## **Electronic Supplementary Information**

## **Experimental section**

*Materials*: Anatase (TiO<sub>2</sub>), potassium carbonate (K<sub>2</sub>CO<sub>3</sub>), ammonium chloride (NH<sub>4</sub>Cl), hydrazine hydrate (N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O), sodium hypochlorite (NaClO), sodium hydroxide (NaOH), sodium salicylate (C<sub>7</sub>H<sub>5</sub>O<sub>3</sub>Na), sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>), hydrochloric acid (HCl), ethanol (CH<sub>3</sub>CH<sub>2</sub>OH), and carbon paper were bought from Beijing Chemical Corporation. Para-(dimethylamino) benzaldehyde (C<sub>9</sub>H<sub>11</sub>NO), sodium nitroferricyanide (III) dihydrate (Na<sub>2</sub>Fe(CN)<sub>5</sub>NO·2H<sub>2</sub>O), and Nafion were purchased from Aladdin Ltd. (Shanghai, China). The water used throughout all experiments was purified through a Millipore system.

*Preparation of K*<sub>2</sub>*Ti*<sub>4</sub>*O*<sub>9</sub>*:* The Potassium titanate (K<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub>) were synthesized through the solid-sate reaction route at high temperature with K<sub>2</sub>CO<sub>3</sub> and TiO<sub>2</sub> as the K and Ti sources respectively. The mixture of K<sub>2</sub>CO<sub>3</sub> and TiO<sub>2</sub> at the molar ratio of 1:3 was heated at 800 °C in air for 20 h, and for another 20 h after grinding.

*Preparation of*  $K_2Ti_4O_9/CP$ : The carbon paper is used as support for test because it has good electrical conductivity and is easy to handle. In a typical synthesis of working electrode, the catalyst suspension was prepared by blending 10 mg catalyst powder with 40 µL Nafion binder, 720 µL ethanol and 240 µLwater and further ultrasonic bath for 30 min. Then, 10 µL of the suspension was loaded onto a carbon paper electrode with area of 1 x 1 cm<sup>2</sup> and dried under ambient condition for measurement.

*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). 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 UV-Vis absorbance spectra were measured on a SHIMADZU UV-1800 UV-Vis

spectrophotometer.

*Electrochemical measurements*: Before NRR measures, the Nafion proton exchange film was pretreated by heating in 5% H<sub>2</sub>O<sub>2</sub> solution, 0.5 M H<sub>2</sub>SO<sub>4</sub> and ultrapure water at 80 °C for 1.5 h, respectively. Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system using K<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub> 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 KOH aqueous solution, E (vs RHE) =E (vsAg/AgCl) + 0.059 × pH + 0.197 V. All experiments were carried out at room temperature. For N<sub>2</sub> reduction experiments, the 0.1 M KOH electrolyte was purged with N<sub>2</sub> for 30 min before the measurement. Electrochemical test was conducted in N<sub>2</sub>-saturated 0.1 M KOH solution in a two-compartment cell, which was separated by Nafion 211 membrane.

*Determination of NH*<sub>3</sub>: The produced NH<sub>3</sub> was spectrophotometrically determined by indophenol blue method.<sup>1</sup> Typically, 2 mL 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<sub>5</sub>FeN<sub>6</sub>Na<sub>2</sub>O·2H<sub>2</sub>O were add into the above solution. After standing at room temperature for 2 h, UV-Vis absorption spectrum was measured. The concentration-absorbance curves were calibrated using standard NH<sub>3</sub> solution with a serious of concentrations. The fitting curve (y = 0.41x + 0.040, R<sup>2</sup> = 0.999) shows good linear relation of absorbance value with NH<sub>3</sub> concentration.

*Determination of*  $N_2H_4$ : The amount of  $N_2H_4$  present in the electrolyte was determined by the method of Watt and Chrisp.<sup>2</sup> The mixture of  $C_9H_{11}NO$  (5.99 g), HCl (30 mL), and  $C_2H_5OH$  (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 =0.74x+0.049, R<sup>2</sup> = 0.999) shows good linear relation of absorbance value with N<sub>2</sub>H<sub>4</sub> concentration (Supplementary Fig. 2). *Calculations of NH<sub>3</sub> formation rate and FE:* NH<sub>3</sub> formation rate was calculated using the following equation:

NH<sub>3</sub> formation rate = [NH<sub>3</sub>]×V/( $m_{cat.}$ ×t)

FE was calculated according to following equation:

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

Where  $[NH_3]$  is the measured  $NH_3$  concentration; V is the volume of the cathodic reaction electrolyte; t is the potential applied time;  $m_{cat.}$  is the loaded quality of catalyst; F is the Faraday constant; and Q is the quantity of applied electricity.



Fig. S1. (a) UV-Vis absorption spectra of various  $NH_3$  concentrations after incubated for 2 h at room temperature. (b) Calibration curve used for calculation of  $NH_3$  concentrations.



Fig. S2. (a) UV-Vis absorption spectra of various  $N_2H_4$  concentrations after incubated for 10 min at room temperature. (b) Calibration curve used for calculation of  $N_2H_4$ concentration.



Fig. S3. CV curves of  $K_2Ti_4O_9/CP$  and CP in Ar- and  $N_2$ -saturated 0.1 M KOH.



Fig. S4. NH<sub>3</sub> yields and FEs of TiO<sub>2</sub>/CP for NRR at -0.50 V.



Fig. S5.  $NH_3$  yields of  $K_2Ti_4O_9/CP$  in (1)  $N_2$ -saturated solution at -0.50 V, (2) Arsaturated solution at -0.50 V and (3)  $N_2$ -saturated solution at open circuit potential.



Fig. S6. The amount of  $NH_3$  produced vs. reaction time over  $K_2Ti_4O_9/CP$  at -0.50 V.



Fig. S7. UV-Vis absorption spectra of the 0.1 M KOH electrolytes estimated by the method of Watt and Chrisp after 2-h electrolysis in  $N_2$  at each given potential.



**Fig. S8.** UV-Vis absorption spectra of the electrolytes coloured with indophenol indicator after electrolysis under different conditions for 2 h.



Fig. S9. UV-Vis absorption spectra of the electrolytes (obtained by repeating electrolysis for 6 times) coloured with indophenol indicator in 0.1 M KOH at -0.50 V.



Fig. S10. SEM image of  $K_2T_4O_9$  after stability test.



**Fig. S11.** XRD pattern of  $K_2T_4O_9/CP$  after stability test.



Fig. S12. XPS spectra of  $K_2T_4O_9$  in the (a) K 2p and (b) Ti 2p regions after stability test.

**Table S1.** Comparison of the electrocatalytic NRR performance of  $K_2Ti_4O_9$  with other aqueous-based NRR electrocatalysts at room temperature.

Catalyst	Electrolyte	NH <sub>3</sub> yield	FE (%)	Ref.
K <sub>2</sub> Ti <sub>4</sub> O <sub>9</sub>	0.1 M KOH	22.88 μg h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	5.87	This work
Ag nanosheet	0.1 M HCl	$4.62 \times 10^{-11}  \text{mol s}^{-1}  \text{cm}^{-2}$	4.8	3
Au nanorods	0.1 M KOH	6.042 μg h–1 mg–1cat.	4	4
Ru/C	2.0 M KOH	$0.21 \ \mu g \ h^{-1} \ cm^{-2}$	0.28	5
Rh nanosheets	0.1 M KOH	23.88 $\mu$ g h <sup>-1</sup> cm <sup>-2</sup>	0.217	6
Fe <sub>2</sub> O <sub>3</sub> -CNT	KHCO3	$0.22 \ \mu g \ h^{-1} \ cm^{-2}$	0.15	7
Fe <sub>3</sub> S <sub>4</sub>	0.1 M HCl	75.4 $\mu$ g h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	6.45	8
PEBCD/C	0.5 M Li <sub>2</sub> SO <sub>4</sub>	$1.58 \ \mu g \ h^{-1} \ cm^{-2}$	2.85	9
MoS <sub>2</sub> /CC	0.1 M Na <sub>2</sub> SO <sub>4</sub>	4.94 $\mu$ g h <sup>-1</sup> cm <sup>-2</sup>	1.17	10
Mo nanofilm	0.01 M H <sub>2</sub> SO <sub>4</sub>	$1.89 \ \mu g \ h^{-1} \ cm^{-2}$	0.72	11
Bi <sub>4</sub> V <sub>2</sub> O <sub>11</sub> /CeO <sub>2</sub>	0.1 M HCl	23.21 $\mu$ g h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	10.16	12
TiO <sub>2</sub> nanosheets array	0.1 M Na <sub>2</sub> SO <sub>4</sub>	$9.16 \times 10^{-11} \text{ mol s}^{-1} \text{ cm}^{-2}$	2.5	13
TiO <sub>2</sub> -rGO	0.1 M Na <sub>2</sub> SO <sub>4</sub>	$15.13 \ \mu g \ h^{-1} \ mg^{-1}_{cat.}$	3.3	14
B-TiO <sub>2</sub>	0.1 M Na2SO4	$14.4 \ \mu g \ h^{-1} \ mg^{-1}_{cat.}$	3.4	15
TA-reduced Au/TiO <sub>2</sub>	0.1 M HCl	21.4 $\mu$ g h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	8.11	16
Nb <sub>2</sub> O <sub>5</sub> nanofiber	0.1 M HCl	43.6 $\mu$ g h <sup>-1</sup> mg <sup>-1</sup> <sub>cat.</sub>	9.26	17

MoN NA/CC	0.1 M HCl	$18.42 \ \mu g \ h^{-1} \ cm^{-2}$	1.15	18
B <sub>4</sub> C nanosheet	0.1 M HCl	$26.57 \ \mu g \ h^{-1} \ cm^{-2}$	15.95	19
Mn <sub>3</sub> O <sub>4</sub> nanocube	0.1 M Na <sub>2</sub> SO <sub>4</sub>	$11.6 \ \mu g \ h^{-1} \ mg^{-1}_{cat.}$	3.0	20
Fe <sub>2</sub> O <sub>3</sub> /TiO <sub>2</sub>	1.0 M KOH	$16.52 \ \mu g \ h^{-1} \ m g^{-1}{}_{cat.}$	0.31	21
Fe <sub>2</sub> O <sub>3</sub>	0.1 M KOH	$0.46 \ \mu g \ h^{-1} \ cm^{-2}$	6.04	22
γ-Fe <sub>2</sub> O <sub>3</sub>	0.1 M KOH	$0.212 \ \mu g \ h^{-1} \ m g^{-1}{}_{cat.}$	1.9%	23
30% Fe <sub>2</sub> O <sub>3</sub> -CNT	0.5 M KOH	$0.4125 \ \mu g \ h^{-1} \ cm^{-2}$	0.028	24

## References

- 1 D. Zhu, L. Zhang, R. E. Ruther and R. J. Hamers, *Nat. Mater.*, 2013, **12**, 836–84.
- 2 G. W. Watt and J. D. Chrisp, Anal. Chem., 1952, 24, 2006–2008.
- H. Huang, L. Xia, X. Shi, A. M. Asiri and X. Sun, *Chem. Commun.*, 2018, 54, 11427–11430.
- 4 D. Bao, Q. Zhang, F. Meng, H. Zhong, M. Shi, Y. Zhang, J. Yan, Q. Jiang and X. Zhang, *Adv. Mater.*, 2017, **29**, 1604799.
- 5 V. Kordali, G. Kyriacou and C. Lambrou, *Chem. Commun.*, 2000, **17**, 1673– 1674.
- H. Liu, S. Han, Y. Zhao, Y. Zhu, X. Tian, J. Zeng, J. Jiang, B. Xia and Y. Chen, J. Mater. Chem. A, 2018, 6, 3211–3217.
- S. Chen, S. Perathoner, C. Ampelli, C. Mebrahtu, D. Su and G. Centi, *Angew. Chem., Int. Ed.*, 2017, 56, 2699–2703.
- X. Zhao, X. Lan, D. Yu, H. Fu, Z. Liu and T. Mu, *Chem. Commun.*, 2018, 54, 13010–13013.
- 9 G. Chen, X. Cao, S. Wu, X. Zeng, L. Ding, M. Zhu and H. Wang, J. Am. Chem. Soc., 2017, 139, 9771–9774.
- 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.
- 11 D. Yang, T. Chen and Z. Wang, J. Mater. Chem. A, 2017, 5, 18967–18971.
- 12 C. Lv, C. Yan, G. Chen, Y. Ding, J. Sun, Y. Zhou and G. Yu, Angew. Chem., Int. Ed., 2018, 57, 6073–6076.
- R. Zhang, X. Ren, X. Shi, F. Xie, B. Zheng, X. Guo and X. Sun, ACS Appl. Mater. Interfaces, 2018, 10, 28251–28255.
- 14 X. Zhang, Q. Liu, X. Shi, A. M. Asiri, Y. Luo, X. Sun and T. Li, J. Mater. Chem. A, 2018, 6, 17303–17306.
- 15 Y. Wang, K. Jia, Q. Pan, Y. Xu, Q. Liu, G. Cui, X. Guo and X. Sun, ACS Sustainable Chem. Eng., 2019, 7, 117–122.

- M. Shi, D. Bao, B. Wulan, Y. Li, Y. Zhang, J. Yan and Q. Jiang, *Adv. Mater.*, 2017, 29, 1606550.
- 17 J. Han, Z. Liu, Y. Ma, G. Cui, F. Xie, F. Wang, Y. Wu, S. Gao, Y. Xu and X. Sun, *Nano Energy*, 2018, **52**, 264–270.
- 18 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.
- W. Qiu, X. Xie, J. Qiu, W. Fang, R. Liang, X. Ren, X. Ji, G. Cui, A. M. Asiri,G. Cui, B. Tang and X. Sun, *Nat. Commun.*, 2018, 9, 3485.
- X. Wu, L. Xia, Y. Wang, W. Lu, Q. Liu, X. Shi and X. Sun, *Small*, 2018, 14, 1803111.
- R. Manjunatha, A. Karajic, V. Goldstein and A. Schechter, *ACS Appl. Mater*. *Interfaces*, 2019, **11**, 7981–7989.
- X. Cui, C. Tang, X. M. Liu, C. Wang, W. Ma and Q. Zhang, *Chem. Eur. J.*, 2018, 24, 18494–18501.
- J. Kong, A. Lim, C. Yoon, J. H. Jang, H. C. Ham, J. Han, S. Nam, D. Kim, Y.
  E. Sung, J. Choi and H. S. Park, *ACS Sustainable Chem. Eng.*, 2017, 5, 10986–10995.
- 24 S. Chen, S. Perathoner, C. Ampelli, C. Mebrahtu, D. Su and G. Centi, ACS Sustainable Chem. Eng., 2017, 5, 7393–7400.