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$\begin{array}{c} \mbox{Electronic supplementary information (ESI)}\\ \mbox{Efficient N_2 Reduction with VS_2}\\ \mbox{Electrocatalyst: Identifying the Active Sites}\\ \mbox{and Unraveling the Reaction Pathway} \end{array}$

Liang Zhao, Rui Zhao, Yixiang Zhou, Xiaoxuan Wang, Xinyue Chi, Yuanyuan Xiong, Cheng Li, Yufei Zhao, Huaizhi Wang, Zhiyu Yang, Yi-Ming Yan*

State Key Lab of Organic-Inorganic Composites, Beijing Advanced Innovation Center

for Soft Matter Science and Engineering, Beijing University of Chemical Technology,

Beijing, 100029, People's Republic of China

*Corresponding Authors.

Email: <u>bityanyiming@163.com</u>

Experimental Section

Materials

Sodium orthovanadate (Na₃VO₄·12H₂O) and thioacetamide (TAA, CH₃CSNH₂) were commercially available from Shanghai Chemical Reagent Co. Ltd. Hydrazine hydrate (N₂H₄·H₂O) and ethanol (C₂H₃OH) were purchased from Beijing Tongguang Fine Chemical Co., Ltd. Hydrochloric acid (HCl), salicylic acid (C₇H₆O₃, \geq 99.7%), ammonium chloride (NH₄Cl, 99.998%), p–dimethylaminobenzaldehyde (p–C₉H₁₁NO, 99%), trisodium sodium citrate dehydrate (C₆H₅Na₃O₇·2H₂O, 99%), sodium nitroferricyanide dihydrate (C₅FeN₆Na₂O·2H₂O, 99%), sodium hypochlorite solution (NaClO, available chlorine 6–10%) were purchased from Beijing Chemical Corp. Nafion (5 wt%) was purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. All the chemicals were used without further purification. Ultrapure Smart-S15 water (18.2 MΩ) was used in all experiments.

Synthesis of Flower-like VS₂

2 mmol Na₃VO₄·12 H₂O and 12 mmol TAA powders were dissolved in 30 mL DI water in a glass jar, which was then stirred for 1 h to form a homogeneous solution and transferred to a 50 mL Teflon-lined autoclave. The autoclave was sealed and heated at 160 °C for 24 h. After it was cooled down to room temperature, a black precipitate was collected by centrifugation and washed several times with DI water and absolute ethanol.

Synthesis of Sphere-like VS₂

The preparation process of sphere-like VS_2 is the same as that of flower-like VS_2 , which only needs to be sealed in an autoclave and heated at 160 °C for 2 hours.

Preparation of Flower-like VS₂/CP and Sphere-like VS₂/CP electrode

Flower-like VS₂/CP as prepared as following: First, 5 mg of flower-like VS₂ catalyst and 20 μ L of Nafion solution (5 wt%) were dispersed in 980 μ L mixed solution contain ethanol and H₂O (V:V=2:1) by 1h sonication to form a homogeneous ink. Then 20 μ L of the flower-like VS₂ ink was loaded on a carbon paper (1 cm × 1 cm) (TGP-H-060) and dried. The sphere-like VS₂/CP prepared by following the same method.

Characterizations

The X-ray diffraction (XRD, Rigaku D/MAX 2550) equipped with Cu K α radiation ($\lambda = 1.54178$ Å) by scanning from $2\theta = 5^{\circ}$ to 90° was used to analyze crystalline structures. A field emission scanning electron microscopy (SEM, JEOL JSM-6700F) was used to analyze the surface morphology of samples. The high-resolution TEM, TEM images were recorded on a Zeiss Libra 200FE TEM operated at 200 kV. The chemical compositions of the materials were characterized by X-ray photoelectron spectroscopy (XPS, Physical Electronics 5400 ESCA). The surface area of the samples was estimated by method of Brunauer-Emmett-Teller (BET) and the estimation of the distribution of mesoporous and microporous was made by application of the Barrett-Joyner-Halenda (BJH) method to the adsorption data. The chemical composition was investigated by using energy dispersive X-ray spectroscopy (EDX) and Raman spectroscopy. The Raman spectrum was recorded on a HORIBA Raman microscope with a laser

wavelength of 532 nm (LabRAM Aramis, HORIBA Jobin Yvon S.A.S, France) for surface characterization. N₂-Temperature programmed desorption (N₂-TPD) were carried out on an AutoChem II 2920 system. The absorbance data of spectrophotometer were measured on UV-8000S UV-Vis spectrophotometer(Shanhai Metash Instruments Co.,Ltd).

Electrochemical Measurements

Before NRR measures, the Nafion membrane was pretreated by heating in H_2O_2 solution (3 wt%), 0.5M H₂SO₄, and ultrapure water at 80°C for 2 h, respectively. Electrochemical measurements N₂ reduction experiments were carried out in a typical H-type electrolytic cell (the volume of the H-type cell is 50 mL), which was separated by the Nafion 117 membrane. The electrochemical experiments were performed with a CHI 760E electrochemical analyzer (CH Instruments, Inc., Shanghai, China) using a standard three-electrode system including prepared flower-like VS₂/CP electrode, platinum gauze electrode and Ag/AgCl (3M) electrode serving as the working electrode, counter electrode and reference electrode, respectively. The potentials reported in this work were converted to RHE scale via calibration with the following equation: E (vs RHE) = E (vs Ag/AgCl) + $0.197 + 0.0591 \times \text{pH}$. For N₂ reduction experiments, the 0.1 M HCl electrolyte was purged with N₂ for 30 min before the measurement. N₂ electrochemical reduction was conducted in N2-saturated 0.1 M HCl solution. Before the controlled potential electrolysis for hours, N2 was purged into HCl solution for at least 30 min to remove residual air.

The LSV curves were carried out at the scan rate of 10 mV s⁻¹ under Ar- or N₂saturated 0.1 M HCl solution with the CHI 760e electrochemical workstation. The ECSA was measured according the capacitive current associated with double-layer charging, as the double-layer capacitance (C_{dl}) is proportional to the surface area. Cyclic voltammetry (CV) curves were conducted between 0.007 and 0.107 V vs RHE at the scan rates of 20, 40, 60, 80, 100, 120, and 180 mV s⁻¹

Determination of NH3

Concentration of produced NH₃ was determined by the indophenol blue method. In detail, 2 ml post-tested solution was removed from the cathodic chamber, and then added into 2 ml 1.0 M NaOH solution containing $C_7H_6O_3$ and $C_6H_5Na_3O_7 \cdot 2H_2O$ (5 wt%), then added 1 ml NaClO (0.05 M) and 0.2 ml Na₂[Fe(NO)(CN)₅] $\cdot 2H_2O$ (1 wt%) aqueous solution in turn. After standing at room emperature for 2 h, the UV–Vis absorption absorption spectrum was measured. The concentration-absorbance curves were calibrated using standard NH₄Cl solution (0.1 M HCl as mother solution) with a serious of concentrations. Typically, 100 µg mL⁻¹ NH₄Cl solution was prepared and diluted to 2 µg mL⁻¹. Then, 0.0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 mL NH₄Cl solution with concentration of 2 µg mL⁻¹ were poured into test tubes and separately diluted to 2 mL with 0.1 M HCl and the resulting concentrations of NH₄Cl in the solutions are 0.0, 0.1, 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 µg mL⁻¹. The concentration of indophenol blue was determined using the absorbance at a wavelength of 655 nm. The fitting curve (y = 0.1356x + 0.0503, $R^2 = 0.9978$) shows good linear relation of absorbance value with NH₄Cl concentration by three times independent calibrations.

In addition, determination of ammonia by ion chromatography (IC). The concentrations of NH_3 in the electrolytes were also determined by IC on a Metrohm 883 ion chromatograph equipped with a Metrosep C4 cation column. Typically, 10 mL of the 0.1 M HCl electrolyte was adjusted the pH value by adding 1.01 mL of 1 M KOH solution to meet the requirement of IC test. The NH_4^+ peak appeared at 9.4 min and the calibration curve was obtained by using 0.1 M HCl electrolyte with known concentrations of NH_4 Cl to quantify the concentration of ammonium ion.

Determination of N₂H₄

The hydrazine present in the electrolyte was estimated via the method of Watt and Chrisp. A mixture of p–C₉H₁₁NO (5.99 g), HCI (concentrated, 30 mL) and C₂H₅OH (300 mL) was used as a color reagent. In detail, 2 mL electrolyte was removed from the electrochemical reaction vessel and added into 2 mL above prepared color reagent and stirring 15 min at room temperature. The absorbance of the resulting solution was measured at 455 nm. The concentration absorbance curves were calibrated using standard N₂H₄·H₂O solution with a series of concentrations. The fitting curve (y = 0.4777x + 0.0167, R² = 0.9974) shows good linear relation of absorbance value with N₂H₄ concentration.

Calculations of NH₃ formation rate and Faradaic efficiency (FE)

The rate of formation of NH₃ was calculated using the following equation:

$$V(\mu g h^{-1} m g_{cat}^{-1}) = \frac{17 \times c_{NH_4Cl} \times V}{53.5 \times t \times m_{cat}}$$

The FE was calculated according to the following equation:

$$FE = \frac{3 \times F \times c_{NH_4Cl} \times V \times 10^{-6}}{53.5 \times 0} \times 100\%$$

where ${}^{C_{NH_4}Cl}$ (µg mL⁻¹) is the measured concentration of NH₄Cl; V (mL) is the volume of electrolyte (in our work 30 mL); t (h) is the reduction reaction time; ${}^{m_{cat}}$ (mg) is the mass loading of catalyst on CP; F is Faraday constant (96500 C mol⁻¹); Q (C) is the quantity of applied charge/electricity.

Calculation details

Spin-polarized density functional theory (DFT) simulations were performed to calculate the adsorption of N₂ molecule using the Vienna ab initio simulation package (VASP). The Perdew-Burke-Ernzerhof (PBE) functional within the framework of generalized gradient approximation (GGA) was applied to describe the exchange–correlation interactions. DFT–D2 method was adopted to consider the van der Waals (vdW) interaction. For structural optimization, the Brillouin zone was sampled by $3\times3\times1$ k-points for plane-wave basis, together with a energy cutoff of 400 eV. All the atoms were allowed to relax until the residue forces on each atom were less than 0.02 eV/Å. The convergence criterions were set to 10^{-5} eV for total energy. In order to avoid interactions between periodic images, a vacuum space of 15 Å was applied to

all calculations. The formation Gibbs free energy (ΔG) of the NRR intermediates is calculated as:

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S$$

where ΔE is the electronic energy difference directly obtained from DFT calculations, ΔZPE is the change of zero-point energies, ΔZPE is the zero point energy difference, T is the temperature (T = 298.15K), and ΔS is the entropy changes. The entropy of gas molecules are taken from standard values.



Fig. S1 (a) SEM and (b) TEM images of $SL-VS_2$. (c–e) EDX mappings of $SL-VS_2$ reveal the homogeneous distribution of V (red), S (green). (f) HRTEM image of $SL-VS_2$. (g) SAED pattern of $SL-VS_2$.



Fig. S2 XPS wide survey (a) and C 1s (b) of $FL-VS_2$ and $SL-VS_2$.



Fig. S3 (a) UV–Vis absorption spectra of various NH_4^+ concentrations after incubated for 2h at room temperature. (b) Calibration curve used for calculating NH_4^+ concentrations.



Fig. S4 (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 concentrations.



Fig. S5 Chronoamperometric curves of $FL-VS_2/CP$ at different potentials for 2 h.



Fig. S6 A comparison of V_{NH^3} (µg h⁻¹ m_{cat}⁻¹) and FE(%) of NRR electrocatalysts reported in our work and other recently works, as listed in Table S2.



Fig. S7 UV–Vis absorption spectra of the electrolytes estimated by the Watt and Chrisp's method after NRR electrolysis at a series of potentials.



Fig. S8 Time-dependent current density curve of $FL-VS_2/CP$ at -0.70 V vs RHE.



Fig. S9 XRD pattern of after-NRR FL-VS₂/CP.



Fig. S10. (a) Ion chromatogram for the NH_4^+ ions. (b) Calibration curve used for estimation of NH_4^+ .



Fig. S11 (a) UV–Vis absorption Spectra of electrolytes corresponding to $FL-VS_2$ and $SL-VS_2$. (b) Average NH₃ yield and Faraday efficiency for $FL-VS_2$ and $SL-VS_2$ at -0.70 V vs. RHE.



Fig. S12 CVs of (a) $FL-VS_2$ and (b) $SL-VS_2$ at various scan rates (20–160 mV s⁻¹) in the region of 0.007 to 0.107 V vs. RHE. (c) The capacitive current densities as a function of scan rates for $FL-VS_2$ and $SL-VS_2$.



Fig. S13 (a) N_2 adsorption-desorption isotherms of FL–VS₂ and SL–VS₂. (b) Normalization of NH_3 yield by BET specific surface area.



Fig. S14 Chronoamperometry curves recorded at -0.70 V vs RHE in N₂-saturated electrolyte for FL–VS₂ with in situ addition of tannic acid.



Fig. S15 The re-recorded bridge-on configuration.



Fig. S16 the optimized structures of different intermediates.



Fig. S17 Free Energy Diagram of nitrogen reduction of VS_2 structure in hybrid 1 and 2 paths.

1	8				
Sample	$I_{(001)}/I_{(011)}$	Grain thickness (nm)	Grain diameter (nm)	Thickness -diameter ratio	$d_{(001)}({ m \AA})$
FL-VS ₂	1.12	16.94	13.48	1.26	5.73
SL-VS ₂	0.45	6.05	21.00	0.29	5.60

Table S1 Crystal structure properties of $FL-VS_2$ and $SL-VS_2$ obtained by analyzing their XRD patterns in Fig. 2(a).

 $I_{(001)}/I_{(011)}$ is the intensity ratio of the (001) and (011) peaks. Based on Scherrer equation, the grain thickness is calculated by the profiles fitting of (001) peaks and the grain diameter is calculated by the profiles fitting of (011), (012) and (110) peaks.

Catalyst	System/C onditions	NH ₃ Yield Rate	FE (%)	Detection method	Ref
FL-VS ₂	0.1 M HCl	34.62 μg h ⁻¹ mg _{cat} ⁻¹ (-0.7 V vs RHE)	2.09	Indophenol blue method	this work
Au/TiO ₂	0.1 M HCl	21.4 μg h ⁻¹ mg _{cat} ⁻¹ (-0.2 V vs RHE)	8.11	Indophenol blue method	1
Au nanorods	0.1 М КОН	1.648 μg h ⁻¹ cm ⁻² (-0.2 V vs RHE)	3.87	Nesslers method	2
Au/CeO _x -RGO	0.1 M HCl	8.3 μg h ⁻¹ mg _{cat} ⁻¹ (-0.2 V vs RHE)	10.1	Nesslers method	3
Polymeric carbon nitride	0.1 M KOH	8.09 μg h ⁻¹ mg _{cat} ⁻¹ (-0.2 V vs RHE)	11.59	Indophenol blue method	4
N doped porous carbon	0.05 M H ₂ SO ₄	23.8 μg h ⁻¹ mg _{cat} ⁻¹ (-0.9 V vs RHE)	1.42	Nesslers method	5
Rh nanosheets	0.1 M KOH	23.88 μg h ⁻¹ mg _{cat} ⁻¹ (-0.2 V vs RHE)	0.2	Phenolhypochl o rite method	6
Mo ₂ C/C	0.5 M LiSO ₄	11.3 μg h ⁻¹ mg _{cat} ⁻¹ (-0.3 V vs RHE)	7.8	Nesslers method	7
Amorphous Pd _{0.2} Cu _{0.8} /RGO	0.1 M KOH	2.8 μg h ⁻¹ mg _{cat} ⁻¹ (-0.2 V vs RHE)	0.6	Indophenol blue method	8
Defect-rich MoS ₂ nanoflower	0.1 M Na ₂ SO ₄	29.28 μg h ⁻¹ mg _{cat} ⁻¹ (-0.2 V vs RHE)	8.34	Indophenol blue method	9
Nb ₂ O ₅ nanofiber	0.1 M HCl	43.6 μ g h ⁻¹ mg _{cat} ⁻¹ (-0.55 V vs. RHE)	9.26	Indophenol blue method	10
Fe/Fe ₃ O ₄	0.1 M PBS (pH = 7.2)	~0.19 μ g h ⁻¹ mg _{cat} ⁻¹ (-0.3 V vs RHE)	8.29	Indophenol blue method	11
B ₄ C nanosheet	0.1 M HCl	26.57 μg h ⁻¹ mg _{cat} ⁻¹ (-0.75 V vs RHE)	15.95	Indophenol blue method	12
Hollow Cr ₂ O ₃ microspheres	0.1 M Na ₂ SO ₄	25.3 μg h ⁻¹ mg _{cat} ⁻¹ (-0.55 V vs RHE)	9.26	Indophenol blue method	13
PdRu tripods	0.1 M KOH	37.23 μg h ⁻¹ mg _{cat} ⁻¹ (-0.2 V vs RHE)	1.85	Indophenol blue method	14
Pd ₃ Cu ₁ alloy	0.1 M KOH	39.9 μg h ⁻¹ mg _{cat} ⁻¹ (-0.15 V vs RHE)	0.6	Indophenol blue method	15
Black phosphorus nanosheets	0.1 M KOH	31.37 μg h ⁻¹ mg _{cat} ⁻¹ (-0.6 V vs RHE)	5.07	Indophenol blue method	16
MoS ₂ with Li–S interactions	0.5M LiSO4	43.4 μ g h ⁻¹ mg _{cat} ⁻¹ (-0.2 V vs RHE)	9.81	Indophenol blue method	17
Au@CeO ₂	0.01M H ₂ SO ₄	$28.2 \ \mu g \ h^{-1} \ m g_{cat}^{-1}$ (-0.4 V vs RHE)	9.5	Indophenol blue method	18

 Table S2. The comparison of our work and other recently reported NRR electrocatalysts.

MoC nanorod	0.1 M HCl	95.1 μg h ⁻¹ mg _{cat} ⁻¹ (-0.3 V vs RHE)	8.13	Indophenol blue method	19
Defect-rich fluorographene nanosheet	0.1 M Na ₂ SO ₄	9.3 μg h ⁻¹ mg _{cat} ⁻¹ (-0.7 V vs RHE)	4.2	Indophenol blue method	20
Au/Ti ₃ C ₂	0.1 M HCl	30.06 μg h ⁻¹ mg _{cat} ⁻¹ (-0.2 V vs RHE)	18.34	Indophenol blue method	21
Fe _{SA} –N–C	0.1 M KOH	7.48 μ g h ⁻¹ mg _{cat} ⁻¹ (0.0 V vs RHE)	56.55	Indophenol blue method	22
SA-Mo/NPC	0.1 M KOH	$34.0 \pm 3.6 \ \mu g \ h^{-1} \ mg_{cat}^{-1}$ (-0.3 V vs RHE)	14.6 ±1.6	Nesslers method	23
OVs-rich MoO ₂	0.1 M HCl	12.20 μg h ⁻¹ mg _{cat} ⁻¹ (-0.15 V vs RHE)	8.2	Indophenol blue method	24
TiO ₂ /Ti ₃ C ₂ T _x	0.1 M HCl	32.17µg h ⁻¹ mg _{cat} ⁻¹ (-0.45 V vs RHE)	16.07	Indophenol blue method	25
Fe-N/C-carbon nanotube	0.1 М КОН	34.83µg h ⁻¹ mg _{cat} ⁻¹ (-0.2 V vs RHE)	9.28	Indophenol blue method	26
MnO/TM	0.1 M Na ₂ SO ₄	1.11×10 ⁻¹⁰ mol s ⁻¹ cm ⁻² (−0.39 V vs RHE)	8.02	Indophenol blue method	27
Bismuth nanosheet (Bi NS)	0.1 M Na ₂ SO ₄	~13.23µg h ⁻¹ mg _{cat} ⁻¹ (-0.8 V vs RHE)	10.46 ± 1.45	Indophenol blue method	28
NPC-500	0.05 M H ₂ SO ₄	22.27 μg h ⁻¹ mg _{cat} ⁻¹ (-0.4 V vs RHE)	9.98	Indophenol blue method	29
MoS ₂ /C ₃ N ₄	0.1 M HCl	18.5 μg h ⁻¹ mg _{cat} ⁻¹ (-0.3 V vs RHE)	17.8	Indophenol blue method	30
IrTe ₄ PNRs	0.1 М КОН	51.1 μg h ⁻¹ mg _{cat} ⁻¹ (-0.2 V vs RHE)	15.3	Indophenol blue method	31
C18@CoP/TM	0.1 M Na ₂ SO ₄	5.18µg h ⁻¹ mg _{cat} ⁻¹ (-0.2 V vs RHE)	14.03	Indophenol blue method	32
TiB ₂	0.1 M HCl	6.3 μ g h ⁻¹ mg _{cat} ⁻¹ (-0.3 V vs RHE)	11.37	Indophenol blue method	33
1T‴ MoS ₂	0.1 M Na ₂ SO ₄	9.09 μg h ⁻¹ mg _{cat} ⁻¹ (-0.3 V vs RHE)	13.6	Indophenol blue method	34
Mn–O3N1	0.1 M HCl	66.41 μg h ⁻¹ mg _{cat} ⁻¹ (-0.35 V vs RHE)	8.91	Indophenol blue method	35
np-OVs-NiO/MoO ₃	0.1 M PBS	$35.4 \ \mu g \ h^{-1} \ m g_{cat}^{-1}$ (-0.4 V vs RHE)	10.3	Indophenol blue method	36

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