperscript{-1} cm\textsuperscript{-2}</td>
<td>6.2% at -0.4 V vs RHE</td>
<td>This work</td>
</tr>
</tbody>
</table>
References:


2018, **54**, 11332–11335.