Electronic Supplementary Information

Experimental section

Materials: Chromium acetate ($C_6H_9O_6Cr$), polyacrylonitrile (PAN), and dimethylformamide (DMF) were purchased from Aladdin Ltd. (Shanghai, China). All reagents were analytical reagent grade and used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

Preparation of Cr_2O_3 nanofibers: 1.0 g PAN was dissolved in 13 mL DMF solution with stirring to obtain a homogeneous solution. Then 1.5 g $C_6H_9O_6Cr$ was added to above solution with gentle stirring for 24 h. A viscous solution can be obtained after gentle stirring for 24 h. Subsequently, the precursor solution was loaded into a plastic syringe for electrospinning by applying a high voltage of 20 kV and the aluminum foil collector with a distance of 15 cm. Next, the obtained precursor nanofibers were calcinated at 230 °C for 1 h with a heating rate of 1 °C min^{-1} and then at 600 °C for 2 h with a heating rate of 2 °C min^{-1} in air. The obtained Cr_2O_3 nanofibers were washed with water for several times and collected by centrifugation, followed by drying at 60 °C.

Preparation of Cr_2O_3/CPE: 4 mg Cr_2O_3 and 10 μL of Nafion solution (5 wt%) were dispersed in 990 μL mixed solution contain 490 μL ethanol and 500 μL H_2O by 1 h sonication to form a homogeneous ink. Then 25 μL catalyst ink was loaded on a CPE with area of 1 x 1 cm^2 and dried under ambient condition.

Characterizations: XRD data were recorded using a LabX XRD-6100 X-ray diffractometer, with a Cu Kα radiation (40 kV, 30 mA) of wavelength 0.154 nm (SHIMADZU, Japan). SEM images were obtained on a Hitachi S-4800 field emission scanning electron microscope at an accelerating voltage of 20 kV. TEM characterization was performed using 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. UV-Vis spectra were acquired on a SHIMADZU UV-1800 ultraviolet-visible spectrophotometer. The ion chromatography data were collected on Swiss Wangtong ECO.

Electrocatalytic N_2 reduction measurements: The N_2 reduction experiments were carried out in a two-compartment cell separated by a Nafion 211 membrane under ambient condition using a CHI 660E electrochemical analyzer. The membrane was protonated by first boiling in ultrapure water for 1 h and treating in H_2O_2 (5%) aqueous solution at 80 °C for another 1 h, respectively. And then, the membrane was treaded in 0.5 M H_2SO_4 for 3 h at 80 °C and finally in water for 6 h. The electrochemical experiments using a three-electrode configuration with prepared electrodes, 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: E (vs. RHE) = E (vs. Ag/AgCl) + 0.256 V and the presented current density was normalized to the geometric surface area. For electrochemical N_2 reduction, chrono-amperometry tests were conducted in N_2-saturated 0.1 M HCl solution. All NRR experiments were carried out at room temperature and atmospheric pressure. Prior to each test, the electrolyte was bubbled with Ar or N_2 for 30 min.

Determination of NH_3: Concentration of produced NH_3 was spectrophotometrically determined by the indophenol blue method.[1] Typically, 2 mL HCl electrolyte was taken from the cathodic chamber, and then 2 mL of 1 M NaOH solution containing 5% salicylic acid and 5% sodium citrate was added into this solution. Subsequently, 1 mL of 0.05 M NaClO and 0.2 mL of 1% $C_5FeN_6Na_2O \cdot 2H_2O$ were add into the above solution. After standing at room temperature for 2 h, the UV-Vis absorption absorption spectrum was measured at a wavelength of 655 nm. The concentration-absorbance curves were calibrated using standard NH_4Cl solution with a serious of concentrations. The fitting curve ($y = 0.370x + 0.076$, $R^2 = 0.999$) shows good linear relation of absorbance value with NH_4Cl concentration by three times independent calibrations.

Determination of N_2H_4: The N_2H_4 presented in the electrolyte was estimated by the method of Watt and Chrisp.[2] A mixed solution of 5.99 g $C_9H_{11}NO$, 30 mL HCl and 300 mL ethanol was used as a color reagent. Calibration curve was plotted as follow: first, preparing a series of reference solutions; second, adding 5 mL above prepared color reagent and stirring 20 min at room temperature; finally, the absorbance of the resulting solution was measured at 455 nm, and the yields of N_2H_4 were estimated from a standard curve using 5 mL residual electrolyte and 5 mL color reagent. Absolute calibration of this method was achieved using $N_2H_4 \cdot H_2O$ solutions of known concentration as standards, and the fitting curve shows good linear relation of absorbance with $N_2H_4 \cdot H_2O$ concentration ($y = 1.01x + 0.045$, $R^2 = 0.998$) by three times independent calibrations.

Determination of FE: The FE for N_2 reduction was defined as the amount of electric charge used for synthesizing NH_3 divided the total charge passed through the electrodes during the electrolysis. The total amount of NH_3 produced was measured using colorimetric methods. Assuming three electrons were needed to produce one NH_3 molecule, the FE could be calculated as follows:

$$FE=3\times F\times [NH_3]\times V/17\times Q$$

The rate of NH_3 formation was calculated using the following equation:

$$v_{NH_3}=[NH_3]\times V/t\times m_{cat.}$$

Where F is the Faraday constant, $[NH_3]$ is the measured NH_3 concentration, V is the volume of the HCl electrolyte for NH_3 collection, t is the reduction time and $m_{cat.}$ is the catalyst loading mass.

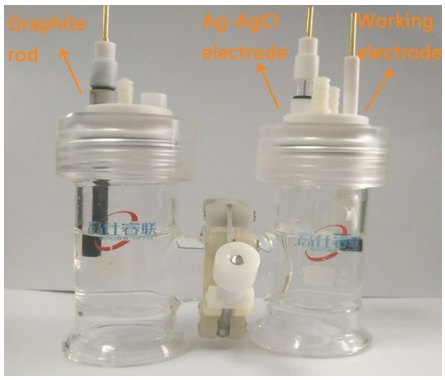

Fig. S1. The construction of two-compartment cell with three-electrode cell and the working electrode connections of NRR process.

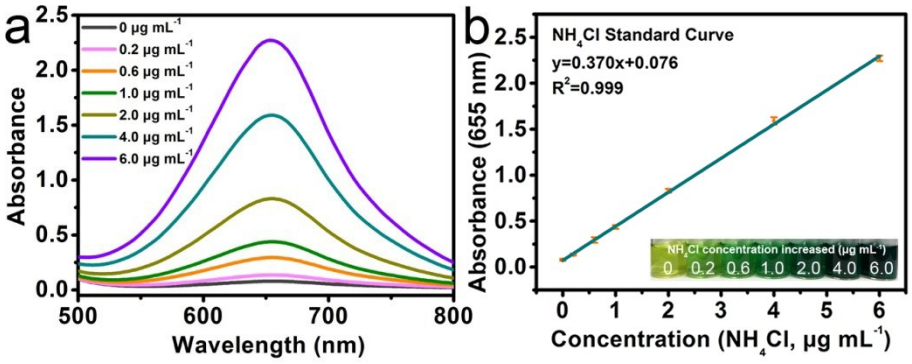

Fig. S2. (a) UV-Vis spectra of indophenol assays with NH_4Cl after incubated for 2 h at room temperature. (b) Calibration curve used for estimation of NH_4Cl.

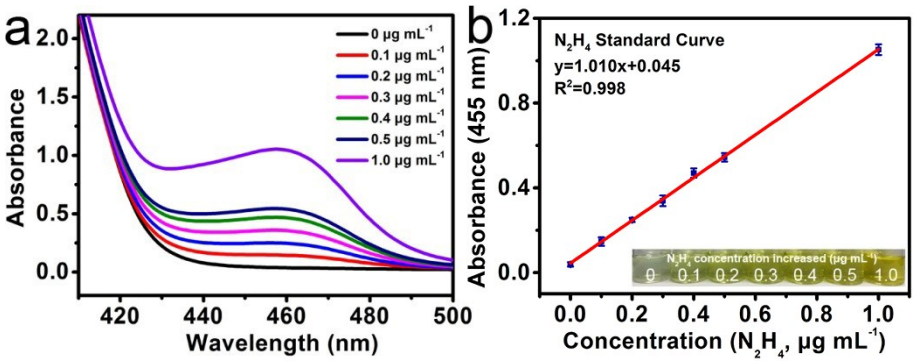

Fig. S3. (a) UV-Vis spectra of various N_2H_4 concentration after incubated for 20 min at room temperature. (b) Calibration curve used for calculation of N_2H_4 concentrations.

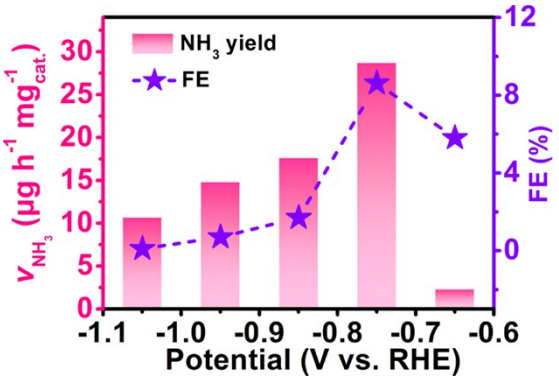

Fig. S4. NH_3 yields and FEs for Cr_2O_3/CPE at a series of potentials for 2-h determined by ion chromatography analysis.

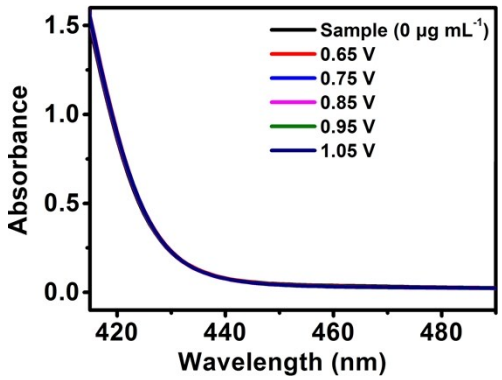

Fig. S5. UV-Vis spectra of the electrolyte estimated by the method of Watt and Chrisp before and after 2-h electrolysis in N_2 atmosphere at each given potential under ambient conditions.

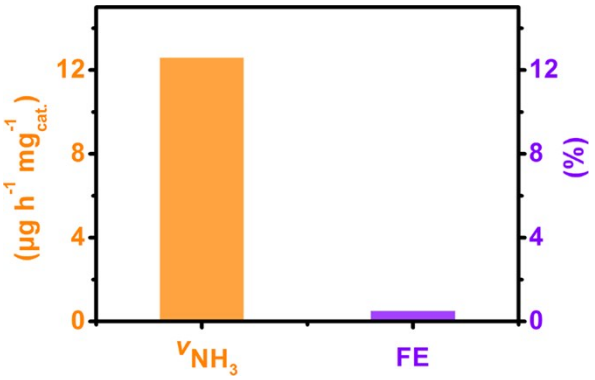

Fig. S6. NH_3 yield and FE for Ru/C at the potential of –0.75 V under ambient conditions in 0.1 M HCl.

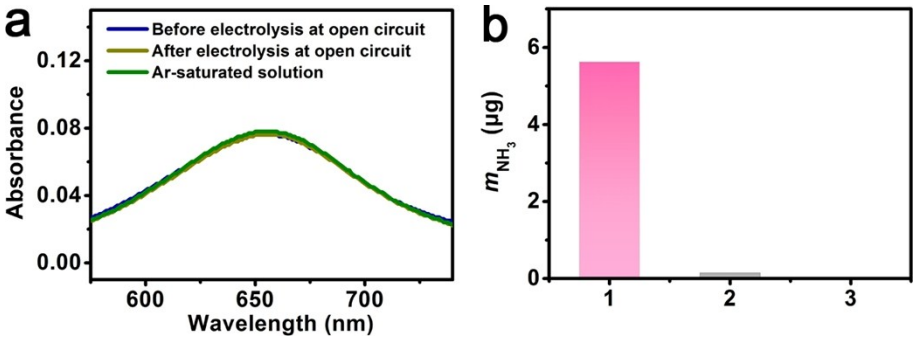

Fig. S7. (a) UV-Vis spectra of the electrolyte stained with indophenol indicator before and after 2-h electrolysis at open potential in N_2-saturated solution and at the potential of –0.75 V in Ar-saturated solution on Cr_2O_3/CPE. (b) Production of NH_3 with Cr_2O_3/CPE under different conditions: In N_2-saturated solution and at the potential of –0.75 V (Column 1); In Ar-saturated solution and at the potential of –0.75 V (Column 2); In N_2-saturated solution and at open potential (Column 3).

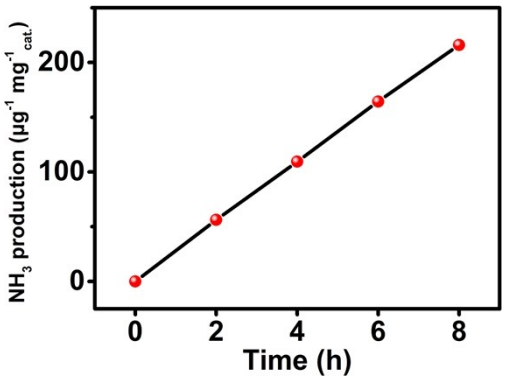

Fig. S8. The curve of NH_3 amount vs. reaction time at –0.75 V.

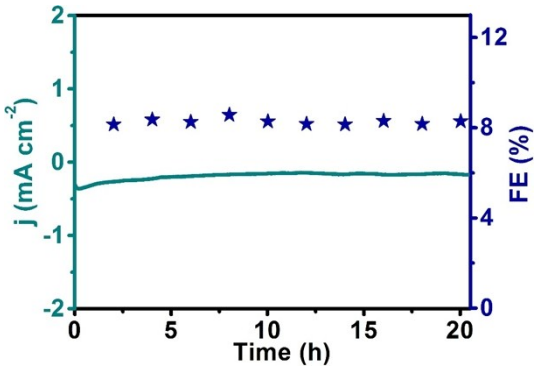

Fig. S9. Chronoamperometry and FE data for Cr_2O_3/CPE at the potential of –0.75 V in N_2-saturated 0.1 M HCl.

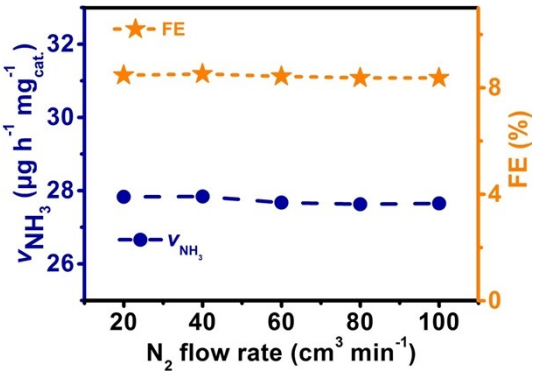

Fig. S10. NH_3 yield and FE for Cr_2O_3/CPE at the potential of –0.75 V with different N_2 flow rates.

Table S1. Comparison of the electrocatalytic N_2 reduction performance for Cr_2O_3 nanofiber with other NRR catalysts under ambient conditions.

Catalyst	Electrolyte	V_{NH3}	FE	Ref.
Cr_2O_3/CPE	**0.1 M HCl**	**28.13 μg h^{-1} $mg^{-1}_{cat.}$**	**8.56%**	**This work**
TA-reduced Au/TiO_2	0.1 M HCl	21.40 μg h^{-1} $mg^{-1}_{cat.}$	8.11%	[3]
α-Au/CeO_x-RGO	0.1 M HCl	8.31 μg h^{-1} $mg^{-1}_{cat.}$	10.1%	[4]
Au nanorods	0.1 M KOH	6.04 μg h^{-1} $mg^{-1}_{cat.}$	4%	[5]
AuHNCs	0.5 M $LiClO_4$	3.90 μg h^{-1} cm^{-2}	30.2%	[6]
Ag-Au@ZIF	THF-based electrolyte	0.61 μg h^{-1} cm^{-2}	18%	[7]
Ru/Ti	0.5 M H_2SO_4	7.34 μg h^{-1} cm^{-2}	-	[8]
Ru/C	2 M KOH	0.21 μg h^{-1} cm^{-2}	0.28%	[9]
$Bi_4V_2O_{11}/CeO_2$	0.1 M HCl	23.21 μg h^{-1} $mg^{-1}_{cat.}$	10.16%	[10]
MoO_3	0.1 M HCl	29.43 μg h^{-1} mg^{-1}	1.9%	[11]
Mo_2N	0.1 M HCl	78.4 μg h^{-1} $mg^{-1}_{cat.}$	4.5%	[12]
MoN	0.1 M HCl	0.06 μg h^{-1} cm^{-2}	1.15%	[13]
MoS_2/CC	0.1 M Na_2SO_4	0.02 μg h^{-1} cm^{-2}	1.17%	[14]
Mo nanofilm	0.01 M H_2SO_4	1.89 μg h^{-1} cm^{-2}	0.72%	[15]
PEBCD/C	0.5 M Li_2SO_4	1.58 μg h^{-1} cm^{-2}	2.85%	[16]
Fe_2O_3-CNT	$KHCO_3$	0.22 μg h^{-1} cm^{-2}	0.15%	[17]
Fe_3O_4/Ti	0.1 M Na_2SO_4	0.012 μg h^{-1} cm^{-2}	2.6%	[18]
N-doped nanocarbon	0.05 M H_2SO_4	27.20 μg h^{-1} $mg^{-1}_{cat.}$	1.42%	[19]
B_4C	0.1 M HCl	26.57 μg h^{-1} $mg^{-1}_{cat.}$	15.95%	[20]
Au flowers	0.1 M HCl	25.57 μg h^{-1} $mg^{-1}_{cat.}$	6.05%	[21]
Ag nanosheet	0.1 M HCl	4.62×10^{-11} mol s^{-1} cm^{-2}	4.8%	[22]

β-FeOOH nanorods	0.5 M $LiClO_4$	23.32 μg h^{-1} $mg^{-1}_{cat.}$	6.7%	[23]
TiO_2–rGO	0.1 M Na_2SO_4	15.13 μg h^{-1} $mg^{-1}_{cat.}$	3.3%	[24]

Table S2. Data obtained from the ion chromatography for NH_4^+ concentrations after electrolysis for 2-h at a series of potentials.

Potential	**Concentration (NH_4^+, ppm)**
–0.65 V	0.013
–0.75 V	0.164
–0.85 V	0.101
–0.95 V	0.085
–1.05 V	0.061

References

[1] D. Zhu, L. Zhang, R. E. Ruther and R. J. Hamers, *Nat. Mater.,* 2013, **12**, 836–841.

[2] G. W. Watt and J. D. Chrisp, *Anal. Chem.,* 1952, **24**, 2006–2008.

[3] M. Shi, D. Bao, B. Wulan, Y. Li, Y. Zhang, J. Yan and Q. Jiang, *Adv. Mater.,* 2017, **29** 1606550.

[4] S. Li, D. Bao, M. Shi, B. Wulan, J. Yan and Q. Jiang, *Adv. Mater.,* 2017, **29**, 1700001.

[5] D. Bao, Q. Zhang, F. Meng, H. Zhong, M. Shi, Y. Zhang, J. Yan, Q. Jiang and X. Zhang, *Adv. Mater.,* 2017, **29**, 1604799.

[6] M. Nazemi, S. R. Panikkanval and M. A. El-Sayed, *Nano Energy,* 2018, **49**, 316–323.

[7] H. K. Lee, C. S. L. Koh, Y. H. Lee, C. Liu, I. Y. Phang, X. Han, C. K. Tsung, X. Ling, *Sci. Adv,.* 2018, **4**, eaar3208.

[8] K. Kugler, M. Luhn, J. A. Schramm, K. Rahimi and M. Wessling, *Phys. Chem. Chem. Phys.,* 2015, **17**, 3768–3782.

[9] V. Kordali, G. Kyriacou and C. Lambrou, *Chem. Commun.,* 2000, **17**, 1673–1674.

[10] C. Lv, C. Yan, G. Chen, Y. Ding, J. Sun, Y. Zhou and G. Yu, *Angew. Chem. Int. Ed.,* 2018, **57**, 6073–6076.

[11] 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.

[12] X. Ren, G. Cui, L. Chen, F. Xie, Q. Wei, Z. Tian and X. Sun, *Chem. Commun.,* 2018, **54**, 8474–8477.

[13] L. Zhang, X. Ji, X. Ren, Y. Luo, X. Shi, A. M. Asiri, B. Zheng and X. Sun, *ACS Sustainable Chem. Eng.,* 2018, **6**, 9550–9554.

[14] L. Zhang, X. Ji, X. Ren, Y. Ma, X. Shi, Z. Tian, A. M. Asiri, L. Chen, B. Tang and X. Sun, *Adv. Mater.,* 2018, **30**, 1800191.

[15] D. Yang, T. Chen and Z. Wang, *J. Mater. Chem. A,* 2017, **5**, 18967–18971.

[16] G. Chen, X, Cao, S. Wu, X. Zeng, L. Ding, M. Zhu, H. Wang, *J. Am. Chem. Soc.,* 2017, **139**, 9771–9774.

[17] S. Chen, S. Perathoner, C. Ampelli, C. Mebrahtu, D. Su, G. Centi, *Angew. Chem. Int. Ed.,* 2017, **56**, 2699–2703.

[18] Q. Liu, X. Zhang, B. Zhang, Y. Luo, G. Cui, F. Xie and X. Sun, *Nanoscale,* 2018, **10**, 14386–14389.

[19] Y. Liu, Y. Su, X. Quan, X. Fan, S. Chen, H. Yu, H. Zhao, Y. Zhang and J. Zhao, *ACS Catal.,* 2018, **8**, 1186–1191.

[20] W. Qiu, X. Xie, J. Qiu, W. Fang, R. Liang, X. Ren, X. Ji, G. Cui, A. M. Asiri, G. Cui, Bo Tang and X. Sun, *Nat. Commun.,* 2018, **9**, 3485.

[21] Z. Wang, Y. Li, H. Yu, Y. Xu, H. Xue, X. Li, H. Wang and L. Wang, *ChemSusChem,* 2018, DOI: 10.1002/cssc.201801444.

[22] H. Huang, L. Xia, X. Shi, A. M. Asirie and X. Sun, *Chem. Commun.,* 2018, DOI: 10.1039/C8CC06365F.

[23] X. Zhu, Z. Liu, Q. Liu, Y. Luo, X. Shi, A. M. Asiri, Y. Wu and X. Sun, *Chem. Commun.,* 2018, DOI: 10.1039/C8CC06366D.

[24] X. Zhang, Q. Liu, X. Shi, A. M. Asiri, Y. Luo, X. Sun and T. Li, *J. Mater. Chem. A,* 2018, **6**, 17303–17306.