Electronic Supplementary Information

Experimental Section

Materials: Sodium hydroxide (NaOH), ammonium chloride (NH$_4$Cl), sodium sulfate (Na$_2$SO$_4$), ethylalcohol (C$_2$H$_5$OH), hydrochloric acid (HCl), sodium nitrite (NaNO$_2$, 99.0%), sodium salicylate (C$_7$H$_5$O$_3$Na), sodium nitroferricyanide dihydrate (C$_5$FeN$_6$Na$_2$O·2H$_2$O), sodium hypochlorite solution (NaClO), and p-dimethylaminobenzaldehyde (C$_9$H$_{11}$NO) were purchased from Aladdin Ltd. (Shanghai, Chain). Sulfuric acid (H$_2$SO$_4$), hydrogen peroxide (H$_2$O$_2$), sodium hypophosphite (NaH$_2$PO$_2$), and hydrazine monohydrate (N$_2$H$_4$·H$_2$O) were bought from Beijing Chemical Corporation. (China). Titanium plate (TP) (thickness is 0.2 mm) was purchased from Qingyuan Metal Materials Co., Ltd (Xingtai, China) and treated with 2 M HCl for 30 minutes before hydrothermal reaction. All reagents used in this work were analytical grade and direct use without further purification.

Preparation of Cu@TiO$_2$/TP: Firstly, TP was cut into a small piece (2.0 × 4.0 cm^2) and sonicated in acetone, ethanol, and distilled water for 15 min, respectively. After then, TP was put into 30 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 sample was moved out, washed with deionized water and ethanol several times and dried at 60 °C for 10 min. Then the resultant Na-titanate/TP was immersed in 0.1 M Cu(CH$_3$COO)$_2$·H$_2$O for 1 h to exchange Na$^+$ with Cu^{2+}, followed by rinsing several times with deionized water and then dried at 60 °C. Subsequently, Cu-titanate/TP was annealed in H$_2$/Ar atmosphere at 500 °C for 3 h to obtain Cu@TiO$_2$/TP.

Preparation of TiO$_2$/TP: TiO$_2$/TP nanobelt array was synthesized using the same methods but with 1 M HCl for ion-exchange. The prepared H$_2$Ti$_2$O$_5$·H$_2$O was then washed with distilled water and ethanol several times and dried at 60 °C. Subsequently, H$_2$Ti$_2$O$_5$·H$_2$O was annealed in H$_2$/Ar atmosphere at 500 °C for 3 h. After cooling to room temperature, TiO$_2$/TP was finally obtained.

Preparation of Cu/TP: Briefly, The Cu nanoparticles were prepared by pyrolysis of 0.199 g of Cu(CH$_3$COO)$_2$·H$_2$O at 500 °C for 3 h in H$_2$/Ar atmosphere. The Cu powder was prepared into ink and dropped on TP, then dried in air, Cu/TP was finally obtained.

Characterizations: The crystal structure of as-prepared materials was identified through X-ray diffraction (XRD, Philip D8). Scanning electron microscopy (SEM, ZISS 300) and transmission electron microscopy (TEM, JEM-F200, JEOL Ltd.) were carried out to reveal the morphology information of samples. Energy dispersive X-ray (EDX) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Xi) were utilized to analyze chemical compositions. The absorbance data of spectrophotometer was measured on UV-Vis spectrophotometer (Shimadzu UV-2700). Gas chromatography (GC-2014C, SHIMADZU) was utilized to quantitatively detect H_2 and N_2. ^1H NMR spectra were collected on Varian VNMRS 600 MHz (the USA).

Electrochemical measurements: All electrochemical measurements were carried on the CHI660E electrochemical workstation (Shanghai, Chenhua), using Cu@TiO$_2$/TP (0.5 × 0.5 cm^2, the average loading of Cu@TiO$_2$: 3.2 mg/cm^2) as the working electrode, graphite rod as the counter electrode, and Ag/AgCl as the reference electrode, respectively. All the potentials reported in our work were converted to reversible hydrogen electrode via calibration with the following equation: E (vs. RHE) = E (vs. Ag/AgCl) + 0.059 × pH + 0.197 V, and the presented current densities were normalized to the geometric area of the electrode. ECSA was measured by CV at the potential window from 0.325 to 0.425 V, with different scan rates of 20, 40, 60, 80, and 100 mV s^{-1}. The double layer capacitance (C_{dl}) was estimated by plotting the $\Delta j = (j_a - j_c)/2$ at 0.375 V against the scan rates, in which the j_a and j_c were the anodic and cathodic current density, respectively. The slope is that of the C_{dl} value. C_{dl} was used to represent the ECSA.

Determination of NH$_3$: The concentration of produced NH$_3$ was determined by colorimetry (the obtained electrolyte was diluted 40 times) using the indophenol blue method.[1] In detail, a certain amount of electrolyte was taken out from the electrolytic cell and diluted to 4 mL to the detection range. Then, 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%) were dropped into the collected electrolyte solution. After standing at room temperature for 1 h, the ultraviolet-visible (UV-Vis) absorption spectrum was measured. The concentration of NH$_3$ was determined using the absorbance at a wavelength of 660 nm. The concentration-absorbance curve was calibrated using the standard NH$_4$Cl solution with NH$_3$ concentrations of 0, 0.2, 0.5, 1.0, 2.0 and 5.0 ppm in 0.1 M Na$_2$SO$_4$ solution. The fitting curve (y =

0.4299 x + 0.0341, R^2 = 0.9998) shows a good linear relation of absorbance value with NH_3 concentration.

Calculations of the FE and NH_3 yield:

The amount of NH_3 (n_{NH3}) was calculated by the following equation:

$$n_{NH3} = [NH_3] \times V$$

FE of NH_3 was calculated by the following equation:

$$FE = (6 \times F \times [NH_3] \times V) / (M_{NH3} \times Q) \times 100\% \quad (1)$$

NH_3 yield was calculated using the following equation:

$$NH_3 \text{ yield} = ([NH_3] \times V) / (M_{NH3} \times t \times A) \quad (2)$$

Where F is the Faradic constant (96500 C mol^{-1}), [NH_3] is the measured NH_3 concentration, V is the volume of electrolyte in the cathode compartment (35 mL), M_{NH3} is the molar mass of NH_3, Q is the total quantity of applied electricity; t is the electrolysis time (1 h) and A is the geometric area of catalyst (0.5 × 0.5 cm^2).

Determination of N_2H_4: In this work, we used the method of Watt and Chrisp to determine the concentration of produced N_2H_4.[2] The chromogenic reagent was a mixed solution of 5.99 g $C_9H_{11}NO$, 30 mL HCl and 300 mL C_2H_5OH. 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_2H_4 concentration with a standard curve of hydrazine (y = 0.6996 x + 0.0755, R^2 = 0.9995).

^{15}N isotopic labelling experiment: The generated NH_3 was verified by an isotope-labelled tracer experiment using 0.1 M $^{15}NO_2^-$ as a N source. After 1 h of electroreduction at −0.6 V, the electrolyte (2 mL) in the cathodic chamber was neutralized by HCl aqueous solution (1.2 M). After that, the neutralized electrolyte (500 μL) was mixed with deuterium oxide (D_2O, 50 μL). And the mixture was sealed into a nuclear magnetic resonance (NMR) tube (5 mm in diameter, 600 MHz) for further test.
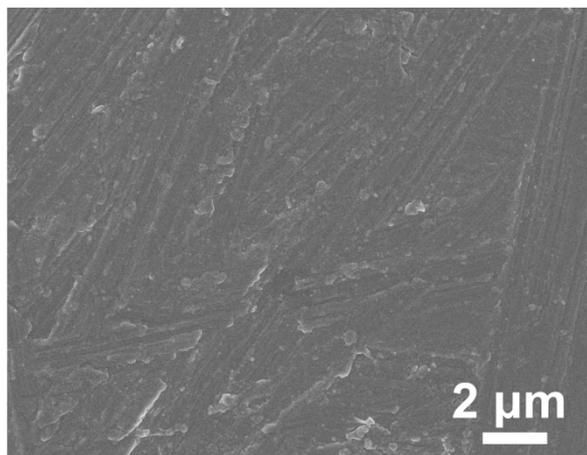
Fig. S1. SEM image of bare TP.
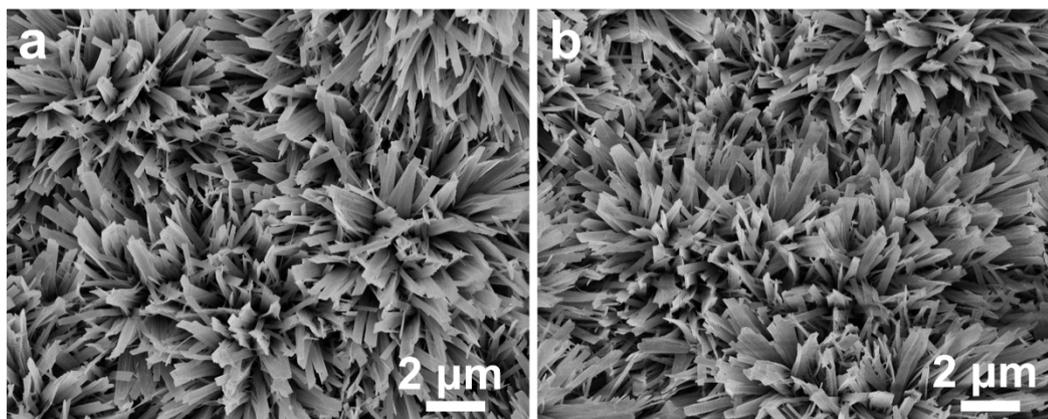
Fig. S2. SEM images of (a) Na-titanate/TP and (b) Cu-titanate/TP.
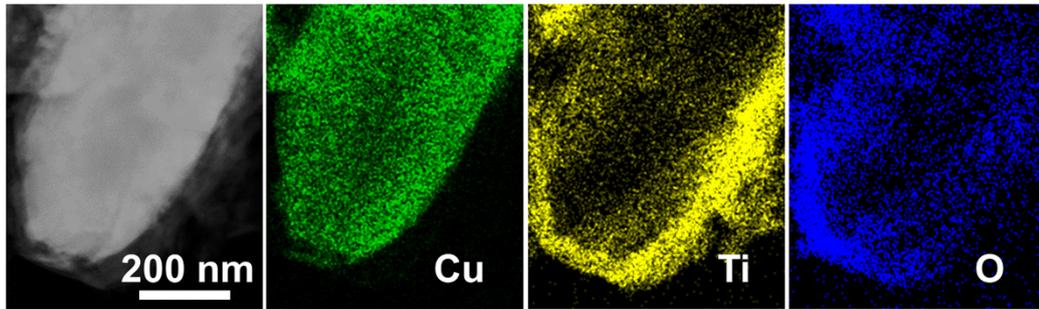
Fig. S3. TEM image and corresponding EDS elemental mapping images of Cu@TiO$_2$.
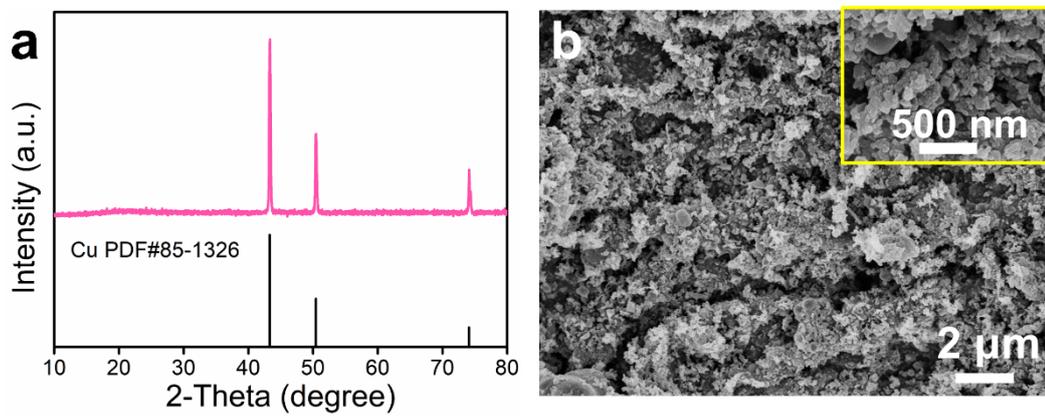
Fig. S4. (a) XRD pattern and (b) SEM images of Cu nanoparticles.
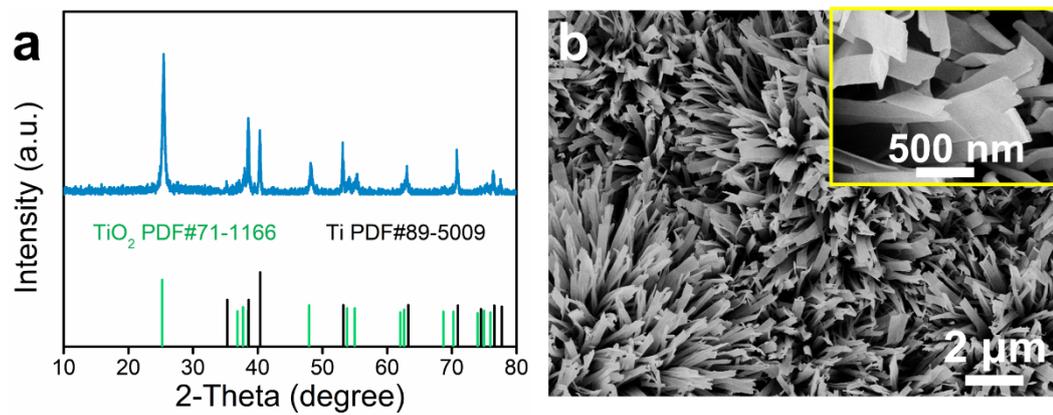
Fig. S5. (a) XRD pattern and (b) SEM images of TiO_2/TP.
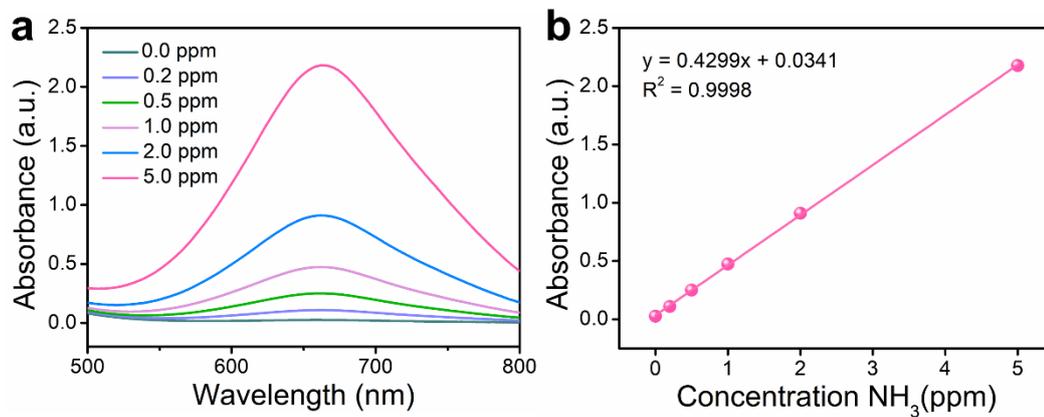
Fig. S6. (a) UV-Vis absorption spectra of indophenol assays kept with different concentrations of NH$_3$ after incubated for 1 h at room temperature. (b) Corresponding calibration curve used for calculation of NH$_3$ concentration.
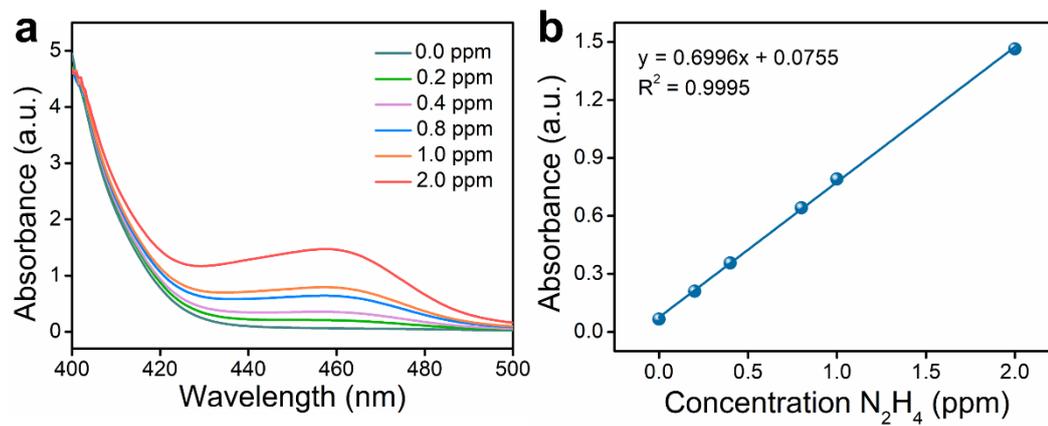
Fig. S7. (a) UV-Vis absorption spectra various N_2H_4 concentrations after incubated for 15 min at room temperature. (b) Corresponding calibration curve used for calculation of N_2H_4 concentration.
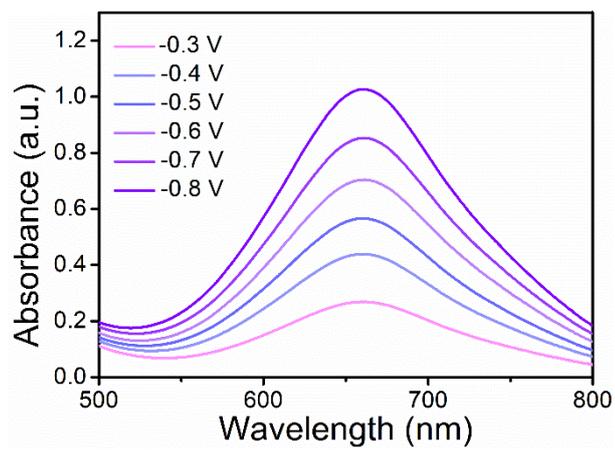
Fig. S8. UV-Vis absorption spectra of the electrolytes for calculation of NH$_3$ concentration at each given potential.
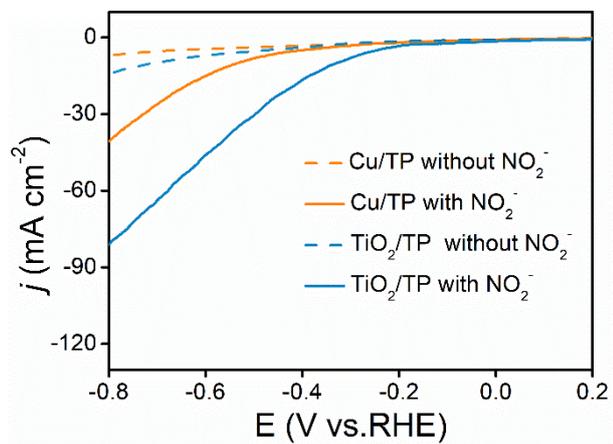
Fig. S9. LSV curves of Cu/TP and TiO$_2$/TP in 0.1 M Na$_2$SO$_4$ with and without 0.1 M NO$_2^-$.
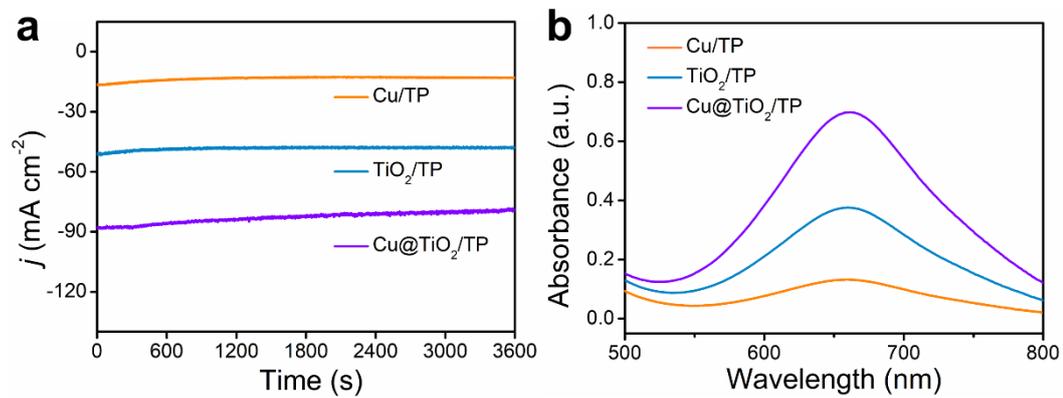
Fig. S10. (a) Chronoamperometry curves of Cu/TP, TiO$_2$/TP, and Cu@TiO$_2$/TP for NO$_2^-$RR at −0.6 V. (b) Corresponding UV-Vis absorption spectra of the electrolytes for calculation of NH$_3$ concentration.
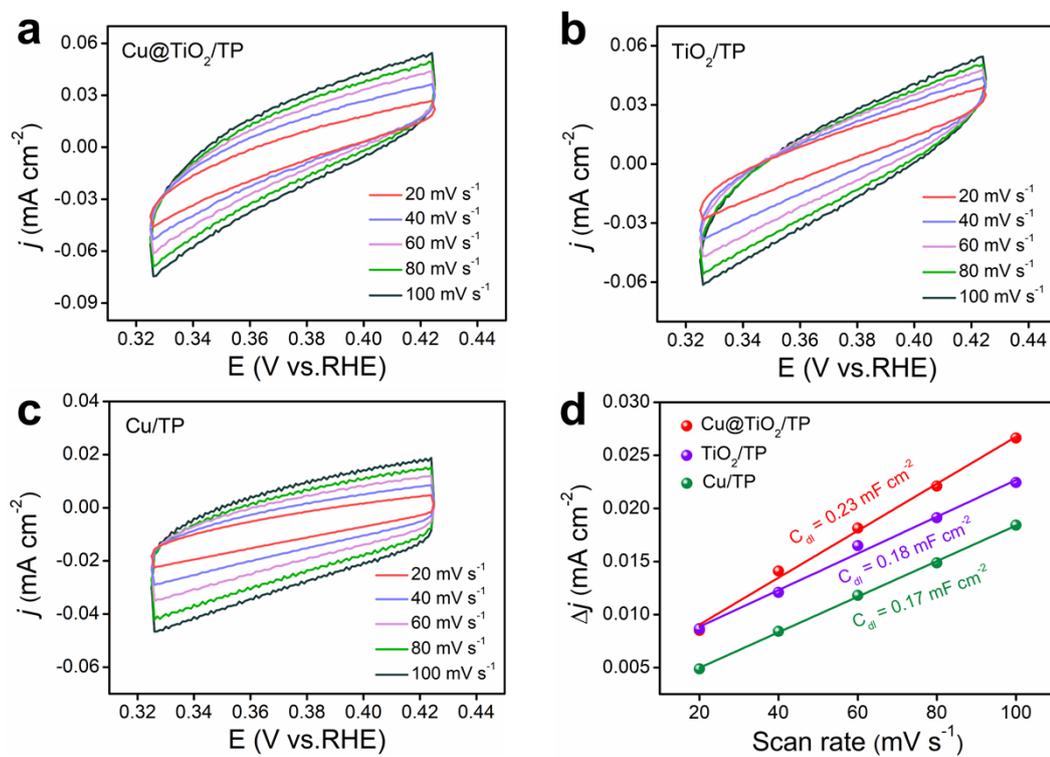
Fig. S11. Cyclic voltammograms recorded at a series of scan rates for (a) Cu@TiO$_2$/TP, (b) TiO$_2$/TP, and (c) Cu/TP. (d) Corresponding electrochemical double layer capacitances of Cu@TiO$_2$/TP, TiO$_2$/TP, and Cu/TP.
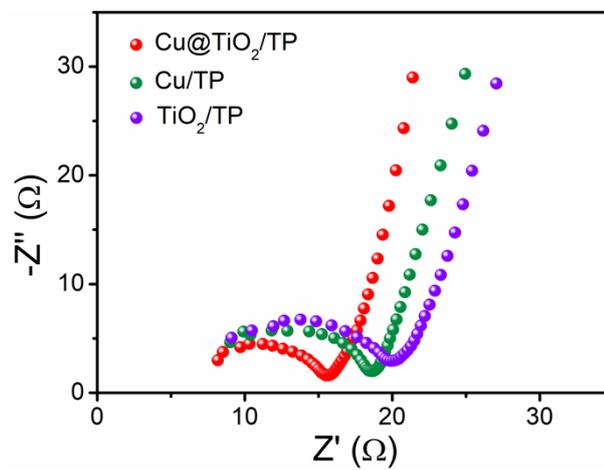
Fig. S12. Nyquist plots of Cu@TiO$_2$/TP, Cu/TP, and TiO$_2$/TP in 0.1 M Na$_2$SO$_4$ with 0.1 M NO$_2^-$.
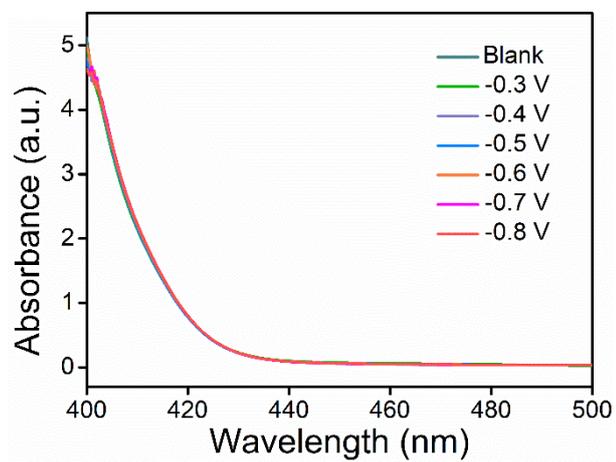
Fig. S13. UV-Vis absorption spectra of the electrolytes estimated by the method of Watt and Chrisp for the calculation of N_2H_4 concentration.
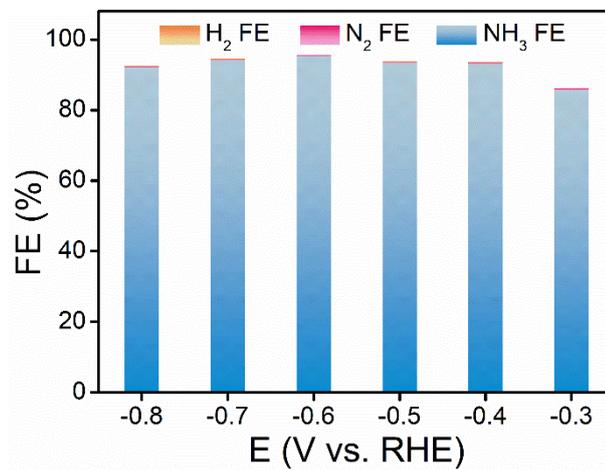
Fig. S14. FEs of NH_3, N_2, and H_2 of Cu@TiO$_2$/TP at different given potentials.
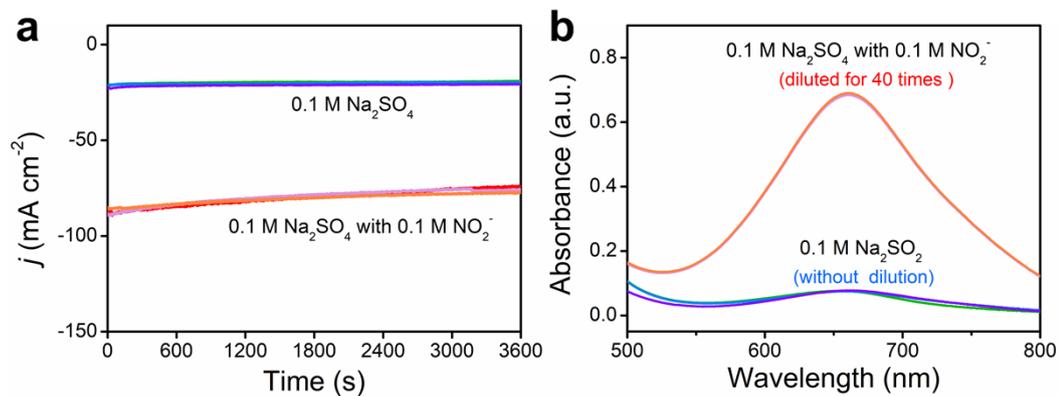
Fig. S15. (a) Chronoamperometry curves and (b) corresponding UV-Vis absorption spectra of Cu@TiO$_2$/TP for electrochemical catalytic production of NH$_3$ during the alternating experiments between NO$_2^-$-containing and NO$_2^-$-free 0.1 M Na$_2$SO$_4$ solution.
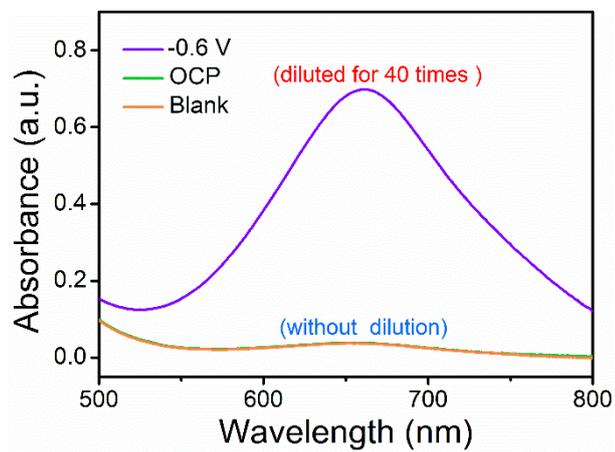
Fig. S16. UV-Vis absorption spectra of NH$_3$ concentrations at different conditions.
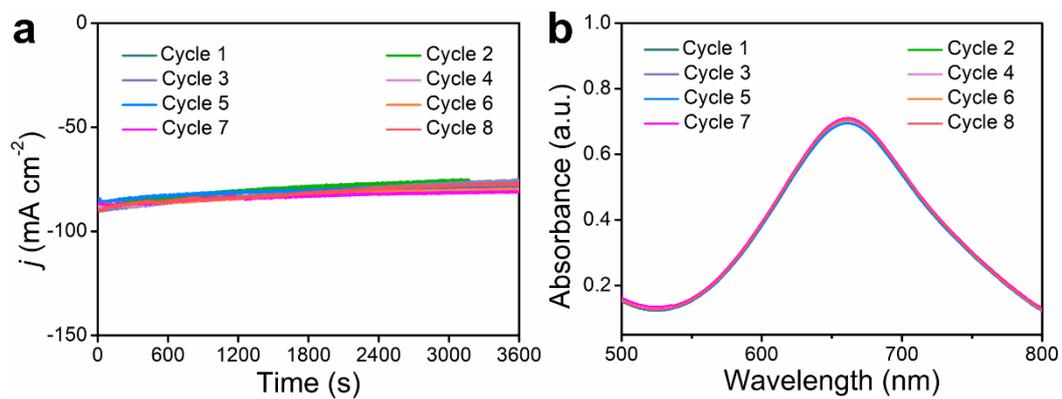
Fig. S17. (a) Chronoamperometry curves and (b) corresponding UV-Vis absorption spectra of Cu@TiO$_2$/TP for electrochemical catalytic production of NH$_3$ during cyclic tests at –0.6 V.
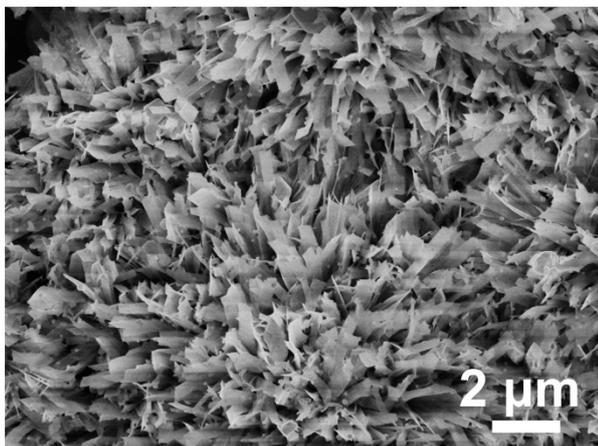
Fig. S18. SEM image of Cu@TiO$_2$/TP after 12-h electrolysis.
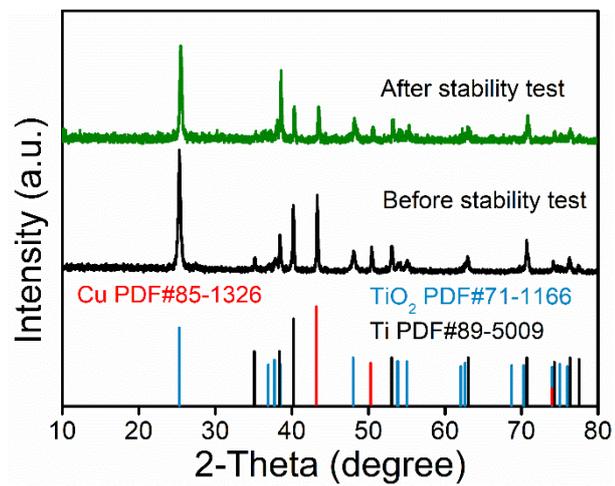
Fig. S19. XRD patterns of Cu@TiO$_2$/TP before and after stability test.

Table S1 Comparison of the catalytic performances of Cu@TiO$_2$/TP with other reported NO$_2^-$RR electrocatalysts under ambient conditions.

Catalyst	Electrolyte	NH$_3$ yield	FE (%)	Ref
Cu@TiO$_2$/TP	0.1 M Na$_2$SO$_4$ (0.1 M NO$_2^-$)	760.5 μmol h^{-1} cm^{-2}	95.3	This work
Cu phthalocyanine complexes	0.1 M KOH (NaNO$_2$)	\	78	3
TiO$_{2-x}$ NBA/TP	0.1 M NaOH (0.1 M NaNO$_2$)	464.6 μmol h^{-1} cm^{-2}	92.7	4
Ag@NiO/CC	0.1 M NaOH (0.1 M NO$_2^-$)	338.3 μmol h^{-1} cm^{-2}	97.7	5
CoP NA/TM	0.1 M PBS (500 ppm NaNO$_2$)	132.9 μmol h^{-1} cm^{-2}	90	6
Cu/JDC/CP	0.1 M NaOH (0.1 M NO$_2^-$)	523.5 μmol h^{-1} mg$_{cat.}^{-1}$	93.2	7
Ni$_2$P/NF	0.1 M PBS (200 ppm NaNO$_2$)	191.3 ± 6.6 μmol h^{-1} cm^{-2}	90.2 ± 3.0	8
Anatase TiO$_{2-x}$	0.1 M NaOH (0.1 M NaNO$_2$)	719.4 ± 23.9 μmol h^{-1} cm^{-2}	91.1 ± 5.5	9
CF@Cu$_2$O	0.1 M PBS (0.1 M NaNO$_2$)	441.8 μmol h^{-1} cm^{-2}	94.2	10
Cu$_3$P NA/CF	0.1 M PBS (0.1 M NO$_2^-$)	95.6 μmol h^{-1} cm^{-2}	91.2	11
Ni-NSA-V$_{Ni}$	0.2 M Na$_2$SO$_4$ (200 ppm NaNO$_2$)	235.98 μmol h^{-1} cm^{-2}	88.9	12
P-TiO$_2$/TP	0.1 M Na$_2$SO$_4$ (0.1 M NO$_2^-$)	560.8 μmol h^{-1} cm^{-2}	90.6	13

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