Electronic Supplementary Information

Experimental section

Materials: GO, commercial TiO$_2$ powder, ammonium chloride (NH$_4$Cl), hydrazine hydrate (N$_2$H$_4$·H$_2$O), sodium hypochlorite (NaClO), sodium hydroxide (NaOH), sodium salicylate (C$_7$H$_5$O$_3$Na), sodium sulfate (Na$_2$SO$_4$), hydrochloric acid (HCl), ethanol (CH$_3$CH$_2$OH), and carbon paper were bought from Beijing Chemical Corporation. Para-(dimethylamino) benzaldehyde (C$_9$H$_{11}$NO), sodium nitroferricyanide (III) dihydrate (Na$_2$Fe(CN)$_5$NO·2H$_2$O), and Nafion were purchased from Aladdin Ltd. (Shanghai, China). The water used throughout all experiments was purified through a Millipore system.

Preparation of TiO$_2$-rGO: TiO$_2$ powder was dissolved in homogeneous GO aqueous dispersion under stirring for about 1 h. After that, the mixture was sealed in a 50 mL Teflon-lined autoclave and maintained at 180 °C for 2 h. The autoclave was naturally cooled down to room temperature. Finally, a black cylinder was obtained.

Preparation of TiO$_2$-rGO/CP electrode: 10 mg TiO$_2$-rGO powders and 20 µL of Nafion solution (5 wt%) were dispersed in 980 µL mixed solution contain 600 µL ethanol and 380 µL H$_2$O by 2 h sonication to form a homogeneous ink. Then, 10 µL TiO$_2$-rGO was loaded on a CP with area of 0.5 x 0.5 cm$^2$ and dried under ambient condition.

Characterizations: XRD patterns were obtained from a Shimazu XRD-6100 diffractometer with Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (Japan). SEM images were collected from the tungsten lamp-equipped SU3500 scanning electron microscope at an accelerating voltage of 20 kV (HITACHI, Japan). Scanning electron microscope (SEM) measurements were recorded on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM images were obtained from a Zeiss Libra 200FE transmission electron microscope 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 were measured on SHIMADZU UV-1800 ultraviolet-visible (UV-
Vis) 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.

**Electrochemical measurements**: Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) using a standard three-electrode system using TiO₂-rGO/CP as the working electrode, graphite rod as the counter electrode, and saturated Ag/AgCl electrode as the reference electrode. In all measurements, saturated Ag/AgCl electrode was calibrated with respect to reversible hydrogen electrode as following: in 0.1 M Na₂SO₄ aqueous solution, E(RHE) = E(Ag/AgCl) + 0.059 × pH + 0.197 V. All experiments were carried out at room temperature. For N₂ reduction experiments, the 0.1 M Na₂SO₄ electrolyte was purged with N₂ for 30 min before the measurement. Potentiostatic test was conducted in N₂-saturated 0.1 M Na₂SO₄ solution (35 mL) in a two-compartment cell, which was separated by Nafton 211 membrane.

**Determination of NH₃**: The concentration of NH₄⁺ was prepared as follows. Firstly, 50 µg mL⁻¹ NH₄⁺ solution was prepared and diluted to 1 µg mL⁻¹. Then, 0.0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0 mL NH₄⁺ solution with concentration of 1 µg mL⁻¹ were poured into 10 mL test tubes and separately diluted to 10 mL with 0.1 M Na₂SO₄ and the resulting concentrations of NH₄⁺ in the solutions are 0.00, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30 µg mL⁻¹. The produced NH₃ was detected with indophenol blue by ultraviolet spectroscopy. In detail, 4 mL electrolyte was obatined from the cathodic chamber and mixed with 50 µL oxidizing solution containing NaClO (pCl = 4 ~ 4.9) and NaOH (0.75 M), 500 µL coloring solution containing 0.4 M C₇H₆O₃ and 0.32 M NaOH, and 50 µL catalyst solution (1 wt% Na₂[Fe(CN)₅NO]) for 2 h. Absorbance measurements were performed at λ = 660 nm. The concentration-absorbance curve was calibrated using standard NH₄⁺ solution with a serious of concentrations. The fitting curve (y = 0.682x + 0.029, R² = 0.999) shows good linear relation of absorbance value with NH₄⁺ concentration.

**Determination of N₂H₄**: The concentration of N₂H₄ was prepared as follows. Firstly, 2 mg mL⁻¹ N₂H₄ solution was prepared and diluted to 2 µg mL⁻¹. Then, 0.0, 0.5, 1.0, 1.5,
2.0, 2.5, 5.0 mL $N_2H_4$ solution with concentration of 2 μg mL$^{-1}$ were poured into 10 mL test tubes and separately diluted to 5 mL with 0.1 M Na$_2$SO$_4$ and the resulting concentrations of $N_2H_4$ in the solutions are 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 2.0 μg mL$^{-1}$. The $N_2H_4$ present in the electrolyte was determined by the method of Watt and Chrisp. The mixture of C$_9$H$_{11}$NO (5.99 g), HCl (30 mL), and C$_2$H$_5$OH (300 mL) was used as a color reagent. In detail, 5 mL electrolyte was removed from the electrochemical reaction vessel, and added into 5 mL above prepared color reagent and stirring 10 min at room temperature. Moreover, the absorbance of the resulting solution was measured at a wavelength of 455 nm. The concentration absorbance curves were calibrated using standard $N_2H_4$ solution with a series of concentrations. The fitting curve ($y = 0.4909x + 0.047$, $R^2 = 0.999$) shows good linear relation of absorbance value with $N_2H_4$ concentration.

*Calculations of NH$_3$ formation rate and FE:* NH$_3$ formation rate was calculated using the following equation:

$$\text{NH}_3 \text{ formation rate} = [\text{NH}_4^+] \times \text{V}/(\text{m}_{\text{cat.}} \times \text{t})$$

FE was calculated according to following equation:

$$\text{FE} = 3 \times \text{F} \times [\text{NH}_4^+] \times \text{V}/(18 \times \text{Q})$$

Where $[\text{NH}_4^+]$ is the measured NH$_4^+$ concentration; V is the volume of the cathodic reaction electrolyte; t is the potential applied time; $m_{\text{cat.}}$ is the loaded quality of catalyst; F is the Faraday constant; and Q is the quantity of applied electricity.
Fig. S1. TGA curve of TiO$_2$-rGO.
Fig. S2. SEM images of TiO$_2$ and TiO$_2$-rGO.
Fig. S3. SAED pattern taken from TiO$_2$-rGO.
Fig. S4. XPS spectrum of GO in the C 1s.
Fig. S5. (a) LSV curves and (b) corresponding Tafel plots of TiO$_2$-rGO/CP in Ar- and N$_2$-saturated 0.1 M Na$_2$SO$_4$. 
Fig. S6. CV curves of TiO$_2$-rGO/CP in Ar- and N$_2$-saturated 0.1 M Na$_2$SO$_4$. 
Fig. S7. (a) UV-Vis absorption spectra of indophenol assays with NH$_4^+$ concentrations after incubated for 2 h at room temperature. (b) Calibration curve used for calculation of NH$_4^+$ concentrations.
Fig. S8. (a) UV-Vis absorption spectra of various N$_2$H$_4$ concentrations after incubated for 10 min at room temperature. (b) Calibration curve used for calculation of N$_2$H$_4$ concentrations.
Fig. S9. UV-Vis absorption spectra of electrolytes stained with indophenol indicator before and after 2 h electrolysis at the potential of –0.90 V under different electrochemical conditions.
Fig. S10. UV-Vis absorption spectra of the 0.1 M Na$_2$SO$_4$ electrolyte stained with indophenol indicator after continuously supplying N$_2$ or Ar with no applied voltage.
Fig. S11. UV-Vis absorption spectra of the electrolytes estimated by the method of Watt and Chrisp before and after 2 h electrolysis in N₂ atmosphere at –0.90 V.
Fig. S12. CVs of (a) TiO$_2$-rGO/CP and (b) TiO$_2$/CP with various scan rates (20-220 mV s$^{-1}$) in the region of –0.1 to –0.2 V vs. Ag/AgCl. The capacitive current densities at –0.15 V vs. Ag/AgCl as a function of scan rates for (c) TiO$_2$-rGO/CP and (d) TiO$_2$/CP.
Fig. S13. Nyquist plots of TiO$_2$-rGO/CP and TiO$_2$/CP.
Fig. S14. NH$_3$ yields and FEs of TiO$_2$-rGO/CP with different N$_2$ flow rate.
Fig. S15. XRD patterns for CP and TiO$_2$-rGO/CP after long-term electrolytic reaction in 0.1 M Na$_2$SO$_4$. 
Fig. S16. XPS spectra in the (a) Ti 2p and (b) O 1s regions after long-term electrolytic reaction in 0.1 M Na$_2$SO$_4$. 
Table S1. Comparison of the electrocatalytic NRR performance of TiO$_2$-rGO with other aqueous-based NRR electrocatalysts at room temperature.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>NH$_3$ yield</th>
<th>FE (%)</th>
<th>Ref.</th>
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</thead>
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<tr>
<td>TiO$_2$-rGO</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>15.13 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>3.3</td>
<td>This work</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>
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<td>3</td>
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<td>α-Au/CeO$_x$-RGO</td>
<td>0.1 M HCl</td>
<td>8.31 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>10.1</td>
<td>4</td>
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<tr>
<td>TA-reduced Au/TiO$_2$</td>
<td>0.1 M HCl</td>
<td>21.4 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>8.11</td>
<td>5</td>
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<tr>
<td>Pd/C</td>
<td>0.1 M PBS</td>
<td>4.5 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>8.2</td>
<td>6</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>NPC</td>
<td>0.05 M H$_2$SO$_4$</td>
<td>23.8 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>1.42</td>
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<tr>
<td>γ-Fe$_2$O$_3$</td>
<td>0.1 M KOH</td>
<td>0.212 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>1.9</td>
<td>9</td>
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<tr>
<td>Bi$_4$V$<em>2$O$</em>{11}$/CeO$_2$</td>
<td>0.1 M HCl</td>
<td>23.21 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>10.16</td>
<td>10</td>
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<tr>
<td>MoS$_2$/CC</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>4.94 µg h$^{-1}$ cm$^{-2}$</td>
<td>1.17</td>
<td>11</td>
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<tr>
<td>Mo$_2$N</td>
<td>0.1 M HCl</td>
<td>78.4 µg h$^{-1}$ mg$^{-1}$cat.</td>
<td>4.5</td>
<td>12</td>
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<tr>
<td>MoN NA/CC</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>Mo nanofilm</td>
<td>0.01 M H$_2$SO$_4$</td>
<td>1.89 µg h$^{-1}$ cm$^{-2}$</td>
<td>0.72</td>
<td>14</td>
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<tr>
<td>PEBCD/C</td>
<td>0.5 M Li$_2$SO$_4$</td>
<td>1.58 µg h$^{-1}$ cm$^{-2}$</td>
<td>2.85</td>
<td>15</td>
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<td>Fe$_2$O$_3$-CNT</td>
<td>KHCO$_3$</td>
<td>0.22 µg h$^{-1}$ cm$^{-2}$</td>
<td>0.15</td>
<td>16</td>
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<tr>
<td>Fe$_3$O$_4$/Ti</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>3.43 µg h$^{-1}$ cm$^{-2}$</td>
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<tr>
<td>MoO$_3$</td>
<td>0.1 M HCl</td>
<td>29.43 µg h$^{-1}$ mg$^{-1}$cat.</td>
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<tr>
<td>VN/TM</td>
<td>0.1 M HCl</td>
<td>5.14 µg h$^{-1}$ cm$^{-2}$</td>
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<td>Nb$_2$O$_5$ 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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</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.