Electronic Supplementary Information

Experimental section

Materials: Sodium hydroxide (NaOH), ammonium chloride (NH₄Cl), salicylic acid (C₇H₆O₃), sodium citrate dehydrate (C₆H₅Na₃O₇·2H₂O), p-dimethylaminobenzaldehyde (C₉H₁₁NO), sodium nitroferricyanide dihydrate (C₅FeN₆Na₂O·2H₂O), sodium nitrate (NaNO₃) and sodium hypochlorite (NaClO), were purchased from Aladdin Ltd. (Shanghai, China). Sulfuric acid (H₂SO₄), hydrogen peroxide (H₂O₂), hydrochloric acid (HCl), hydrazine monohydrate (N₂H₄·H₂O), phosphoric acid (H₃PO₄), N, N-dimethylformamide (DMF, C₃H₇NO), ethylalcohol (C₂H₅OH), and sopropyl alcohol (C₃H₇OH) were purchased from Beijing Chemical Corporation. (China). chemical Ltd. in Chengdu. Cobalt nitrate (Co(NO₃)₂·6H₂O), adenine (C₅H₅N₅), were purchased from Chengdu Kelong Chemical Regent Co. Ltd. Carbon paper (CP) was purchased from Qingyuan Metal Materials Co., Ltd (Xingtai, China). All reagents used in this work were analytical grade without further purification. The ultrapure water purified on a Millipore system was used in all experiments.

Preparation of Co-Adenine MOF: In a 250 mL round-bottom flask, 2.0 mmol adenine was added into 80 mL DMF and heated at 140 °C to form a transparent solution. Then, 1.0 mmol Co(NO₃)₂·6H₂O was ultrasonically dissolved in 20 mL DMF, and added to the above flask under vigorous stirring. The color of this mixture immediately turned to purple blue and gradually changed to brown. The reaction was allowed to proceed for 4 h, and the mixture was left to cool down to room temperature. Co-Adenine (identified as Co-Ade) MOF were collected by centrifugation, and then washed with water and ethanol for several times. The samples were finally dried at 160 °C overnight.

Preparation of Co@NC: the as-prepared Co-Ade MOF was heated to 700 °C at a heating rate of 5 °C min⁻¹ and maintained for 1 h in Ar atmosphere.

Preparation of NC: As a control, the NC was prepared by the direct carbonization of adenine at the same conditions.
Characterizations: XRD dates were acquired by a LabX XRD-6100 X-ray diffraction instrument. SEM measurements were carried out on a Gemini Sigma 300/VP microscope. TEM images were collected on a HITACHI H-8100 electron microscopy. XPS spectra were recorded on an ESCALABMK II X-ray photoelectron spectrometer. UV-Vis absorption spectra were obtained on a SHIMADZU UV-2700 spectrophotometer. Gaseous products from nitrate reduction reaction were determined by GC with SHIMADZU GC-2014 gas chromatograph. A GC run was initiated per 1200 s. Argon (99.999%) was used as the carrier gas. A flame ionization detector with a thermal conductivity detector (TCD) was used to quantify H₂ and N₂. The electrolyzer outlet was introduced into a condenser before being vented directly into the gas sampling loop of the gas chromatograph. ¹H NMR spectra were acquired on a Brüker spectrometer operating at 400 MHz.

Electrochemical measurements: All electrochemical measurements were performed in a two-compartment cell separated by a treated Nafion 117 membrane using the CHI760E electrochemical workstation (Shanghai, Chenhua) with a standard three-electrode setup including catalyst coated on carbon paper as the working electrode, a Hg/HgO as the reference electrode, and a graphite rod as the counter electrode. Co@NC ink was obtained by mixing 10 mg of Co@NC catalyst, 960 μL of sopropyl alcohol, and 40 μL of Nafion (5 wt%) to achieve a catalyst concentration of 10 mg mL⁻¹ via sonication for 60 min. Co@NC coated on carbon paper (identified by Co@NC/CP) was prepared by dropping 20 μL of the Co@NC ink onto carbon paper (mass loading: 0.2 mg) and drying in air. Electrolyte solution was Ar-saturated 0.1 M NaOH with additional 0.1 M NaNO₃. Before the long-term stability test, a thin tube was inserted into H-cell and fixed below the electrolyte level. At each sampling time, 0.5 mL of electrolyte was pipetted into the centrifugal tube for subsequent testing. All potentials reported in our work were converted to reversible hydrogen electrode (RHE) scale and the current density was normalized by the geometrical area of the electrode (0.25 cm²).

Determination of NH₃: The NH₃ concentration was quantitatively determined by indophenol blue method.¹ Firstly, 2.0 mL of sample solution was mixed with 1.0 mL
of chromogenic reagent, 1.0 mL of oxidizing reagent, and 0.2 mL of catalysing reagent. The absorbance at 655 nm was then measured by a UV-Vis spectrophotometer after 2 h of dark incubation. The concentration-absorption spectra were calibrated using standard NH₄Cl solution with different concentration.

**Determination of NO₂⁻:** The NO₂⁻ concentration was quantitatively determined by Griess method.² Firstly, 1.0 mL of deionized water, 1.0 mL of sample solution, and 2.0 mL of Griess reagent were sequentially added to a 10 mL of centrifuge tube. The absorbance at 540 nm was then measured by a UV-Vis spectrophotometer after 15 min of dark incubation. The concentration-absorption spectra were calibrated using standard NaNO₂ solution with different concentration.

**Determination of N₂H₄:** The N₂H₄ concentration was quantitatively determined by Watt and Chrisp method.³ Firstly, 1.0 mL of sample solution was mixed with 1.0 mL of chromogenic reagent. The absorbance at 455 nm was then measured by a UV-Vis spectrophotometer after 15 min of dark incubation. The concentration-absorption spectra were calibrated using standard N₂H₄ solution with different concentration.

**Determination of NH₃ yield and FE:**

\[
\text{FE} = \frac{nCVF}{MQ}
\]

\[
\text{NH₃ yield} = \frac{CV}{17tA}
\]

Where \( n \) is the number of electrons transferred during NO₃RR, \( C \) is the concentration of products, \( V \) is the volume of cathodic electrolyte (35 mL), \( F \) is the Faradaic constant (96500 C mol⁻¹), \( M \) is the molar mass of products, \( Q \) is the total quantity of applied electricity, \( t \) is the electrolysis time, and \( A \) is the geometric area of working electrode (0.5 × 0.5 cm²).
Fig. S1. XRD pattern of Co-Ade MOF.
Fig. S2. XRD pattern of NC.
Fig. S3. (a) Low- and (b) high-magnification SEM images of NC.
Fig. S4. LSV curves of (a) NC/CP and (b) bare CP in 0.1 M NaOH without and with 0.1 M NO$_3^-$.
Fig. S5. (a) UV-Vis absorption spectra and (b) corresponding calibration curve used for calculation of NH$_4^+$ concentration.
Fig. S6. (a) UV-Vis absorption spectra and (b) corresponding calibration curve used for calculation of NO$_2^-$ concentration.
Fig. S7. (a) UV-Vis absorption spectra and (b) corresponding calibration curve used for calculation of N$_2$H$_4$ concentration.
**Fig. S8.** CA curves for the NO$_3$RR process on Co@NC/CP at different applied potentials.
Fig. S9. UV-Vis absorption spectra of generated $\text{N}_2\text{H}_4$ for Co@NC/CP at different applied potentials.
Fig. S10. Partial current densities of NO$_2^-$, H$_2$, N$_2$, and NH$_3$. 
Fig. S11. NH₃ yields and FEs during the alternate cycle tests in NO₃⁻-containing and NO₃⁻-free 0.1 M NaOH at −0.5 V.
Fig. S12. (a) CA curves, (b) Q values, and (c) corresponding UV-Vis absorption spectra for generated NH$_3$ during recycling tests at $-0.5$ V.
Fig. S13. Long-term stability test of Co@NC/CP at –0.5 V in 0.1 M NaOH with 0.1 M NO$_3^-$ and corresponding NH$_3$ concentration for Co@NC/CP.
Table S1. Comparison of catalytic performance of Co@NC with other reported non-noble-metal NO₃RR electrocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>FE (%)</th>
<th>NH₃ yield</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co@NC</td>
<td>0.1 M NaOH (0.1 M NaNO₃)</td>
<td>96.5</td>
<td>758.0 µmol h⁻¹ mg₉₉ cat⁻¹</td>
<td>This work</td>
</tr>
<tr>
<td>Co-NCNT</td>
<td>0.1 M NaOH (0.1 M NaNO₃)</td>
<td>92.0</td>
<td>580.3 µmol h⁻¹ cm⁻²</td>
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<tr>
<td>Co/CoO NSA</td>
<td>0.1 M Na₂SO₄ (3.23 mM NaNO₃)</td>
<td>93.8</td>
<td>194.5 µmol h⁻¹ cm⁻²</td>
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<tr>
<td>Co₃O₄@NiO</td>
<td>0.5 M Na₂SO₄ (3.23 mM NaNO₃)</td>
<td>55.0</td>
<td>6.9 µmol h⁻¹ mg₉₉ cat⁻¹</td>
<td>6</td>
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<tr>
<td>Co-P/TP</td>
<td>0.2 M Na₂SO₄ (3.23 mM NaNO₃)</td>
<td>93.6</td>
<td>24.5 µmol h⁻¹ cm⁻²</td>
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<tr>
<td>CoO@NCNT</td>
<td>0.1 M NaOH (0.1 M NaNO₃)</td>
<td>93.8</td>
<td>531.8 µmol h⁻¹ cm⁻²</td>
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<tr>
<td>Fe SAC</td>
<td>0.1 M K₂SO₄ (0.5 M KNO₃)</td>
<td>75.0</td>
<td>1176.5 µmol h⁻¹ mg₉₉ cat⁻¹</td>
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<tr>
<td>Fe-PPy SACs</td>
<td>0.1 M KOH (0.1 M KNO₃)</td>
<td>100</td>
<td>30.0 µmol h⁻¹ mg₉₉ cat⁻¹</td>
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<tr>
<td>Fe₃O₄/SS</td>
<td>0.1 M NaOH (0.1 M NaNO₃)</td>
<td>91.6</td>
<td>721.4 µmol h⁻¹ cm⁻²</td>
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<tr>
<td>Cu₃P NA/CF</td>
<td>0.1 M PBS (0.1 M NaNO₃)</td>
<td>62.9</td>
<td>49.9 µmol h⁻¹ cm⁻²</td>
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<tr>
<td>Cu/Cu₃O NWAs</td>
<td>0.5 M Na₂SO₄ (3.23 mM NaNO₃)</td>
<td>95.8</td>
<td>244.9 µmol h⁻¹ cm⁻²</td>
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<tr>
<td>Cu₅₀Ni₅₀</td>
<td>1 M KOH (0.01 M KNO₃)</td>
<td>93.0</td>
<td>/</td>
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<tr>
<td>In-S-G</td>
<td>0.1 M KOH (0.1 M KNO₃)</td>
<td>75.0</td>
<td>220.0 µmol h⁻¹ mg₉₉ cat⁻¹</td>
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<td>Pd/TiO₂</td>
<td>0.5 M NaOH (0.25 M NaNO₃)</td>
<td>92.1</td>
<td>66.0 µmol h⁻¹ cm⁻²</td>
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<td>TiO₂₋ₓ</td>
<td>0.5 M Na₂SO₄ (0.81 mM NaNO₃)</td>
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<td>45.0 µmol h⁻¹ cm⁻²</td>
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<td>Ni₃N/N-C-800</td>
<td>0.5 M Na₂SO₄ (0.05 M NaNO₃)</td>
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<td>688.8 µmol h⁻¹ mg₉₉ cat⁻¹</td>
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<td>BCN@Ni</td>
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<td>1706 µmol h⁻¹ mg₉₉ cat⁻¹</td>
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<td>Ni₃B@NiB₂.₇₄</td>
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<td>98.7</td>
<td>198.3 µmol h⁻¹ cm⁻²</td>
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</table>
References


