Electronic Supplementary Information

Experimental section

Materials: Ammonium vanadate (NH₄VO₃, purity >99.0%), glucose (C₆H₁₂O₆, purity >99.0%), ammonium chloride (NH₄Cl), hydrazine hydrate (N₂H₄·H₂O), sodium hypochlorite (NaClO), hydrochloric acid (HCl), salicylic acid (C₇H₆O₃), sodium citrate (C₆H₅O₇Na₃), sodium hydroxide (NaOH), sodium sulfate (Na₂SO₄), ethanol (CH₃CH₂OH), and carbon paper were bought from Beijing Chemical Corporation. Para-(dimethylamino) benzaldehyde (C₉H₁₁NO), sodium nitroferricyanide (III) dihydrate (Na₂Fe(CN)₅NO·2H₂O), and Nafion were purchased from Aladdin Ltd. (Shanghai, China). The water used throughout all experiments was purified through a Millipore system.

*Preparation of V*₈C₇/*C powders:* 0.47 g NH₄VO₃ and 4.0 g C₆H₁₂O₆ (molar ratio of 1:5) were put into 40 mL hot de-ionized water and mixed uniformly. The mixture solution was then transferred to a 50 ml Teflon-lined autoclave and heated at 160 °C for 15 h. The brown precipitates were then filtered and washed with deionized water and absolute alcohol to remove soluble species before being dried in a vacuum oven at 70 °C overnight. Finally, the products were heated at 1000 °C under the flowing of high-purity Ar (40 ml min⁻¹) for 3 h. The similar experiment without V-source was also carried out to prepare carbon powder (C) for comparison.^{1,2}

 NH_4VO_3 was used as vanadium source because it can easily dissolve into heated water and it is easy to be reduced by glucose. V_8C_7 nanoparticles could be prepared by thermal processing the precursor under a high-purity Ar atmosphere:

$$16 \text{ NH}_4 \text{VO}_3 + 9 \text{ C}_6 \text{H}_{12} \text{O}_6 \rightarrow 2 \text{ V}_8 \text{C}_7 + 40 \text{ CO} + 16 \text{ NH}_3 + 62 \text{ H}_2 \text{O}$$
(1)

Preparation of V_8C_7/CP : The carbon paper (CP) was cleaned via brief sonication with ethanol and water for several times. It 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 μ L Nafion binder, 720 μ L ethanol, and 240 μ Lwater and further ultrasonic bath for 30 min. Then, 10 μ L of the suspension was loaded onto a CP electrode with area of 1 × 1 cm² and dried under ambient condition for measurement.

Characterizations: XRD patterns were obtained from a Shimazu XRD-6100 diffractometer with Cu Ka 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 Xray photoelectron spectrometer using Mg as the exciting source. Elemental analysis for V was carried out using an inductively coupled plasma-atomic emission spectrometry (ICP-AES, Thermo IRIS Intrepid IIXSP, USA). The UV-Vis absorbance spectra were measured on a SHIMADZU UV-1800 UV-Vis spectrophotometer. Raman spectra were obtained by a Renishaw inVia confocal Raman microprobe under 633 nm laser excitation. A gas chromatograph (SHIMADZU, GC-2014C) equipped with MolSieve 5A column and Ar carrier gas was used for H₂ quantifications. Gas-phase product was sampled every 1000 s using a gas-tight syringe (Hamilton). ¹H nuclear magnetic resonance (NMR) spectra were collected on a superconducting-magnet NMR spectrometer (Bruker AVANCE III HD 500 MHz) and dimethyl sulphoxide was used as an internal to calibrate the chemical shifts in the spectra. TPD data were collected using a TP-5076 multiple adsorption instrument. Briefly, 0.16 g of the catalyst was first pretreated with pure He at a flow rate of 30 mL·min⁻¹ at 300 °C for 30 min, followed by cooling down to room temperature in the same atmosphere and then dosed with pure N₂. To remove residual N₂, the catalyst was purged with pure He at a flow rate of 30 mL·min⁻¹ for 30 min. The N₂ TPD measurement was subsequently performed up to 600 °C at a heating rate of 10 °C·min⁻¹ in pure He.

Electrochemical measurements: N₂ (99.999%) reduction experiments were carried out in a two-compartment cell under ambient condition, which was separated by Nafion 211 membrane. The membrane was pre-treated by boiling in ultrapure water for 1 h and treating in H₂O₂ (5 wt%) aqueous solution at 80 °C for another 1 h, respectively. And then, it was treated in 0.5 M H₂SO₄ for 3 h at 80 °C and finally in water for 6 h. The electrochemical experiments were carried out with an electrochemical workstation (CHI 660E) 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) + $0.059 \times pH$ + 0.197 V and the presented current densities were normalized to the geometric surface area. For electrochemical N2 reduction, chrono-amperometry tests were conducted in N₂-saturated electrolyte solution. Before the NRR measurements, the HCl electrolyte was bubbled with high-purity N₂ (99.999%) for 20 min. All experiments were performed at ambient conditions.

Determination of NH_3 (0.1 *M* HCl as electrolyte): Concentration of produced NH₃ was spectrophotometrically determined by the indophenol blue method.³ In detail, 2 mL of post-tested solution was got from the electrochemical reaction vessel and mixed with 2 mL of colouring solution (containing 5 wt% C₇H₆O₃, 5 wt% C₆H₅O₇Na₃ and 1 M NaOH solution), 1 mL of 0.05 M NaClO solution and 0.2 mL of 1 wt% Na₂[Fe(CN)₅NO] solution, sequentially. After standing the mixture solution at 25 °C

for 2 h, the concentration of NH₃ was determined using the absorbance at the wavelength of 655 nm. The concentration-absorbance curves were calibrated using the standard NH₄Cl solution with a series of concentrations. The fitting curve (y = 0.389 x + 0.078, R² = 0.999) shows good linear relation of absorbance value with NH₃ concentration by three times independent calibrations.³

Determination of NH₃ (0.1 M Na₂SO₄ as electrolyte): 4 mL of sample was removed from the cathodic chamber, then added into 50 µL of oxidizing solution containing NaClO (ρ Cl = 4~4.9) and NaOH (0.75 M), then added 500 µL colouring solution containing 0.4 M C₆H₅Na₃O₇·2H₂O and 0.32 M NaOH and 50 µL catalyst solution (0.1 g Na₂[Fe(CN)₅NO]·2H₂O diluted to 10 ml with deionized water) in turn. Absorbance measurements were performed after one hour at λ = 662 nm. The calibration curve (y = 0.560 x + 0.016, R² = 0.999) shows good linear relation of absorbance value with NH₃ concentration by three times independent calibrations.³

Determination of N_2H_4 : The N₂H₄ was estimated by the method of Watt and Chrisp.⁴ A mixed solution containing 5.99 g C₉H₁₁NO, 30 mL concentrated HCl and 300 ml ethanol was used as a colour reagent. The calibration curve was plotted as follow: firstly, preparing a series of N₂H₄ solutions of known concentration as standards; secondly, adding 5 mL colour reagent to above N₂H₄ solution, separately, and standing for 20 min at room temperature; finally, the absorbance of the resulting solution was measured at 455 nm. The fitting curve shows good linear relation of absorbance with N₂H₄·H₂O concentration (y = 0.697 x + 0.022, R² = 0.999) by three times independent calibrations.

Determination of Faradaic efficiency (FE) and NH_3 formation rate (R_{NH3}): 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 NH₃ produced was measured using colorimetric methods. Assuming three electrons were needed to produce one NH₃ molecule, the FE could be calculated as follows:

$$FE = 3 \times F \times [NH_3] \times V / (17 \times Q) \times 100\%$$

The NH₃ yield was calculated using the following equation:

$$NH_3$$
 yield = $[NH_3] \times V / (m_{cat.} \times t)$

Where F is the Faraday constant, $[NH_3]$ is the measured NH_3 concentration, V is the volume of the electrolyte in the cathodic chamber, Q is the total quantity of applied electricity, t is the reduction time, and $m_{cat.}$ is the loaded mass of catalyst on carbon paper.



Fig. S1. SEM image of V_8C_7/C_1 .



Fig. S2. TEM microscopy images of V_8C_7/C at different magnifications.



Fig. S3. The particle size distribution of V_8C_7 .



Fig. S4. EDX spectrum for V_8C_7/C .



Fig. S5. XPS survey spectrum of V_8C_7/C .



Fig. S6. XPS spectrum in the O 1s energy region of V_8C_7/C .



Fig. S7. Raman spectra of V_8C_7/C in region of 50~1100 cm⁻¹.



Fig. S8. The reaction device.



Fig. S9. (a) UV-Vis absorption spectra of various NH₃ concentrations after incubation for 2 h at room temperature. (b) Calibration curve used for calculation of NH₃ concentrations (0.1 M HCl as electrolyte).



Fig. S10. (a) UV-Vis absorption spectra of various N_2H_4 concentrations after incubation for 20 min at room temperature. (b) Calibration curve used for calculation of N_2H_4 concentrations (0.1 M HCl as electrolyte).



Fig. S11. UV-Vis absorption spectra of the electrolytes estimated by the method of Watt and Chrisp for 2 h electrolysis in N₂ atmosphere before and after 2 h electrolysis at -0.40 V using V₈C₇/C-CP as the working electrode.



Fig. S12. (a) UV-Vis absorption spectra of various NH₃ concentrations after incubation for 1 h at room temperature. (b) Calibration curve used for calculation of NH₃ concentrations (0.1 M Na₂SO₄ as electrolyte).



Fig. S13. (a) UV-Vis absorption spectra of the electrolytes coloured with indophenol indicator after electrolysis in 0.1 M Na₂SO₄ at different potentials for 2 h. (b) NH₃ yields and FEs for V_8C_7/C -CP at a series of potentials.



Fig. S14. NH₃ yields of before (blank) and after 2 h electrolysis under different conditions: –

0.40~V in $N_2\text{,}$ open circuit in $N_2\text{,}$ and –0.40 V in Ar.



Fig. S15. ¹⁵N isotope labelling experiment. ¹H NMR spectra for the post-electrolysis 0.1 M HCl electrolytes with ¹⁵N₂, ¹⁴N₂ as the feeding gas. Also shown are the spectra for ¹⁵NH₄⁺ and $^{14}NH_{4}^{+}$ standard samples.



Fig. S16. NH₃ yields and FEs at -0.40 V for 2 h over initial V₈C₇/C-CP and V₈C₇/C-CP

subjected to 22-h operation.



Fig. S17. TEM image for V_8C_7/C after stability test.



Fig. S18. XPS V 2p of V_8C_7/C before and after stability test.



Fig. S19. XRD pattern for V_8C_7/C before and after test.



Fig. S20. N_2 TPD curves of C and V_8C_7/C .



Fig. S21. Nyquist plots of V_8C_7/C and C in the frequency range from 1000 kHz to 1Hz with a voltage amplitude of 5 mV, and all the three electrodes are in one compartment cell being full of 0.1 M HCl solution at room temperature (25 °C).

Catalyst	Electrolyte	NH ₃ yield	FE (%)	Ref.
V ₈ C ₇ /C	0.1 M HCl	$34.62 \ \mu g \ h^{-1} \ mg^{-1}_{cat.}$	12.20	This work
VN Nanosheet Array	0.1 M HCl	$\frac{8.40\times10^{-11}\ mol\ s^{-1}}{cm^{-2}}$	2.25	5
VN nanowire array	0.1 M HCl	$\begin{array}{c} 2.48 \times 10^{-10} \ mol \ s^{-1} \\ cm^{-2} \end{array}$	3.58	6
VN nanoparticles	0.1 M HCl	$3.3 \times 10^{-10} \text{ mol s}^{-1} \text{ cm}^{-2}$	6.0	7
V ₂ O ₃ /C	0.1 M Na ₂ SO ₄	$12.3 \ \mu g \ h^{-1} \ m g^{-1}{}_{cat.}$	7.28	8
VO ₂ hollow microsphere	0.1 M Na ₂ SO ₄	14.85 $\mu g h^{-1} m g^{-1}_{cat.}$	3.97	9
TiO ₂ nanosheets array	0.1 M Na ₂ SO ₄	$\begin{array}{c} 2.48 \times 10^{-10} \ mol \ s^{-1} \\ cm^{-2} \end{array}$	2.50	10
V-TiO ₂ nanorod	0.5 M LiClO ₄	17.73 μg h ⁻¹ mg ⁻¹ cat.	15.3	11
TiC/C nanofiber	0.1 M HCl	14.1 $\mu g h^{-1} m g^{-1}_{cat.}$	5.8	12
MoS ₂ nanoflower	0.1 M Na ₂ SO ₄	29.28 μ g h ⁻¹ mg ⁻¹ _{cat.}	8.34	13
Mo ₂ C nanorod	0.1 M HCl	95.1 μg h ⁻¹ mg ⁻¹ _{cat.}	8.13	14
Cr ₂ O ₃ nanofiber	0.1 M HCl	28.13 μg h ⁻¹ mg ⁻¹ cat.	8.56	15
Cr ₃ C ₂ /C nanofiber	0.1 M HCl	23.9 μ g h ⁻¹ mg ⁻¹ cat.	8.6	16
MnO	0.1 M Na ₂ SO ₄	7.92 μ g h ⁻¹ mg ⁻¹ _{cat.}	8.02	17
Nb ₂ O ₅ nanofiber	0.1 M HCl	43.6 μ g h ⁻¹ mg ⁻¹ _{cat.}	9.26	18
CeO ₂ nanorod	0.1 M Na ₂ SO ₄	$16.4 \ \mu g \ h^{-1} \ m g^{-1}_{cat.}$	3.7	19
LaF ₃ nanoplate	0.5 M LiClO ₄	55.9 μg h ⁻¹ mg ⁻¹ _{cat.}	16.0	20
La ₂ O ₃	0.1 M Na ₂ SO ₄	$17.04 \ \mu g \ h^{-1} \ mg^{-1}_{cat.}$	4.76	21
SnO ₂	0.1 M Na ₂ SO ₄	$1.47 \times 10^{-10} \text{ mol s}^{-1} \ \text{cm}^{-2}$	2.17	22

Table S1. Comparison of the catalytic performances of V_8C_7/C with previous V-based and transition metal NRR catalysts at ambient conditions.

β-FeOOH nanorod	0.5 M LiClO ₄	23.32 μ g h ⁻¹ mg ⁻¹ _{cat.}	6.7	23
WO ₃ nanosheet	0.1 M HCl	$17.28 \ \mu g \ h^{-1} \ m g^{-1}_{cat.}$	7.0	24

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