Electronic Supplementary Information

Experimental Section

Materials: Sodium hydroxide (NaOH), ammonium chloride (NH₄Cl), potassium sulfate (K₂SO₄), hydrochloric acid (HCl), salicylic acid (C₇H₆O₃), sodium citrate dehydrate (C₆H₅Na₃O₇·2H₂O), p-dimethylaminobenzaldehyde (C₉H₁₁NO), Nafion solution (5 wt %), anhydrous alcohol, sodium nitroferricyanide dihydrate (C₅FeN₆Na₂O·2H₂O), sodium nitrite (NaNO₂) and sodium hypochlorite (NaClO) were purchased from Aladdin Ltd. (Shanghai, China). Nitric acid (HNO₃), sulfuric acid (H₂SO₄), hydrogen peroxide (H₂O₂), hydrazine monohydrate (N₂H₄·H₂O), phosphoric acid (H₃PO₄) and ethyl alcohol (C₂H₅OH) were purchased from Beijing Chemical Corp. (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.

Synthesis of TiO₂-x NBA/TP: The fabrication process of TiO₂-x NBA/TP were as follows: Firstly, titanium plates were cut into small pieces (2.0 × 4.0 cm²) and sonicated in acetone, ethanol, and distilled water for 15 min, respectively. After then, they were put into 40 mL of 5 M NaOH aqueous solution in 50 mL Teflon-lined autoclave. The autoclave was kept in an electric oven at 180°C for 24 h. After the autoclave was cooled down naturally to room temperature, the samples were moved out, washed with deionized water and ethanol several times and dried at 60 °C for 30 min. Then the samples were immersed in 1 M HCl for 1 h in order to exchange Na⁺ with H⁺. The as-prepared H₂Ti₂O₅·H₂O NBA/TP were rinsed with deionized water and ethanol several times and dried at 60 °C for 30 min. Subsequently, H₂Ti₂O₅·H₂O NBA/TP were annealed in a tubular furnace at 500 °C for 2 h. After cooling to room temperature, TiO₂-x NBA/TP were finally obtained.

Preparation of the TiO₂/TP: Typically, 10 mg of the commercial TiO₂ nanoparticle powder and 10μL of Nafion solution (5 wt %) were scattered in a mixture of 500μL water and 500μL anhydrous alcohol by ultrasonic treatment for 1 h to form a homogeneous liquid. Then, 50μL of the dispersion was loaded on a TP with an area of 1 × 0.5 cm² and dried in the N₂ atmosphere at 60 °C for 1 h.

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 Gemini SEM 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 were measured on UV-Vis spectrophotometer. TEM image was obtained from a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. EPR spectrum was recorded on a Bruker EMX spectrometer at room temperature.

**Electrochemical measurements:** All electrochemical measurements were carried on the CHI660E electrochemical workstation (Shanghai, Chenhua) using a standard three-electrode setup. Electrolyte solution was Ar-saturated of 0.1 M NaOH with 0.1 M NO$_2^-$, using TiO$_{2-x}$ NBA/TP (1.0 × 0.5 cm$^2$) as the working electrode, graphite rod as the counter electrode and a Hg/HgO 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 via calibration with the following equation: $E_{(RHE)} = E_{(Hg/HgO)} + (0.098 + 0.0591 \times \text{pH}) \text{ V}$ and the presented current density was normalized to the geometric surface area.

**Determination of NH$_3$:** The NH$_3$ concentration in the solution was determined by colorimetry (the obtained electrolyte was diluted 40 times) using the indophenol blue method.$^1$ In detail, 2 mL of the solution after reaction, and 2 mL of 1 M NaOH chromogenic solution containing 5% salicylic acid and 5% sodium citrate. Then, 1 mL oxidizing solution of 0.05 M NaClO and 0.2 mL catalyst solution of C$_5$FeN$_6$Na$_2$O (1 wt%) were added to the above solution. After standing in the dark for 2 h, the UV-Vis absorption spectra were measured. The concentration of NH$_3$ was identified using the absorbance at a wavelength of 655 nm. The concentration-absorbance curve was calibrated using the standard NH$_4$Cl solution with NH$_3$ concentrations of 0.25, 0.50, 0.75, 1.0, 1.50, 2.50, 3.50 and 5.0 ppm in 0.1 M NaOH solution. The fitting curve ($y = 0.3896 x + 0.0178, R^2 = 0.9996$) shows good linear relation of absorbance value with NH$_3$ concentration.

**Determination of N$_2$H$_4$:** In this work, we used the method of Watt and Chrisp to estimate whether N$_2$H$_4$ produced.$^2$ The chromogenic reagent was a mixed solution of 5.99 g C$_9$H$_{11}$NO, 30 mL HCl and 300 mL C$_2$H$_5$OH. In detail, 1 mL electrolyte was added into 1 mL prepared color reagent and standing for 15 min in the dark. The absorbance at 455 nm was measured to quantify the N$_2$H$_4$ concentration with a standard curve of hydrazine ($y = 0.6497 x + 0.07655, R^2 = 0.9995$).

**Calculations of the FE and NH$_3$ yield rate:**

$^{\text{FE toward NH}_3}$ via NO$_2$RR was calculated by the following equation (the reduction of NO$_2^-$ to...
NH₃ consumes six electrons):

$$\text{FE} = \frac{(6 \times F \times [\text{NH}_3] \times V)}{(M_{\text{NH}_3} \times Q)} \times 100\% \quad (1)$$

NH₃ yield rate was calculated using the following equation:

$$\text{NH}_3 \text{ yield rate} = \frac{([\text{NH}_3] \times V)}{(M_{\text{NH}_3} \times t \times A)} \quad (2)$$

Where $F$ is the Faradic constant (96500 C mol⁻¹), $[\text{NH}_3]$ is the measured NH₃ concentration, $V$ is the volume of electrolyte in the cathode compartment (70 mL), $M_{\text{NH}_3}$ is the molar mass of NH₃, $Q$ is the total quantity of applied electricity; $t$ is the electrolysis time and $A$ is the loaded area of catalyst (1.0 × 0.5 cm²).

**DFT calculation details:**

First-principles calculations with spin-polarized were carried out based on density functional theory (DFT) implemented in the VASP package, and the interaction between valence electrons and ionic core were expanded using the projector augmented wave (PAW) approach with a cutoff of 450 eV. Perdew-Burke-Ernzerhof functional (PBE) with semi-empirical corrections of DFT-D3 was adopted to describe exchange-correlation functional effect based on general gradient approximation (GGA). TiO₂(101) surface was modeled using a 2 × 2 supercell with three trilayers (O-Ti-O), of which the bottom trilayer was fixed. The thickness of the vacuum region is > 15 Å to avoid the spurious interaction. Hubbard U model was implemented with an effective $U = 4$ eV for Ti 3d orbitals. The Brillouin zone was sampled by 2 × 3 × 1 special k-points using the Monkhorst Pack scheme for structural configuration optimizations. The force convergence thresholds are 0.02 eV/Å and the total energy less than 1E-5 eV, respectively. The theoretical calculation results were processing and analyzed by VASPKIT software.
Fig. S1 Cross-section SEM image of TiO$_{2-x}$ NBA/TP.
Fig. S2 The ratio of Ti and O of TiO$_{2-x}$ NBA/TP.
Fig. S3 EPR spectra of the commercial TiO$_2$ (black curve) and the TiO$_{2-x}$ NBA (red curve).
Fig. S4 LSV curves of TiO$_2$/TP and bare TP in 0.1 M NaOH with and without 0.1 M NO$_2^-$.
Fig. S5 (a) UV-Vis absorption spectra and corresponding (b) calibration curve used for calculation of NH$_3$ concentration.
Fig. S6 (a) UV-Vis absorption spectra and corresponding (b) calibration curve used for calculation of $N_2H_4$ concentration.
Fig. S7 Calculated NH$_3$ yields and FEs of TiO$_{2-x}$ NBA/TP, TiO$_2$/TP and bare TP toward NO$_2$RR in 0.1 M NaOH with 0.1 M NO$_2^-$ at −0.7 V.
Fig. S8 (a) LSV curves of TiO$_{2-x}$ NBA/TP in 0.1 M K$_2$SO$_4$ in the presence and absence of 0.1 M NO$_2^-$. (b) CA curves (from −0.4 V to −0.9 V) and (c) corresponding UV-Vis spectra of TiO$_{2-x}$ NBA/TP. (d) Calculated NH$_3$ yields and FEs of TiO$_{2-x}$ NBA/TP at different given potentials.
**Fig. S9** UV-Vis absorption spectra of the electrolytes estimated by the method of Watt and Chrissp for the calculation of \( \text{N}_2\text{H}_4 \) concentration.
Fig. S10 (a) Chronoamperometry curves and (b) corresponding UV-Vis absorption spectra of TiO$_{2-x}$ NBA/TP for electrochemical catalytic production of NH$_3$ during cycling tests in 0.1 M NaOH with 0.1 M NO$_2^-$ at $-0.7$ V.
Fig. S11 LSV curves of TiO$_{2-x}$ NBA/TP before and after 12 h electrolysis in 0.1 M NaOH with 0.1 M NO$_2^-$.
**Fig. S12** NH$_3$ yields and FEs for TiO$_{2-x}$ NBA/TP before and after 12 h electrolysis in 0.1 M NaOH with 0.1 M NO$_2^-$ at −0.7 V.
Fig. S13 (a) SEM and (b) TEM images for TiO$_{2-x}$ NBA after 12 h electrolysis.
Fig. S14 XRD patterns for TiO$_{2-x}$ NBA/TP.
Fig. S15 Top views of TiO$_2$ (101) slab model with V$_{O}$. 
Fig. S16 DOS for TiO$_2$ (101) slab model without and with V$_O$. 
Fig. S17 DOS for Ti$_{5c}^{3+}$ and Ti$_{4c}^{3+}$ atoms induced by O$_2$ V$_0$, respectively.
Fig. S18 Calculated free energies for NO$_2^-$ adsorption on TiO$_2$ (101) slab model without and with V$_O$ and corresponding atomic configurations.
**Fig. S19** Top views of NO\(_2^-\) adsorption on TiO\(_2\) (101) surface with V\(_O\).
Fig. S20 Top views of NO$_2^-$ adsorption on pristine TiO$_2$ (101) surface.
Fig. S21 (a) Free energy diagram of different intermediates generated during the NO$_2$RR on TiO$_{2-x}$ (101) along with the optimal pathway and (b) corresponding atomic configurations.
**Table S1** Comparison of the catalytic performances of TiO$_{2-x}$ NBA/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>
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</thead>
<tbody>
<tr>
<td>TiO$_{2-x}$ NBA/TP</td>
<td>0.1 M NaOH (NaNO$_2$)</td>
<td>NH$<em>3$ yield rate: 7898 μg h$^{-1}$ cm$^{-2}$, FE$</em>{NH_3}$: 92.7%</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 × 10$^{-11}$ mol s$^{-1}$ cm$^{-2}$, FE$</em>{NH_3}$: 6%</td>
<td>10</td>
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<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 × 10$^{-10}$ mol s$^{-1}$ cm$^{-2}$, FE$</em>{NH_3}$: 90 ± 3%</td>
<td>11</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>12</td>
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<tr>
<td>Cu phthalocyanine complexes</td>
<td>0.1 M KOH (NaNO$_2$)</td>
<td>FE$_{NH_3}$: 78%</td>
<td>13</td>
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<tr>
<td>[Co(DIM)Br$_2$]$^+$</td>
<td>0.1 M solution of NaNO$_2$</td>
<td>FE$_{NH_3}$: 88%</td>
<td>14</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>FE$_{NH_3}$: 87.6%</td>
<td>15</td>
</tr>
<tr>
<td>Cu$_3$P nanowire array</td>
<td>0.1 M PBS (0.1M NaNO$_2$)</td>
<td>NH$<em>3$ yield rate: 1626.6 ± 36.1 μg h$^{-1}$ cm$^{-2}$, FE$</em>{NH_3}$: 91.2 ± 2.5%</td>
<td>16</td>
</tr>
<tr>
<td>CoP nanoarray</td>
<td>0.1 M PBS (500 ppm NaNO$_2$)</td>
<td>NH$<em>3$ yield rate: 2260.7 ± 51.5 μg h$^{-1}$ cm$^{-2}$, FE$</em>{NH_3}$: 90 ± 2.3%</td>
<td>17</td>
</tr>
<tr>
<td>Ni$_2$P nanosheet array</td>
<td>0.1 M PBS (200 ppm NaNO$_2$)</td>
<td>NH$<em>3$ yield rate: 2692.2 ± 92.1 μg h$^{-1}$ cm$^{-2}$, FE$</em>{NH_3}$: 90.2 ± 3%</td>
<td>18</td>
</tr>
<tr>
<td>Oxo-MoS$_x$</td>
<td>0.1 M NaNO$_2$ in 0.2 M citric acid (pH = 5)</td>
<td>FE$_{NH_3}$: 13.5%</td>
<td>19</td>
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</table>
Table S2 Standard electrode potentials for nitrite redox reactions.

<table>
<thead>
<tr>
<th>Chemical reaction equation</th>
<th>Standard electrode potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2 \text{NO}_2^- + 8 \text{H}^+ + 6 \text{e}^- \rightleftharpoons \text{N}_2 \ (g) + 4 \text{H}_2\text{O})</td>
<td>(E^0 = 1.520 \text{ V (vs. NHE)})</td>
</tr>
<tr>
<td>(2 \text{NO}_2^- + 2 \text{H}^+ + \text{e}^- \rightleftharpoons \text{NO} \ (g) + \text{H}_2\text{O})</td>
<td>(E^0 = 1.202 \text{ V (vs. NHE)})</td>
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<tr>
<td>(2 \text{NO}_2^- + 6 \text{H}^+ + 4 \text{e}^- \rightleftharpoons \text{N}_2\text{O} \ (g) + 3 \text{H}_2\text{O})</td>
<td>(E^0 = 1.396 \text{ V (vs. NHE)})</td>
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<tr>
<td>(2 \text{NO}_2^- + 6 \text{H}^+ + 4 \text{e}^- \rightleftharpoons \text{NH}_3\text{OH}^+ + \text{H}_2\text{O})</td>
<td>(E^0 = 0.673 \text{ V (vs. NHE)})</td>
</tr>
<tr>
<td>(2 \text{NO}_2^- + 8 \text{H}^+ + 6 \text{e}^- \rightleftharpoons \text{NH}_4^+ + 2 \text{H}_2\text{O})</td>
<td>(E^0 = 0.897 \text{ V (vs. NHE)})</td>
</tr>
<tr>
<td>(2 \text{NO}_2^- \rightleftharpoons \text{NO}_2 + \text{e}^-)</td>
<td>(E^0 = 0.780 \text{ V (vs. NHE)})</td>
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</table>
References