Electronic Supplementary Information

Experimental section

Materials: The kapok fibers were collected in Huaibei, China. Ammonium chloride (NH₄Cl), hydrazine hydrate (N₂H₄·H₂O), hydrochloric acid (HCl) and ethanol (C₂H₅OH) were purchased from Chengdu Kelong Chemical Reagent Factory. Nitroferricyanide (III) dihydrate (Na₂Fe(CN)₅NO·2H₂O) and Nafion (5 wt%) sodium were purchased from Aladdin Ltd (Shanghai). Para-(dimethylamino) benzaldehyde (C₉H₁₁NO), sodium salicylate (C₇H₅O₃Na), sodium hypochlorite (NaClO), sodium hydroxide (NaOH) and carbon paper (CP) were bought from Beijing Chemical Corporation. Aqueous solutions were prepared with ultrapure water and all chemical reagents are of analytical grade and used without further purification.

Synthesis of O-KFCNTs: Kapok fibers were first soaked in an acetone solution for two hours and then rinsed with ethanol and dried at 80 °C to obtain the cleaned kapok fibers. Then, the treated kapok fibers were heated in a furnace under an argon atmosphere at 600 °C for 2 h with an elevating rate of 2 °C min⁻¹ from room temperature and then cooled down under an argon atmosphere to room temperature, respectively. The obtained blackish wool-like product is denoted as O-KFCNTs.

Characterization: Scanning electron microscopy (SEM) data were acquired on a XL30 ESEM FEG microscope instrument at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were obtained from a Zeiss Libra 200FE transmission electron microscope operated at 200 kV. The powder X-ray diffraction pattern was obtained using an X-ray diffractometer from a Shimazu XRD-6100 diffractometer with Cu K α radiation (40 kV, 30 mA) of wavelength 0.154 nm (Japan). The X-ray photoelectron spectroscopy (XPS) spectra were performed on an ESCALABMK II X-ray photoelectron spectrometer with the exciting source of Mg. UV-Vis absorption spectra were recorded on a UV-Vis spectrophotometer (Shimadazu, UV-1800).

Electrochemical measurement: Electrochemical measurements were performed in a typical H-cell which cathodic and anodic compartments separated with proton

exchange membrane by using a CHI 660E electrochemical workstation station (CHI Instruments, China) under ambient conditions. The electrocatalytic activity of O-KFCNTs for N₂ reduction experiments were performed on a standard three-electrode system in 0.1 M HCl by using O-KFCNTs/CP as working electrode, Ag/AgCl (saturated KCl electrolyte) as reference electrode and graphite rod as counter electrode. The catalyst ink was prepared by blending 10 mg catalyst powder with 20 µL Nafion binder (5 wt%) and 980 µL ethanol and further ultrasonic bath for 30 min. Then, 10 μ L of the ink (10 mg mL⁻¹) was spread across a 1 × 1 cm² surface area of CP to get the catalyst loading of 0.1 mg cm⁻². All potentials hereafter were recorded with respect to reversible hydrogen electrode via calibration with the following equation: E (vs. RHE) = E (vs. Ag/AgCl) + $0.059 \times pH + 0.197 V$. The proton exchange membrane was first boiled in ultrapure water for 1 h and further treated in H₂O₂ (5%) aqueous solution for another 1 h and then immersed in 0.5 M H₂SO₄ for 3 h, all steps were performed at 80 °C, and finally washed with deionized water to neutral. For every NRR tests, the HCl electrolyte (0.1 M) was bubbled with N₂ for 30 min before the measurement.

Determination of NH₃: The concentration of produced NH₃ was determined by UV-Vis absorption spectrophotometry with indophenol blue method.¹ In detail, 2 mL post-tested electrolyte was obtained from the cathodic chamber and mixed with 2 mL of 1 M NaOH solution containing 5 wt% salicylic acid and 5 wt% sodium citrate, then 1 mL of 0.05 M sodium hypochlorite and 0.2 mL of sodium nitroferricyanide (1 wt%) were added to the above solution successively. Afterwards, the mixture was incubated at 25 °C for 2 h. Then the solution was removed to quartz cell and recorded the UVvis absorption value corresponding to the concentration of indophenol blue. The concentration-absorbance curve was calibrated using standard NH₄Cl solution with NH₃ concentrations of 0.00, 0.05, 0.10, 0.15, 0.20, 0.25, and 0.30 µg mL⁻¹ in 0.1 M HCl and shows a highly linear relationship between the NH₃ concentration and the colorimetric signal with the corresponding equation of y = 0.448 x + 0.036 (R² = 0.999) by three times measurements. **Determination of N₂H₄:** The method of Watt and Chrisp was used to confirm the existence of N₂H₄.² In detail, 5.99 g p-C₉H₁₁NO was added into the mixed solution with HCl (30 mL) and C₂H₅OH (300 mL) and used as a chromogenic substrate. The calibration curve was plotted as follows: a series of 5 mL standard N₂H₄ solutions were prepared with the concentrations of 0.0, 0.2, 0.4, 0.6, 0.8, 1.0 µg mL⁻¹ in 0.1 M HCl, and separately mixed uniformly with 5 mL of the above prepared color reagent. After the mixture was incubated for 20 min in room temperature and then transferred into 4 mL quartz cell for UV-vis spectra record at 455 nm (A₄₅₅). The calibration curve with y = 0.885 x + 0.036 (R² = 0.999) was obtained and shown a good linear relation between absorbance and N₂H₄ concentration by three times independent calibrations. The yields N₂H₄ of the post-tested electrolytes were estimated from a standard curve.

Calculations of NH₃ yield rate and FE: NH₃ yield rate is calculated using the following equation:

NH₃ yield rate = [NH₃] × V / ($m_{cat.} \times t$) (1)

FE is calculated according to following equation:

 $FE = 3 \times F \times [NH_3] \times V / (M(NH_3) \times Q)$ ⁽²⁾

Where $[NH_3]$ (µg mL⁻¹) is the measured NH₃ concentration; V (mL) is the volume of the cathodic reaction electrolyte; m_{cat.} (mg cm⁻²) is the loaded mass of catalyst on carbon paper; t (h) is the potential applied time; F = 96485 C mol⁻¹ is the Faraday constant; M(NH₃) (g mol⁻¹) is the molar mass of NH₃; Q (C) is the total quantity of applied electricity.

Calculation Details: All computations were performed based on spin-polarized density function theory (DFT) as carried out under Vienna Ab-initio Simulation Package (VASP). Perdew-Burke-Ernzerhof (PBE) function along with a generalized gradient approximation (GGA) were employed to describe the electron exchange. The electron-ion interaction was described by the projector augmented wave (PAW) method. The kinetic energy cutoff for planewave was set as 400 eV. A $3 \times 3 \times 1$ k-points grid was used to sample the Brillioun zone. Then the structures were fully optimized until the following convergence criterions were reached: 10–4 eV for

atomic energy and -0.02 eVÅ⁻¹ of atomic force, respectively.³

To accurately model the amorphous carbon, defective graphene and carbon nanotube doping with oxygen atom were both built. In detail, a (4×4) supercell of graphene and a single-walled carbon nanotube with chirality of (8, 0) were built. Oxygen atoms were doped in graphene and SWNT by replacing carbon atoms with oxygen atoms. To ensure the computational accuracy, both model had vacuum layers of 20 Å.



Fig. S1. The XPS survey spectrum of O-KFCNTs.



Fig. S2. (A) UV-Vis absorption spectra of various NH_3 concentrations after incubated with indophenol indicator for 2 h at room temperature. (B) Calibration curve used for calculation of NH_3 concentrations.



Fig. S3. UV-Vis absorption spectra of the electrolytes coloured with indophenol indicator after electrolysis using different electrodes.



Fig. S4. UV-Vis absorption spectra of the electrolytes coloured with indophenol indicator after electrolysis under different conditions for 2 h.



Fig. S5. UV-Vis absorption spectra of the electrolytes coloured with indophenol indicator after electrolysis at different reaction time at -0.85 V.



Fig. S6. UV-Vis absorption spectra of the electrolytes (obtained by repeating electrolysis for 6 times) coloured with indophenol indicator in 0.1 M HCl at -0.85 V.



Fig. S7. SEM image for post-NRR O-KFCNTs.



Fig. S8. XPS spectra for post-NRR O-KFCNTs in (A) C 1s and (B) O 1s regions.



Fig. S9. (A) UV-Vis absorption spectra of various N_2H_4 concentrations after incubated for 20 min at room temperature. (B) Calibration curve used for calculation of N_2H_4 concentration.



Fig. S10. NH₃ yield rates and FE in different electrolytes: A) 0.1 M Na₂SO₄, B) 0.1 M NaOH.



Fig. S11. NH_3 yield rate and FE of O-KFCNTs-400, O-KFCNTs, and O-KFCNTs-800.



Fig. S12. Slab models used in this work and related NRR mechanism.

Catalyst	Potential (V)	Electrolyte	NH ₃ yield rate	FE (%)	Ref.
O-KFCNTs	-0.85	0.1 M HCl	25.1 µg h ⁻¹ mg ⁻¹ _{cat.}	5.7	This work
Fe ₂ O ₃ nanorods	-0.80	0.1 M Na ₂ SO ₄	15.9 μg h ⁻¹ mg ⁻¹ _{cat.}	0.9	4
Mn ₃ O ₄ Nanocube	-0.80	0.1 M Na ₂ SO ₄	$11.6 \ \mu g \ h^{-1} \ mg^{-1}_{cat.}$	3.0	5
β-FeOOH nanorod	-0.75	0.5 M LiClO ₄	23.3 $\mu g h^{-1} m g^{-1}_{cat.}$	6.7	6
γ-Fe ₂ O ₃	0.00	0.1 M KOH	$0.21 \ \mu g \ h^{-1} \ mg^{-1}_{cat.}$	1.9	7
N-doped porous carbon	-0.90	0.05 M H ₂ SO ₄	23.8 $\mu g h^{-1} m g^{-1}{}_{cat.}$	1.4	8
Pd _{0.2} Cu _{0.8} /rGO	-0.20	0.1 M KOH	$2.8 \ \mu g \ h^{-1} \ mg^{-1}_{cat.}$	-	9
Au nanorods	-0.20	0.1 M KOH	$6.042 \ \mu g \ h^{-1} \ m g^{-1}{}_{cat.}$	4.0	10
Hollow Cr ₂ O ₃ microspheres	-0.90	0.1 M Na ₂ SO ₄	25.3 $\mu g h^{-1} m g^{-1}_{cat.}$	6.8	11
TiO ₂ -rGO	-0.90	0.1 M Na ₂ SO ₄	$15.1 \ \mu g \ h^{-1} \ m g^{-1}_{cat.}$	3.3	12
V_2O_3/C	-0.60	0.1 M Na ₂ SO ₄	$12.3 \ \mu g \ h^{-1} \ mg^{-1}_{cat.}$	7.28	13
S-doped carbon nanosphere	-0.70	0.1 M Na ₂ SO ₄	19.07 $\mu g h^{-1} m g^{-1}_{cat.}$	7.47	14
Boron-Doped TiO ₂	-0.80	0.1 M Na ₂ SO ₄	14.4 $\mu g h^{-1} m g^{-1}{}_{cat.}$	3.4	15
C-doped TiO ₂ nanoparticles	-0.70	0.1 M Na ₂ SO ₄	$16.22 \ \mu g \ h^{-1} \ mg^{-1}_{cat.}$	1.84	16
$Ti_3C_2T_x$ nanosheet	-0.40	0.1 M HCl	$20.4 \ \mu g \ h^{-1} \ m g^{-1}{}_{cat.}$	9.3	17
MoO ₃	-0.40	0.1 M HCl	29.43 µg h ⁻¹ mg ⁻¹ _{cat.}	1.9	18

Table S1. Comparison of the NH₃ electrosynthesis activity for O-KFCNTs with other NRR catalysts under ambient conditions.

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 F. Gong, Z. Ding, Y. Fang, C.-J. Tong, D. Xia, Y. Lv, B. Wang, D.V. Papavassiliou, J. Liao and M. Wu, ACS Appl. Mater. Interfaces, 2018, 10, 14614–14621.
- 4 X. Xiang, Z.Wang, X. Shi, M. Fan and X. Sun, *ChemCatChem*, 2018, **10**, 4530–4535.
- 5 X. Wu, L. Xia, Y. Wang, W. Lu, Q. Liu, X. Shi and X. Sun, *Small*, 2018, **14**, 1803111.
- 6 X. Zhu, Z. Liu, Q. Liu, Y. Luo, X. Shi, A. M. Asiri, Y. Wu and X. Sun, *Chem. Commun.*, 2018, **54**, 11332–11335.
- 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.
- 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.
- 9 M. Shi, D. Bao, S. Li, B. Wulan, J. Yan and Q. Jiang, *Adv. Energy Mater.*, 2018, 8, 1800124.
- D. Bao, Q. Zhang, F. Meng, H. Zhong, M. Shi, Y. Zhang, J. Yan, Q. Jiang, X. Zhang, *Adv. Mater.*, 2017, **29**, 1604799.
- 11 Y. Zhang, W. Qiu, Y. Ma, Y. Luo, Z. Tian, G. Cui, F. Xie, L. Chen, T. Li and X. Sun, ACS Catal., 2018, 8, 8540–8544.
- 12 X. Zhang, Q. Liu, X. Shi, A. M. Asiri, Y. Luo, X. Sun and T. Li, J. Mater. Chem. A, 2018, 6, 17303–17306.
- 13 R. Zhang, J. Han, B. Zheng, X. Shi, A. M. Asiri and X. Sun, *Inorg. Chem. Front.*, 2018, DOI: 10.1039/C8QI01145A.

- L. Xia, X. Wu, Y. Wang, Z. Niu, Q. Liu, T. Li, X. Shi, A. M. Asiri and X. Sun, *Small Methods*, 2018, 14, 1800251.
- 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.
- 16 K. Jia, Y. Wang, Q. Pan, B. Zhong, Y. Luo, G. Cui, X. Guo and X. Sun, Nanoscale Adv., 2018, DOI: 10.1039/C8NA00300A.
- J. Zhao, L. Zhang, X. Xie, X. Li, Y. Ma, Q. Liu, W. Fang, X. Shi, G. Cui and X. Sun, J. Mater. Chem. A, 2018, 6, 24031-24035.
- 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.