Electronic Supplementary Information

**Experimental section**

**Materials:** Sodium nitrite (NaNO₂, 99.9%), ammonium chloride (NH₄Cl, 99.5%), sodium hydroxide (NaOH, 98%), ethanol (C₂H₅O, 99.9%), sodium salicylate (C₇H₅NaO₃, 99.5%), trisodium citrate dihydrate (C₆H₅Na₃O₇·2H₂O, 99%), p-dimethylaminobenzaldehyde (C₉H₁₁NO, 99%), sodium nitroferricyanide dihydrate (C₅FeN₆Na₂O·2H₂O, 99%) and sodium hypochlorite solution (NaClO, 5%) were purchased from Aladdin Co., Ltd. (Shanghai, China). Sulfuric acid (H₂SO₄, 99%), hydrogen peroxide (H₂O₂, 99%), hydrochloric acid (HCl, 99%), hydrazine monohydrate (N₂H₄·H₂O, 99%) and ethyl alcohol (C₂H₅OH, 99%) were bought from Beijing Chemical Corporation. (China). Ti plate (thickness is 0.2 mm, 99.9%) was purchased from Qingyuan Metal Materials Co., Ltd (Xingtai, China). All reagents used in this work were analytical grade without further purification.

**Preparation of TiO₂ nanosheets array:** Firstly, Ti plate (2.0 × 3.0 cm²) was cleaned by ultrasonication in acetone, ethanol, and water for 15 min, respectively. Then, Ti plate was put into a 50 mL of Teflon-lined autoclave containing 35 mL of 5 M NaOH solution and heated in an electric oven at 180 °C for 24 h. Subsequently, cation exchange of Na⁺ to H⁺ was carried out by immersing the sample into 1 M HCl for 1 h to obtain H₂Ti₂O₅·H₂O nanosheet array, followed by annealing at 500 °C for 2 h.

**Preparation of CoB@TiO₂ nanoarray:** Amorphous CoB was magnetron sputtered onto as-prepared TiO₂ nanoarray. The sputtering chamber was evacuated to about 8×10⁻⁴ Pa before the sputtering deposition. Ar (50 sccm) was injected to the chamber with a total pressure of 4 Pa and the sputtering voltage was 310 V (direct current voltage). The bias voltage was 60 V and the sputtering time was 5 min. CoB on Ti plate was prepared by the same procedure. The sputtering machine (Z/CM GXZ 05-2020) is purchased from Chengdu CM Photoelectrictechnology Co., Ltd.

**Characterizations:** XRD data were acquired from a LabX XRD-6100 X-ray diffractometer with a Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm
SEM images were collected on a Gemini SEM 300 scanning electron microscope (ZEISS, Germany) at an accelerating voltage of 5 kV. TEM images were acquired on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) operated at 200 kV. XPS measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. The absorbance data of spectrophotometer was measured on UV-vis spectrophotometer (SHIMADZU UV-2700). Gaseous products from nitrate reduction reaction were determined by gas chromatography (GC) with SHIMADZU GC-2014 gas chromatograph.

**Electrochemical measurements:** All electrochemical measurements were carried out on the CHI660E electrochemical workstation (Chenhua, Shanghai). A three-electrode system with an H-type electrolytic cell separated by a Naftion 117 membrane, working electrode of a piece of CoB@TiO$_2$/TP as, reference electrode of Ag/AgCl, and counter electrode of graphite rod are used for the electrochemical tests under magnetic stirring (250 rpm). Electrolyte is 0.1 M Na$_2$SO$_4$ with/without 400 ppm NO$_2^-$.

The potentials reported in this work were converted to the reversible hydrogen electrode (RHE) via the equation of $E$ (vs. RHE) = $E$ (vs. Ag/AgCl) + 0.197 V + 0.059 × pH.

**Determination of NH$_3$:** NH$_3$ concentration was spectrophotometrically determined by the indophenol blue method (the obtained electrolyte was diluted 20 times). In detail, 4 mL diluted electrolyte was mixed with 50 µL oxidizing solution containing NaClO (4.5%) and NaOH (0.75 M), 500 µL coloring solution containing C$_7$H$_5$O$_3$Na (0.4 M) and NaOH (0.32 M), and 50 µL 1 wt% Na$_2$Fe(CN)$_5$NO·2H$_2$O aqueous solution for 1 h in darkness. The concentration-absorbance curve ($y = 0.4506x + 0.0238$, $R^2 = 0.9998$) was prepared from the UV-vis spectra of the standard NH$_4$Cl solutions with known concentrations of 0, 1, 2, 3, 4 mL$^{-1}$ in 0.1 M Na$_2$SO$_4$.

**Determination of N$_2$H$_4$:** N$_2$H$_4$ was estimated by the Watt and Chrisp method. The color reagent was a solution of 18.15 mg mL$^{-1}$ of C$_9$H$_{17}$NO in the mixed solvent of HCl and C$_2$H$_5$OH (V/V: 1/10). In detail, 2 mL electrolyte was added into 2 mL color reagent for 15 min under stirring. The absorbance of such solution was measured to
quantify the hydrazine yields by the standard curve of hydrazine ($y = 0.6878x + 0.1066$, $R^2 = 0.9998$).

**Determination of N$_2$, H$_2$:** H$_2$ was quantified by GC.

**Calculations of the m$_{\text{NH}_3}$, FE and NH$_3$ yield:**

The amount of NH$_3$ ($m_{\text{NH}_3}$) was calculated by the following equation:

$$m_{\text{NH}_3} = [\text{NH}_3] \times V$$

FE of NH$_3$ formation was calculated by the following equation:

$$\text{FE} = \frac{(6 \times F \times [\text{NH}_3] \times V)}{(M_{\text{NH}_3} \times Q)} \times 100\%$$

NH$_3$ yield rate is calculated using the following equation:

$$\text{NH}_3 \text{ yield} = \frac{([\text{NH}_3] \times V)}{(M_{\text{NH}_3} \times t \times A)}$$

Where F is the Faradic constant (96485 C mol$^{-1}$), [NH$_3$] is the NH$_3$ concentration, V is the volume of electrolyte in the anode compartment (40 mL), $M_{\text{NH}_3}$ is the molar mass of NH$_3$ molecule, Q is the total quantity of applied electricity, t is the electrolysis time (1 h) and A is the geometric area of working electrode (0.5 × 0.5 cm$^2$).
Fig. S1. SEM image of TP.
Fig. S2. SEM image of TiO$_2$/TP.
Fig. S3. EDX spectrum of CoB@TiO$_2$/TP.
Fig. S4. (a) UV-vis spectra and (b) corresponding calibration curve for calculation of NH$_4^+$ concentration.
Fig. S5. (a) UV-vis spectra and (b) corresponding calibration curve for calculation of \( \text{N}_2\text{H}_4 \) concentration.
Fig. S6. LSV curves of CoB/TP, TiO$_2$/TP, and bare TP in 0.1 M Na$_2$SO$_4$ with/without 400 ppm NO$_2^-$.
Fig. S7. NH$_3$ yields and FEs of CoB@TiO$_2$/TP, CoB/TP, TiO$_2$/TP, and bare TP in 0.1 M Na$_2$SO$_4$ containing 400 ppm NO$_2^-$ at −0.7 V.
Fig. S8. NO$_3^-$ reduction reaction performance measurements of CoB@TiO$_2$/TP: (a) LSV curves in 0.1 M Na$_2$SO$_4$ with and without 400 ppm NO$_3^-$, (b) Chronoamperometry curves and (c) corresponding UV-vis spectra at a potential range from −0.4 V to −0.9 V. (d) NH$_3$ yields and FE at given potentials.
Fig. S9. UV-vis spectra of N$_2$H$_4$ detection.
Fig. S10. Chromatograph curves of (a) H$_2$ and (b) N$_2$ detected by GC at each given potential.
Fig. S11. NH₃ yields and FEs during alternating cycle tests between NO₂⁻-containing and NO₂⁻-free 0.1 M Na₂SO₄ at −0.7 V.
Fig. S12. Chronoamperometry curve of CoB@TiO$_2$/TP during 12-h stability test.
**Fig. S13.** Time-dependent UV-vis spectra of NH$_4^+$ during long-term stability test.
Fig. S14. LSV curves of CoB@TiO$_2$/TP before and after long-term stability test.
Fig. S15. UV-vis spectra of CoB@TiO$_2$/TP for cycling tests in 0.1 M Na$_2$SO$_4$ containing 400 ppm NO$_2^-$ at −0.7 V.
Fig. S16. SEM image of CoB@TiO$_2$/TP after durability test.
Fig. S17. XRD pattern of CoB@TiO$_2$/TP after durability test.
**Table S1.** Comparison of the catalytic performances of CoB@TiO$_2$/TP with the other reported NO$_2$ RR and NO$_3^-$ RR electrocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>NH$_3$ yield</th>
<th>FE (%)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CoB@TiO$_2$/TP</td>
<td>0.1 M Na$_2$SO$_4$ (400 ppm NaNO$_2$)</td>
<td>233.1 μmol h$^{-1}$ cm$^{-2}$</td>
<td>95.2</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>0.1 M Na$_2$SO$_4$ (400 ppm NaNO$_3$)</td>
<td>195.9 μmol h$^{-1}$ cm$^{-2}$</td>
<td>84</td>
<td></td>
</tr>
<tr>
<td>MnO$_2$ nanoarray</td>
<td>0.1 M Na$_2$SO$_4$ (0.2 M NaNO$_2$)</td>
<td>8.6 × 10$^{-12}$ μmol h$^{-1}$ cm$^{-2}$</td>
<td>6</td>
<td>1</td>
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<tr>
<td>Ni-NSA-V$_{Ni}$</td>
<td>0.2 M Na$_2$SO$_4$ (200 ppm NaNO$_2$)</td>
<td>235.5 μmol h$^{-1}$ cm$^{-2}$</td>
<td>88.9</td>
<td>2</td>
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<tr>
<td>Cobalt-tripeptide complex</td>
<td>1.0 M MOPS (1.0 M NaNO$_2$)</td>
<td>1.1 μmol h$^{-1}$ cm$^{-2}$</td>
<td>90 ± 3</td>
<td>3</td>
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<tr>
<td>Ni$_2$P/NF</td>
<td>0.1 M PBS (200 ppm NaNO$_2$)</td>
<td>158.1 ± 5.4 μmol h$^{-1}$ cm$^{-2}$</td>
<td>90.2 ± 3.0</td>
<td>4</td>
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<tr>
<td>CoP NA/TM</td>
<td>0.1 M PBS (500 ppm NaNO$_2$)</td>
<td>132.7 ± 3.0 μmol h$^{-1}$ cm$^{-2}$</td>
<td>90.0 ± 2.3</td>
<td>5</td>
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<tr>
<td>Cu$_3$P NA/CF</td>
<td>0.1 M PBS (0.1 M NaNO$_2$)</td>
<td>95.5 ± 2.1 μmol h$^{-1}$ cm$^{-2}$</td>
<td>91.2 ± 2.5</td>
<td>6</td>
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<tr>
<td>Cu$<em>{80}$Ni$</em>{20}$</td>
<td>1.0 M NaOH (20 mM NaNO$_2$)</td>
<td>/</td>
<td>87.6</td>
<td>7</td>
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<tr>
<td>Cu phthalocyanine complexes</td>
<td>0.1 M KOH (NaNO$_2$)</td>
<td>/</td>
<td>78</td>
<td>8</td>
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<tr>
<td>[Co(DIM)Br$_2$]$^+</td>
<td>0.1 M NaNO$_2$</td>
<td>/</td>
<td>88</td>
<td>9</td>
</tr>
<tr>
<td>FeN$_3$H$_2$</td>
<td>1.0 M MOPS</td>
<td>/</td>
<td>18</td>
<td>10</td>
</tr>
<tr>
<td>Co$_3$O$_4$@NiO</td>
<td>0.5 M Na$_2$SO$_4$ (2.36 mM NaNO$_3$)</td>
<td>/</td>
<td>55.0</td>
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</tr>
<tr>
<td>System</td>
<td>Solution Details</td>
<td>Activity (μmol h(^{-1}) cm(^{-2}))</td>
<td>Current Efficiency (%)</td>
<td>Turnover Number (h(^{-1}) mg(_{cat.}))</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------------------------------------------------------</td>
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<td>---------------------------------------------</td>
</tr>
<tr>
<td>Co/CoO NSA</td>
<td>0.1 M Na(_2)SO(_4) (200 ppm NaNO(_3))</td>
<td>194.5</td>
<td>93.8</td>
<td>12</td>
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<tr>
<td>Co(_2)AlO(_4)</td>
<td>0.1 M PBS (0.1 M NaNO(_3))</td>
<td>464.7</td>
<td>92.6</td>
<td>13</td>
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<tr>
<td>Pd nanodots on Zr-MOF</td>
<td>0.1 M Na(_2)SO(_4) (500 ppm NO(_3)^–)</td>
<td>16.99</td>
<td>58.1</td>
<td>14</td>
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<tr>
<td>Ru(_x)O(_y) clusters on</td>
<td>0.1 M Na(_2)SO(_4) (100 ppm NO(_3)^–)</td>
<td>16.1</td>
<td>58.8</td>
<td>15</td>
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<tr>
<td>Ni-MOF</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Fe single atom catalyst</td>
<td>0.10 M K(_2)SO(_4) (0.50 M KNO(_3))</td>
<td>~1176</td>
<td>~75</td>
<td>16</td>
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<tr>
<td>Ag@NiO/CC</td>
<td>0.1 M NaOH (0.1 M NaNO(_3))</td>
<td>135.1</td>
<td>75.8</td>
<td>17</td>
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</table>
References


