Electronic Supplementary Information

Experimental Section

Materials: Crystalline tungsten carbide (c-WC, \leq 400 nm, 99.9%), lithium perchlorate (LiClO₄, 99.0%), sodium hydroxide (NaOH, 99.0%), ammonium chloride (NH₄Cl), ethanol (C₂H₆O, 99.0%), sodium salicylate (C₇H₅O₃Na), *p*-dimethylaminobenzaldehyde (C₉H₁₁NO), sodium nitroferricyanide dihydrate (C₅FeN₆Na₂O·2H₂O) and sodium hypochlorite solution (NaClO) were purchased from Aladdin Ltd. (Shanghai, China). Nafion (5 wt%) solution was purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. Nitric acid (HNO₃), sulfuric acid (H₂SO₄), hydrogen peroxide (H₂O₂), hydrazine monohydrate (N₂H₄·H₂O) and ethyl alcohol (C₂H₅OH) were purchased from Beijing Chemical Corp. (China). chemical Ltd. in Chengdu. The ultrapure water used throughout all experiments was purified through a Millipore system. All reagents were analytical reagent grade without further purification.

Preparation of a-WC/GF: Amorphous WC thin film was magnetron sputtered onto graphite foil (GF) substrate to serve as a self-standing electrode (a-WC/GF). The GF was washed with ethanol, acetone, and deionized water in turn. The sputtering chamber was evacuated to about 8×10^{-4} Pa before the sputtering deposition. The distance between the target and GP was approximately 140 mm. Ar (50 sccm) was injected to the chamber with a total pressure of 10 Pa and the sputtering voltage was 350 V (direct current voltage). The bias voltage was 120 V and the sputtering time was 30 min. After sputtering, cool for 30 min before opening the chamber door to prevent the sample from oxidizing in the air. The sputtering machine (Z/CM GXZ 05-2020) is purchased from Chengdu CM Photoelectrictechnology Co., Ltd.

Characterizations: Power XRD data were acquired by 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 collected on a GeminiSEM 300 scanning electron microscope (ZEISS, Germany) at an accelerating voltage of 5 kV. TEM images were acquired on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) 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 was measured on UV-vis spectrophotometer (SHIMADZU UV-2700). The ion chromatography data were collected on Metrohm 940 Professional IC Vario.

Electrochemical measurements: In this paper, we use an H-type electrolytic cell separated by a Nafion 117 Membrane which was protonated by boiling in ultrapure water, H_2O_2 (5%)

aqueous solution and 0.5 M H₂SO₄ at 80 °C for another 2 h, respectively. A three-electrode configuration is used for electrochemical experiments using a-WC/GF as the working electrode, Ag/AgCl (filled with saturated KCl solution) as the reference electrode, and graphite rod as the counter electrode. The electrochemical experiments were carried out with an electrochemical workstation (CHI 660E) in N₂-saturated 0.5 M LiClO₄ solution. The potentials reported in this work were converted to reversible hydrogen electrode (RHE) scale via calibration with the following equation: E (RHE) = E (vs. Ag/AgCl) + 0.61 V and the presented current density was normalized to the geometric surface area.

Determination of NH₃: Concentration of produced NH₃ was determined by spectrophotometry measurement with indophenol blue method.¹ In detail, 4 mL electrolyte was obatined from the cathodic chamber and mixed with 50 μ L oxidizing solution containing NaClO (4.5%) and NaOH (0.75 M), 500 μ L coloring solution containing C₇H₅O₃Na (0.4 M) and NaOH (0.32 M), and 50 μ L catalyst solution Na₂Fe(CN)₅NO·2H₂O (1 wt%) for 1 h. The concentration-absorbance curve was calibrated using the standard NH₄Cl solution with NH₃ concentration-absorbance curves were calibrated using standard NH₄⁺ solution with a serious of concentrations. The fitting curve (y = 0.489x + 0.018, R² = 0.999) shows good linear relation of absorbance value with NH₄⁺ concentration by three times independent calibrations.

Determination of N₂H₄: The N₂H₄ production was estimated by the method of Watt and Chrisp.² The color reagent was a mixed solution of 5.99 g C₉H₁₁NO, 30 mL HCl and 300 mL C₂H₅OH. In detail, 5 mL electrolyte was removed from the electrochemical reaction vessel, and added into 5 mL prepared color reagent and stirred 15 min at 25 °C. The absorbance of such solution was measured to quantify the hydrazine yields with a standard curve of hydrazine (y = 0.6477x + 0.0623, R² = 0.9999).

Determination of m_{NH3}, R_{NH3} and FE:

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

 $m_{NH3} = c_{NH3} \times V$

 NH_3 yield rate (R_{NH3}) was calculated by the equation:

$$R_{NH3} = \frac{m_{NH3}}{M_{NH3} \times t \times m_{cat}}$$

FE was calculated by the equation:

$$FE = \frac{3F \times m_{NH3}}{M_{NH3} \times Q} \times 100\%$$

Where F is the Faraday constant (96485 C mol⁻¹); M_{NH3} is the molar mass of NH₃ (17.03 g mol⁻¹); c_{NH3} is the calculated NH₃ concentration (µg mL⁻¹); V is the volume of the electrolyte (35 mL) in the cathodic compartment; Q is the quantity of electricity; t is the electrolysis time (7200 s); m_{cat} is the loading quality of a-WC on GF (0.085 mg cm⁻²).

Measurement of electrochemically active surface area:

The electrochemically active surface area (ECSA) was measured by double layer capacitance (C_{dl}) method. Cyclic voltammetry measurement was conducted at the potential form -0.01 V to -0.11 V vs. RHE with different scan rates of 10, 15, 20, 25, 30 mV. By plotting the Δj at -0.06 V vs. RHE against the scan rate, the slope value was calculated to be the C_{dl}.



Fig. S1. SEM image of c-WC particles.

	- 3 -						Ε	en	nent	t	Wt	%	At	omi	с %
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								V	V		94.	22	!	51.5	1
/	2-							Tot	al:		100	.00	1	.00.0	00
cps/eV	1		W												
	-	W	<u>ι</u>				 				W		ww		W
			2		' 4			• 6				' 8			keV

Fig. S2. EDX map sum spectrum of a-WC thin film.



Fig. S3. (a) UV-vis absorption curves of indophenol assays kept with different concentrations of NH_4^+ ions for 1 h at room temperature. (b) Calibration curve used for calculation of NH_4^+ concentration.



Fig. S4. (a) UV-vis curves of various N_2H_4 concentrations after incubated for 15 min at room temperature. (b) Calibration curve used for calculation of N_2H_4 concentration.



Fig. S5. UV-vis absorption spectra of the electrolytes estimated by the method of Watt and Chrisp before and after 2 h electrolysis in N_2 atmosphere at -0.10 V.



Fig. S6. (a) Ion chromatogram of NH_4Cl with different concentrations in 0.5 M LiClO₄ and (b) corresponding standard curve. (c) Ion chromatogram for the electrolytes at a series of potentials after electrolysis for 2 h. (d) NH_3 yields for a-WC/GF at corresponding potentials.



Fig. S7. Time-dependent current density curves of a-WC/GF, c-WC/GF, and bare GF at -0.10 V in 0.5 M LiClO₄.



Fig. S8. Cyclic voltammetry curves of (a) c-WC/GF and (b) a-WC/GF with various scan rates (10-30 mV s⁻¹) in the region of 0.01 to 0.11 V. The capacitive current densities at 0.06 V as a function of scan rates for (c) c-WC/GF and (d) a-WC/GF.



Fig. S9. Nyquist plots of c-WC/GF and a-WC/GF



Fig. S10. UV-vis absorption spectra of the electrolytes colored with indophenol indicator after 2 h electrolysis under different conditions.



Fig. S11. (a) Time-dependent current density curves for a-WC/GF at -0.10 V over 8 cycles. (b) UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after electrolysis for a-WC/GF at -0.10 V over 8 cycles.



Fig. S12. SEM and corresponding EDX elemental mapping images of post-NRR a-WC/GF.

Element	Atomic %					
W	52.04					
С	47.96					

Table S1. Element analysis of a-WC by XPS data.

FE (%) NH₃ yield Ref. Catalyst Electrolyte $43.37 \ \mu g \ h^{-1} \ mg^{-1}_{cat.}$ a-WC/GF 0.5 M LiClO₄ 21.65 This work 17.28 µg h⁻¹ mg⁻¹_{cat.} WO₃ nanosheets 0.1 M HCl 7.0 3 WO₃ 0.1 M HCl 4 4.2 µg h⁻¹ mg⁻¹_{cat.} 12.8 5 Fe-doped W₁₈O₄₉ 0.25 M LiClO₄ 25.7 µg h⁻¹ mg⁻¹_{cat} 20.0 11.66 µg h⁻¹ mg⁻¹_{cat.} 6 0.10 M KOH W_2N_3 11.67 7 0.1 M HCl 40.05 µg h⁻¹ mg⁻¹cat. 19.32 NiWO₄ Mo₂C nanosphere $0.1 \text{ M Li}_2\text{SO}_4$ $6.6 \,\mu g \, h^{-1} \, m g^{-1}_{cat}$ 8 37.2 9 Mo_2C nanorods 0.1 M HCl 95.1 µg h⁻¹ mg⁻¹_{cat.} 8.13 TiC 0.1 M HCl 14.1 µg h⁻¹ mg⁻¹_{cat.} 5.8 10 B_4C 0.1 M HCl 26.57 µg h⁻¹ mg⁻¹_{cat.} 15.95 11 $23.21 \ \mu g \ h^{-1} \ mg^{-1}_{cat.}$ Bi₄V₂O₁₁/CeO₂ 0.1 M HCl 10.16 12 8.3 µg h⁻¹ mg⁻¹cat. a-Au/CeO_x-RGO 0.1 M HCl 10.10 13 BP 0.1 M HCl 26.42 µg h⁻¹ mg⁻¹cat. 14 12.7 NiCoS/C 0.1 M LiClO₄ 26 µg h⁻¹ mg⁻¹_{cat.} 12.90 15 Sb_2O_3 0.1 M KOH 180.4 µg h⁻¹ mg⁻¹_{cat.} 11.6 16 $18.79 \ \mu g \ h^{-1} \ mg^{-1}_{cat.}$ 0.1 M KOH N-doped phosphorene 21.51 17 7.99 µg h⁻¹ mg⁻¹_{cat.} LaF₃ 0.1 M Li₂SO₄ 36.01 18 0.1 M HCl 24.7 µg h⁻¹ mg⁻¹_{cat.} PTCA-rGO 6.9 19 4.22 µg h⁻¹ mg⁻¹cat. Bi@C 0.1 M Na₂SO₄ 15.10 20

Table S2. Comparison of electrocatalytic NRR performance for a-WC with other

 electrocatalysts under ambient conditions.

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