Electronic Supplementary Information

Experimental Section

Materials: Titanium butoxide (C₁₆H₃₆O₄Ti), Para-(dimethylamino) benzaldehyde (C₉H₁₁NO), sodium nitroferricyanide (III) dihydrate (Na₂Fe(CN)₅NO·2H₂O), hydrogen peroxide (H₂O₂) and Nafion (5 wt%) were purchased from Aladdin Ltd. (Shanghai, China). Sulfuric acid (H₂SO₄), ammonium chloride (NH₄Cl), hydrazine hydrate (N₂H₄·H₂O), sodium hypochlorite (NaClO), sodium hydroxide (NaOH), sodium salicylate (C₇H₅O₃Na), sodium sulfate (Na₂SO₄), hydrochloric acid (HCl), ethanol (CH₃CH₂OH) and carbon paper were bought from Beijing Chemical Corporation. The water used throughout all experiments was purified through a Millipore system.

Preparation of C-TiO₂ nanoparticles: Carbon doped TiO₂ nanoparticles have been prepared by a facile calcination assisted hydrothermal method. In a typical hydrothermal synthesis process, 13mL titanium butoxide was added dropwise to 35mL water/ethanol (5:30) mixed solution with continuous stirring for 30 min to form a milk-white solution. Then, the solution was transferred into a 50 mL Teflon-lined stainless steel autoclave and heated at 190°C for 2h. Subsequently, the products were centrifuged, washed with ultrapure water and ethanol three times, respectively, followed by drying in a vacuum oven at 60°C overnight. The as-prepared white precursor powder was calcined at 265°C for 1 h in a muffle furnace to obtain the final products. For comparison, the pure TiO₂ sample was prepared under the same condition without ethanol and calcination.

Preparation of C-TiO₂/CP electrode: 10 mg C-TiO₂ powders and 20 μL of Nafion solution (5 wt%) were dispersed in 980 μL mixed solution contain 735 μL ethanol and 245 μL H₂O by 2 h sonication to form a homogeneous ink. Then 10 μL catalyst ink was loaded on a 1 × 1 cm² carbon paper and dried under ambient condition.

Characterizations: XRD data were recorded using a Shimazu XRD-6100
diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (SHIMADZU, Japan). SEM images were obtained from a tungsten lamp-equipped SU3500 scanning electron microscope at an accelerating voltage of 20 kV (HITACHI, Japan). TEM images were collected from a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) operated at 200 kV. XPS data were acquired on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source. The data of absorbance and UV-vis diffuse reflectance spectra were measured on a SHIMADZU UV-1800 ultraviolet-visible spectrophotometer. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer Model Pyris1 TGA apparatus at a heating rate of 10 °C min⁻¹ in nitrogen atmosphere.

**Electrocatalytic N₂ reduction measurements:** The N₂ reduction experiments were carried out in a two-compartment cell under ambient condition, which was separated by Nafion 211 membrane. The membrane was treated in H₂O₂ (5%) aqueous solution at 80 °C for 1 h and dipped in 0.1 M H₂SO₄ at 80°C for another 1 h. And finally, the membrane was treated in ultrapure water at 80°C for 6h. The electrochemical experiments were carried out with a CHI 660E electrochemical analyzer using a three-electrode configuration with C-TiO₂/CP electrode, graphite rod and Ag/AgCl electrode (saturated KCl electrolyte) as working electrode, counter electrode and reference electrode, respectively. The potentials reported in this work were converted to reversible hydrogen electrode (RHE) scale via calibration with the following equation: in 0.1 M Na₂SO₄ aqueous solution, E (vs. RHE) = E (vs. Ag/AgCl) + 0.059 × pH + 0.197 V. The presented current density was normalized to the geometric surface area. For electrochemical N₂ reduction, chronoamperometry tests were conducted in N₂-saturated 0.1 M Na₂SO₄ solution (40 mL). All experiments were operated under room temperature.

**Determination of NH₃:** Concentration of produced NH₃ was spectrophotometrically determined by spectrophotometry measurement with salicylic acid. Typically, 4 mL of the electrolyte was taken from the cathodic chamber. Then 50 uL of NaClO (4.5%) and NaOH (0.75 M), 500 µL of C₇H₅O₃Na (0.4 M) and NaOH (0.32 M) and 50 uL of
1% Na₂Fe(CN)₆NO·2H₂O were successively added into the above solution. Absorbance measurements were performed after 2 h at a wavelength of 660 nm. The concentration-absorbance curves were calibrated using standard NH₄⁺ solution with a series of concentrations. The fitting curve (y = 0.519x + 0.012, R² = 0.999) shows good linear relation of absorbance value with NH₄Cl concentration.

**Determination of N₂H₄:** The N₂H₄ presented in the electrolyte was estimated by the method of Watt and Chrisp.² A mixed solution of C₉H₁₁NO (5.99 g), HCl (concentrated, 30 mL) and ethanol (300 mL) was used as a color reagent. Typically, 5 mL electrolyte was removed from the cathodic chamber, after that, added into 5 mL above prepared color reagent and stirring 20 min at room temperature. The absorbance of the resulting solution was measured at 455 nm. The concentration absorbance curves were calibrated using standard N₂H₄·H₂O solution with a series of concentrations. The fitting curve (y = 0.566x + 0.037, R² = 0.999) shows good linear relation of absorbance value with N₂H₄ concentration.

**Determination of FE:** The Faradaic efficiency (FE) for N₂ reduction was defined as the amount of electric charge used for synthesizing NH₃ divided the total charge passed through the electrodes during the electrolysis. The total amount of NH₃ produced was measured using colorimetric methods. Assuming three electrons were needed to produce one NH₃ molecule, the FE could be calculated as follows:

\[
FE = \frac{3F \times [\text{NH}_4^+] \times V}{17 \times Q}
\]

The rate of NH₃ formation was calculated using the following equation:

\[
V_{\text{NH}_3} = \frac{[\text{NH}_4^+] \times V}{t \times m_{\text{cat.}}}
\]

Where F is the Faraday constant, [NH₄⁺] is the measured NH₄⁺ concentration, V is the volume of the electrolyte in the cathodic chamber, Q is the total quantity of applied electricity; t is the reduction time; mcat. is the loaded mass of catalyst on carbon paper.
Fig. S1. TGA curve of C-TiO$_2$. 

![TGA curve of C-TiO$_2$](image)
Fig. S2. SEM images of C-TiO$_2$ and TiO$_2$. 
Fig. S3. (a) UV–vis absorption spectra of C-TiO$_2$ and TiO$_2$. (b) the Kubelka–Munk plots for the corresponding reflectance spectra of samples.
Fig. S4. (a) UV–vis absorption spectra of various NH$_4^+$ concentrations after incubated for 2 hours at room temperature. (b) Calibration curve used for calculation of NH$_4^+$ concentrations.
Fig. S5. CVs of (a) C-TiO$_2$/CP and (b) TiO$_2$/CP with various scan rates (20-200 mV s$^{-1}$) in the region of $-0.05$ to $-0.15$ V vs. Ag/AgCl. (c) The capacitive current densities at $-0.10$ V vs. Ag/AgCl as a function of scan rates for C-TiO$_2$/CP and TiO$_2$/CP.
**Fig. S6.** Nyquist plots of C-TiO$_2$/CP and TiO$_2$/CP in the frequency range from 1000 kHz to 1Hz with a voltage amplitude of 5 mV, and all the three electrodes are in one compartment cell being full of 0.1 M Na$_2$SO$_4$ solution.
Fig. S7. UV–vis absorption spectra of the electrolytes stained with indicator before and after 2 h electrolysis (a) at the potential of –0.7 V in Ar-saturated solution (b) at open circuit potential in N₂-saturated solution on C-TiO₂/CP.
**Fig. S8.** NH$_3$ yields and FEs of C-TiO$_2$ at the potential of $-0.7$ V with alternating 2 h cycles between N$_2$-saturated and Ar-saturated solutions for NRR.
Fig. S9. UV–vis absorption spectra of the electrolytes estimated by the method of Watt and Chrisp before and after 2 h electrolysis in N\(_2\)-saturated solution at –0.70 V.
**Fig. S10.** (a) UV–vis absorption spectra of various N$_2$H$_4$ concentrations after incubated for 20 min at room temperature. (b) Calibration curve used for calculation of N$_2$H$_4$ concentrations.
**Fig. S11.** UV–vis spectra of the electrolyte estimated by the method of Watt and Chrisp before and after 2 h electrolysis in N₂ atmosphere at a series of potentials under ambient conditions.
Table S1. Comparison of ambient N₂ reduction performance for C-TiO₂ nanoparticles with other aqueous-based NRR electrocatalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>NH₃ yield</th>
<th>FE (%)</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>C-TiO₂</td>
<td>0.1 M Na₂SO₄</td>
<td>16.22 µg h⁻¹ mg⁻¹ cat.</td>
<td>1.84</td>
<td>This work</td>
</tr>
<tr>
<td>N-doped porous carbon</td>
<td>0.05 M H₂SO₄</td>
<td>23.8 µg h⁻¹ mg⁻¹ cat.</td>
<td>1.42</td>
<td>3</td>
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<tr>
<td>Mo nanofilm</td>
<td>0.01 M H₂SO₄</td>
<td>1.89 µg h⁻¹ cm⁻²</td>
<td>0.72</td>
<td>4</td>
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<tr>
<td>γ-Fe₂O₃</td>
<td>0.1 M KOH</td>
<td>0.212 µg h⁻¹ mg⁻¹ cat.</td>
<td>1.9</td>
<td>5</td>
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<tr>
<td>Pd₀.₂Cu₀.₈/rGO</td>
<td>0.1 M KOH</td>
<td>2.80 µg h⁻¹ mg⁻¹ cat.</td>
<td>4.5</td>
<td>6</td>
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<tr>
<td>Fe₂O₃ nanorods</td>
<td>0.1 M Na₂SO₄</td>
<td>15.9 µg h⁻¹ mg⁻¹ cat.</td>
<td>0.94</td>
<td>7</td>
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<tr>
<td>PEBCD/C</td>
<td>0.5 M Li₂SO₄</td>
<td>1.58 µg h⁻¹ cm⁻²</td>
<td>2.85</td>
<td>8</td>
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<tr>
<td>Fe₂O₃-CNT</td>
<td>KHCO₃</td>
<td>0.22 µg h⁻¹ cm⁻²</td>
<td>0.15</td>
<td>9</td>
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<tr>
<td>Au nanorods</td>
<td>0.1 M KOH</td>
<td>6.042 µg h⁻¹ mg⁻¹ cat.</td>
<td>4.0</td>
<td>10</td>
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<tr>
<td>TA-reduced Au/TiO₂</td>
<td>0.1 M HCl</td>
<td>21.4 µg h⁻¹ mg⁻¹ cat.</td>
<td>8.11</td>
<td>11</td>
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<tr>
<td>α-Au/CeO₂-x-RGO</td>
<td>0.1 M HCl</td>
<td>8.31 µg h⁻¹ mg⁻¹ cat.</td>
<td>10.1</td>
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<tr>
<td>MoN</td>
<td>0.1 M HCl</td>
<td>3.01 × 10⁻¹⁰ mol s⁻¹ cm⁻²</td>
<td>1.15</td>
<td>13</td>
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<tr>
<td>Ru/C</td>
<td>2.0 M KOH</td>
<td>0.21 µg h⁻¹ cm⁻²</td>
<td>0.28</td>
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<td>MoS₂/CC</td>
<td>0.1 M Na₂SO₄</td>
<td>0.02 µg h⁻¹ cm⁻²</td>
<td>1.17</td>
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<tr>
<td>Fe₃O₄/Ti</td>
<td>0.1 M Na₂SO₄</td>
<td>0.012 µg h⁻¹ cm⁻²</td>
<td>2.6</td>
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<tr>
<td>Bi₄V₂O₁₁/CeO₂</td>
<td>0.1 M HCl</td>
<td>23.21 µg h⁻¹ mg⁻¹ cat.</td>
<td>10.16</td>
<td>17</td>
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<tr>
<td>MoO₃</td>
<td>0.1 M HCl</td>
<td>29.43 µg h⁻¹ mg⁻¹ cat.</td>
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<td>18</td>
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<td>VN/TM</td>
<td>0.1 M HCl</td>
<td>5.14 µg h⁻¹ cm⁻²</td>
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<td>19</td>
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<tr>
<td>Nb₂O₅ nanofiber</td>
<td>0.1 M HCl</td>
<td>43.6 µg h⁻¹ mg⁻¹ cat.</td>
<td>9.26</td>
<td>20</td>
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<tr>
<td>TiO₂</td>
<td>0.1 M Na₂SO₄</td>
<td>9.16 × 10⁻¹¹ mol s⁻¹·cm⁻²</td>
<td>2.5</td>
<td>21</td>
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<tr>
<td>TiO₂-rGO</td>
<td>0.1 M Na₂SO₄</td>
<td>15.13 µg h⁻¹ mg⁻¹ cat.</td>
<td>3.3</td>
<td>22</td>
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</tbody>
</table>
References


18 J. Han, X. Ji, X. Ren, G. Cui, L. Li, F. Xie, H. Wang, B. Li and X. Sun, *J. Mater. Chem. A*, 2018, **6**, 12974–12977.


