Experimental Section

Materials: Sodium nitrate (NaNO₃, 99.0%), sodium nitrite (NaNO₂, 99.0%), sodium sulfate (Na₂SO₄), ammonium chloride (NH₄Cl), sodium hydroxide (NaOH), sodium salicylate (C₇H₅NaO₃), trisodium citrate dihydrate (C₆H₅Na₃O₇·2H₂O), p-dimethylaminobenzaldehyde (C₉H₁₁NO), sodium nitroferricyanide dihydrate (C₅FeN₆Na₂O·2H₂O), Na¹⁵NO₃, deuterium oxide (D₂O), 0.8 wt% sulfamic acid solution (H₃NO₃S) and sodium hypochlorite solution (NaClO) were purchased from Aladdin Ltd. (Shanghai, China). Cobalt chloride hexahydrate (CoCl₂·6H₂O), and ammonium sulfate ((NH₄)₂SO₄) were purchased from Chengdu Kelong Chemical Regent Co. Ltd. Sodium hypophosphite (NaH₂PO₂) was bought from Shanghai Macklin Biochemical Co., Ltd. Sulfuric acid (H₂SO₄), hydrogen peroxide (H₂O₂), hydrochloric acid (HCl), hydrazine monohydrate (N₂H₄·H₂O) and ethylalcohol (C₂H₅OH) were bought from Beijing Chemical Corporation. (China). chemical Ltd. in Chengdu. Titanium plate (0.2 mm thick) was purchased from Qingyuan Metal Materials Co., Ltd (Xingtai, China). All reagents used in this work were analytical grade without further purification.

Preparation of Co–P/TP: In brief, CoCl₂·6H₂O (1.19 g), (NH₄)₂SO₄ (3 g), C₆H₅Na₃O₇·2H₂O (3 g) and NaH₂PO₂ (3 g) were dissolved in 50 mL ultrapure water as the electroplating solution. Then, a piece of TP (1 × 1 cm²) as the working electrode was polarized at −1.0 V (vs. SCE) in the above solution for 30 min, with the use of a carbon rod as the auxiliary electrode and a SCE as the reference electrode to obtain Co–P/TP.

Characterizations: XRD data were acquired by a LabX XRD-6100 X-ray diffractometer with a Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (SHIMADZU, Japan). SEM measurements were carried out on a GeminiSEM 300 scanning electron microscope (ZEISS, Germany) at an accelerating voltage of 5 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. The ion chromatography data were collected on Metrohm 940 Professional IC Vario. All $^1$H nuclear magnetic resonance ($^1$H NMR) spectra were collected on Varian VNMRS 600 MHz (the USA) with water suppression.

**Electrochemical measurements:** All electrochemical measurements were carried on the CHI760E electrochemical workstation (Shanghai, Chenhua) using a standard three-electrode setup. Electrolyte solution was Ar-saturated of 0.2 M Na$_2$SO$_4$ with 200 ppm NO$_3^-$, using Co–P/TP (1 × 1 cm$^2$) as the working electrode, a carbon rod as the counter electrode and SCE as the reference electrode. We use a H-type electrolytic cell separated by a Nafion 117 Membrane which was protonated by boiling in ultrapure water, H$_2$O$_2$ (5%) aqueous solution and 0.5 M H$_2$SO$_4$ at 80 °C for another 2 h, respectively. All the potentials reported in our work were converted to reversible hydrogen electrode (RHE) scale via calibration with the following equation: $E_{(\text{RHE})} = E_{(\text{vs. SCE})} + 0.0591 \times \text{pH} + 0.2415$ V and the presented current density was normalized to the geometric surface area.

**Determination of NH$_3$ using the indophenol blue method:** Concentration of produced NH$_3$ was determined by spectrophotometry measurement with indophenol blue method (the obtained electrolyte was diluted 100 times). In detail, 4 mL electrolyte was obtained from the cathodic chamber and 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 catalyst solution Na$_2$Fe(CN)$_5$NO·2H$_2$O (1 wt%) for 1 h. The concentration-absorbance curve was calibrated using the standard NH$_4$Cl solution with NH$_3$ concentrations of 0.0, 0.05, 0.10, 0.15, 0.20, 0.25 and 0.50 µg mL$^{-1}$ in 0.2 M Na$_2$SO$_4$. These solutions were identified via UV-Vis spectroscopy at the wavelength of 660 nm. The concentration-absorbance curves were calibrated using standard NH$_3$ solution with a serious of concentrations. The fitting curve ($y = 0.62334x + 0.02668$, $R^2 = 0.99983$) shows good linear relation of absorbance value with NH$_3$ concentration.
Determination of NH₃ using the ¹H NMR spectroscopy: The amount of produced NH₃ was also determined by the ¹H NMR spectroscopy. After chronoamperometry tests in Ar-saturated 0.2 M Na₂SO₄ with 200 ppm NO₃⁻ at -0.6 V vs. RHE for 2h, the pH of the post-electrolysis electrolyte was adjusted to be 2 with a 0.5 M HCl solution. Then, 0.5 mL of electrolyte and 0.05 mL of deuterium oxide (D₂O) were added into the NMR tube for further NMR (600 MHz) detection. The isotopic labeling experiment was conducted to confirm the origin of ammonium using Ar-saturated 0.2 M Na₂SO₄ with 200 ppm ¹⁵NO₃⁻ as the electrolyte in the same operation described above.

Determination of NO₃⁻: The amount of NO₃⁻ was analyzed by spectrophotometry.² Firstly, 1.0 mL electrolyte was taken out from the electrolytic cell and diluted to 5 mL to detection range. Then, 0.1 mL 1 M HCl and 0.01 mL 0.8 wt% H₃NO₃S solution were added into the aforementioned solution. After 15 minutes, the absorbance was detected by UV-Vis spectrophotometry at a wavelength of 220 nm and 275 nm. The final absorbance of NO₃⁻ was calculated based on the following equation: A=A₂₂₀nm – 2A₂₇₅nm. The calibration curve can be obtained through different concentrations of NaNO₃ solutions and the corresponding absorbance. The fitting curve (y = 0.05841x + 0.0027, R² = 0.99936) shows good linear relation of absorbance value with NO₃⁻ concentration.

Determination of N₂H₄: In this work, we used the method of Watt and Chrisp³ to estimate whether N₂H₄ produced. The chromogenic reagent was a mixed solution of 5.99 g C₉H₁₁NO, 30 mL HCl and 300 mL C₂H₅OH. In detail, 1 mL electrolyte was added into 1 mL prepared color reagent and stirred 15 min in the dark. The absorbance at 455 nm was measured to quantify the N₂H₄ concentration with a standard curve of hydrazine (y = 0.65546x + 0.0556, R² = 0.99998).

Calculations of the conversion rate, FE and NH₃ yield rate:
The conversion rate of NO₃⁻ is calculated using the following equation:
Conversion rate = $\Delta[\text{NO}_3^-] / [\text{NO}_3^-] \times 100\%$ (1)

FE toward NH$_3$ via NO$_3^-$ reduction reaction (NO$_3^-$RR) was calculated by the following equation:

$$\text{FE} = \left(8 \times F \times [\text{NH}_3] \times V\right) / \left(M_{\text{NH}_3} \times Q\right) \times 100\%$$ (2)

FE toward NH$_3$ via NO$_2^-$RR was calculated by the following equation:

$$\text{FE} = \left(6 \times F \times [\text{NH}_3] \times V\right) / \left(M_{\text{NH}_3} \times Q\right) \times 100\%$$ (3)

(Note that the reduction of NO$_3^-$ / NO$_2^-$ to NH$_3$ consumes eight / six electrons.)

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

$$\text{NH}_3 \text{ yield rate} = \left(\left([\text{NH}_3] \times V\right) / \left(M_{\text{NH}_3} \times t \times A\right)\right)$$ (4)

Where $F$ is the Faradic constant (96485 C mol$^{-1}$), $[\text{NH}_3]$ is the measured NH$_3$ concentration, $[\text{NO}_3^-]$ is the initial concentration of NO$_3^-$, $\Delta[\text{NO}_3^-]$ is the concentration difference of NO$_3^-$ before and after electrolysis, $V$ is the volume of electrolyte in the anode compartment (35 mL), $M_{\text{NH}_3}$ is the molar mass of NH$_3$, $Q$ is the total quantity of applied electricity; $t$ is the electrolysis time and $A$ is the loaded area of catalyst (1 $\times$ 1 cm$^2$).
**Fig. S1.** SEM and EDX elemental mapping images of Co–P/TP.
Fig. S2. (a) UV-Vis absorption spectra and corresponding (b) calibration curve used for calculation of NH₃ concentration.
Fig. S3. (a) UV-Vis absorption spectra and corresponding (b) calibration curve used for calculation of N$_2$H$_4$ concentration.
Fig. S4. (a) UV-Vis absorption spectra and corresponding (b) calibration curve used for calculation of NO$_3^-$ concentration.
Fig. S5. LSV curves of Co–P/TP tested in 0.2 M Na₂SO₄ with and without 200 ppm NO₃⁻.
**Fig. S6.** $^1$H NMR spectrum for the products using Na$^{14}$NO$_3$ and Na$^{15}$NO$_3$ as nitrogen sources.
Fig. S7. (a) Ion chromatograms of NH₄⁺ with different concentrations in 0.2 M Na₂SO₄ and (b) corresponding standard curve. (c) Ion chromatograms for the electrolytes at a series of potentials after 2 h electrolysis. (d) NH₃ yield rates and FEs of Co–P/TP at corresponding potentials.
Fig. S8. UV-Vis absorption spectra of the electrolytes estimated by the method of Watt and Chrisp after 2 h electrolysis at each given potential under ambient conditions.
Fig. S9. (a) Time-dependent current density curves of Co−P/TP and bare TP for NO$_3^−$ RR at −0.3 V vs. RHE in 0.2 M Na$_2$SO$_4$ with 200 ppm NO$_3^−$. (b) UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after NO$_3^−$ RR electrolysis.
Fig. S10. (a) UV-Vis absorption spectra and corresponding (b) calibration curve used for calculation of NH$_3$ concentration. Electrochemical tests of Co–P/TP in a two-compartment cell toward NO$_3^-$RR in 0.2 M PBS with 200 ppm NO$_3^-$ (c) UV-Vis absorption spectra of NH$_3$. (d) Calculated FEs and NH$_3$ yield rates of Co–P/TP toward NO$_3^-$ RR at different given potentials.
Fig. S11. LSV curves of Co–P/TP tested in 0.2 M Na$_2$SO$_4$ with and without 200 ppm NO$_2$.
Fig. S12. (a) Time-dependent current density curves of Co–P/TP and bare TP for NO$_2^-$ RR at –0.2 V in 0.2 M Na$_2$SO$_4$ with 200 ppm NO$_2^-$.. (b) UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after NO$_2^-$ RR electrolysis.
Fig. S13. UV-Vis absorption spectra for different operating conditions.
Figure S14. (a) Chronoamperometry curves for Co–P/TP during recycling tests toward NO$_3$–RR at $-0.3$ V in 0.2 M Na$_2$SO$_4$ with 200 ppm NO$_3$–. (b) UV-Vis absorption spectra for NH$_3$ and during recycling tests for NO$_3$–RR at $-0.3$ V in 0.2 M Na$_2$SO$_4$ with 200 ppm NO$_3$–.
Fig. S15. Photographs of pH test strips with 0.5 h of bulk electrolysis and 16 h of bulk electrolysis.

\[
\text{NH}_3\cdot\text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^-, \quad \text{in neutral/alkaline media}
\]

16 h of bulk electrolysis (pH=12)

0.5 h of bulk electrolysis (pH=7)
Fig. S16. XRD patterns for Co–P/TP before and after NO$_3^-$RR.
Fig. S17. XPS spectra in the Co 2p and P 2p regions for Co–P/TP before and after NO$_3^-$ RR.
Table S1. Comparison of catalytic performances of Co–P/TP with other reported NO$_3^-$ RR electrocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Performance</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co–P/TP</td>
<td>0.2 M Na$_2$SO$_4$ (200 ppm NO$_3^-$)</td>
<td>NH$<em>3$ yield rate: 416.0 ± 7.2 µg h$^{-1}$ cm$^{-2}$ (−0.6 V), FE$</em>{NH3}$: 93.6 ± 3.3% (−0.3 V), Conversion rate$_{NH3}$: 86.9% (−0.3 V, 10 h)</td>
<td>This work</td>
</tr>
<tr>
<td>Cu nanosheets</td>
<td>0.1 M KOH</td>
<td>NH$<em>3$ yield rate: 390.1 µg h$^{-1}$ mg$^{-1}$ FE$</em>{NH3}$: 99.7%</td>
<td>4</td>
</tr>
<tr>
<td>PTCDA/O-Cu</td>
<td>0.1 M PBS (500 ppm NO$_3^-$)</td>
<td>NH$<em>3$ yield rate: 436 ± 85 µg h$^{-1}$ cm$^{-2}$ FE$</em>{NH3}$: 85.9%</td>
<td>5</td>
</tr>
<tr>
<td>Pd-In/c-Al$_2$O$_3$</td>
<td>3.28 mM NaHCO$_3$ with nitrate-reservoir</td>
<td>FE$_{NH3}$: 71.5%</td>
<td>6</td>
</tr>
<tr>
<td>Co$_3$O$_4$@NiO HNTs</td>
<td>0.5 M Na$_2$SO$_4$ (200 ppm NO$_3^-$)</td>
<td>NH$<em>3$ yield rate: 6.93 mmol h$^{-1}$ g$^{-1}$ FE$</em>{NH3}$: 54.97%</td>
<td>7</td>
</tr>
<tr>
<td>NiPc complex</td>
<td>0.1 M KOH, in the presence of NO$_3^-$</td>
<td>FE$_{NH3}$: 85%</td>
<td>8</td>
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<tr>
<td>Cu</td>
<td>1 M NaOH (0.1 M NaNO$_3$)</td>
<td>FE$_{NH3}$: 79%</td>
<td>9</td>
</tr>
<tr>
<td>Cu$<em>{50}$Ni$</em>{50}$</td>
<td>1 M KOH (10 mM KNO$_3$)</td>
<td>FE$_{NH3}$: 84 ± 2%</td>
<td>10</td>
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<tr>
<td>Ti/GC</td>
<td>KOH (−0.1 to 0.6 M NO$_3^-$)</td>
<td>FE$_{NH3}$: 82%</td>
<td>11</td>
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<tr>
<td>NTEs</td>
<td>NaCl (0.65 mM NaNO$_3$)</td>
<td>FE$_{NH3}$: 5.6%</td>
<td>12</td>
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</table>
Table S2. Comparison of the catalytic performances of Co–P/TP with other reported NO$_2^-$ RR electrocatalysts under ambient conditions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Performance</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co–P/TP</td>
<td>0.2 M Na$_2$SO$_4$ (200 ppm NO$_2^-$)</td>
<td>NH$<em>3$ yield rate: 661.0 ± 20.1 μg h$^{-1}$ cm$^{-2}$ (–0.6 V), FE$</em>{NH3}$: 93.3 ± 3.2% (–0.2 V)</td>
<td>This work</td>
</tr>
<tr>
<td>MnO$_2$ nanoarrays</td>
<td>0.1 M Na$_2$SO$_4$ (NaNO$_2$)</td>
<td>NH$<em>3$ yield rate: $3.09 \times 10^{-11}$ mol s$^{-1}$ cm$^{-2}$, FE$</em>{NH3}$: 6%</td>
<td>13</td>
</tr>
<tr>
<td>Cobalt-tripeptide complex</td>
<td>1.0 M MOPS (1.0 M NaNO$_2$)</td>
<td>NH$<em>3$ yield rate: $3.01 \times 10^{-10}$ mol s$^{-1}$ cm$^{-2}$, FE$</em>{NH3}$: 90 ± 3%</td>
<td>14</td>
</tr>
<tr>
<td>Poly-NiTRP complex</td>
<td>0.1 M NaClO$_4$ (NaNO$_2$)</td>
<td>NH$_3$ yield rate: 1.1 mM</td>
<td>15</td>
</tr>
<tr>
<td>Cu phthalocyanine complexes</td>
<td>0.1 M KOH (NaNO$_2$)</td>
<td>FE$_{NH3}$: 78%</td>
<td>16</td>
</tr>
<tr>
<td>[Co(DIM)Br$_2$]$^+$ (Carbon rod working electrode)</td>
<td>0.1 M solution of NaNO$_2$</td>
<td>FE$_{NH3}$: 88%</td>
<td>17</td>
</tr>
<tr>
<td>Cu$<em>{80}$Ni$</em>{20}$</td>
<td>1.0 M NaOH (20 mM NaNO$_2$)</td>
<td>FE$_{NH3}$: 87.6%</td>
<td>18</td>
</tr>
</tbody>
</table>
References

15  P. Dreyse, M. Isaacs, K. Calfumán, C. Cáceres, A. Aliaga, M. J. Aguirre and...

