Electronic Supplementary Information

Experimental Section

Materials: salicylic acid ($C_7H_6O_3$), hydroxy rhenium ammoniate (NH_4ReO_4), trisodium citrate dihydrate ($Na_3C_6H_5O_7 \cdot 2H_2O$), sodium hypochlorite (NaClO), sodium nitroferricyanide ($C_5FeN_6Na_2O$), thiourea (CN_2H_4S) and para-(dimethylamino) benzaldehyde ($C_9H_{11}NO$) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. Hydrochloric acid (HCl) and ethanol (C_2H_5OH) were purchased from Aladdin Ltd. (Shanghai, China). Ultrapure water is used throughout all experiments was purified through a Millipore system.

Preparation of ReS_2/CC: ReS_2 nanosheets array on carbon cloth (ReS_2/CC) electrode was prepared by simple hydrothermal method. In a typical step, 0.10 mmol NH_4ReO_4 and 1.0mmol thiourea (CN_2H_4S) were dissolved in 30 mL deionized water to form a clarifying solution. Carbon cloth (2×1 cm^2) was cleaned in deionized water, ethanol, and acetone for 15 minutes, respectively. The above solution and carbon cloth were then transferred to a 50 mL stainless steel autoclave lined with PTFE and sealed for 26 h at 200 °C. After cooling to room temperature, ReS_2/CC is cooled to room temperature. Take out the sample and rinse with the water and ethanol for several times. The ReS_2/CC was dried naturally in the atmosphere.

Electrochemical measurements: Before NRR tests, a salt bridge is built which is filled with agar and saturated KCl solution. Electrochemical measurements were performed with a CHI 660E electrochemical analyzer in a standard three−electrode system using ReS_2/CC as working electrode, Ag/AgCl as reference electrode, and graphite rod as counter electrode. All experiments were carried out at room temperature (25 °C) and all potentials reported in this work were calibrated to RHE, using the following equation:

$$E\ (RHE) = E\ (Ag/AgCl) + (0.197 + 0.059\ pH)\ V$$

Determination of NH_3: The produced ammonia was estimated by indophenol blue method by ultraviolet spectrum. In detail, 5 mL of post−tested solution was got from the electrochemical reaction vessel. Then, 1 mL of 1 M NaOH solution (contains 5 wt%

salicylic acid and 5 wt% sodium citrate) was followed by addition of 0.5 mL of 0.05 M NaClO and 0.1 mL of $C_5FeN_6Na_2O$ (1 wt%). After standing at 25 °C for 2 h, the UV-Vis absorption spectrum was measured. The concentration of indophenol blue was determined using the absorbance at wavelength of 655 nm. The concentration−absorbance curve was calibrated using standard ammonia chloride solution with a series of concentrations. The fitting curve ($Y = 0.299X + 0.084$, $R^2 = 0.996$) shows good linear relation of absorbance value with NH_4Cl concentration by three times independent calibrations.

Determination of N_2H_4: The N_2H_4 present in the electrolyte was determined by the method of Watt and Chrisp. The p-$C_9H_{11}NO$ (5.99 g), HCl (30 mL), and C_2H_5OH (300 mL) were mixed and used as a color reagent. 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 obtained calibration curve of N_2H_4 is $Y = 0.676X + 0.052$, $R^2 = 0.999$.

Calculations of v_{NH3} and FE: v_{NH_3} was calculated using the following equation:

$$v_{NH_3} = [NH_4Cl] \times V/(17 \times 10^6 \times t \times A)\ (mol\ s^{-1}\ cm^{-2})$$

FE was calculated according to following equation:

$$FE = 3 \times F \times [NH_4Cl] \times V/(53.5 \times 10^6 \times Q)$$

Where $[NH_4Cl]$ is the measured NH_4Cl concentration; V is the volume of the cathodic reaction electrolyte; t is the potential applied time; m is the loaded quality of catalyst; F is the Faraday constant; and Q is the quantity of applied electricity.

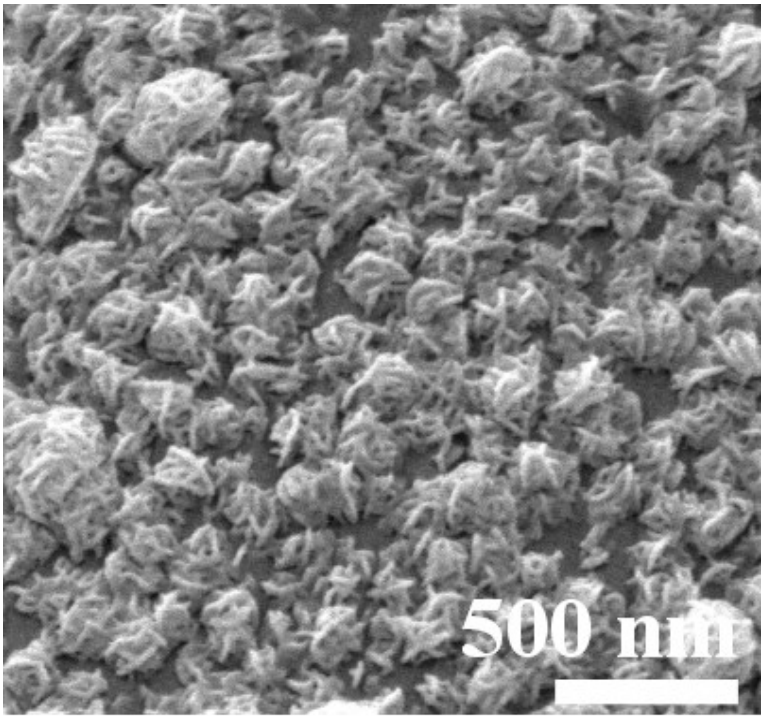

Fig. S1. High-magnifications SEM images of ReS_2/CC.

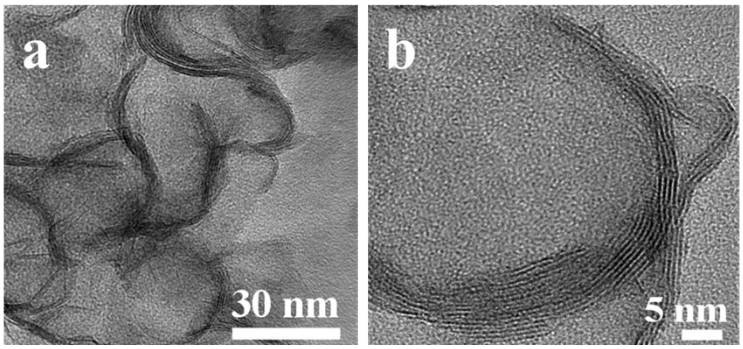

Fig. S2. High-magnification TEM images of ReS_2 nanosheet.

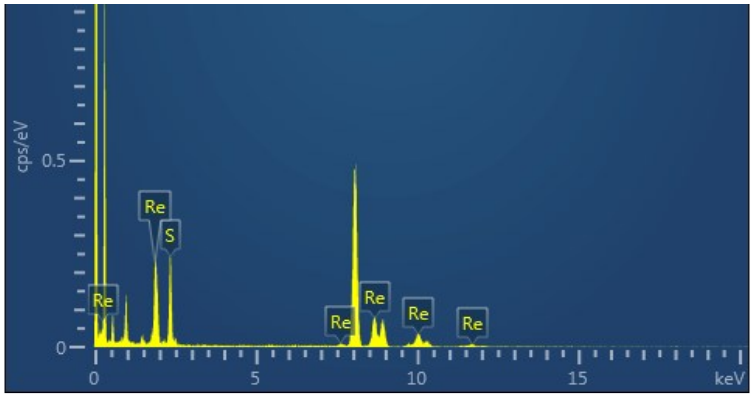

Fig. S3. EDS spectrum of ReS_2 nanosheet.

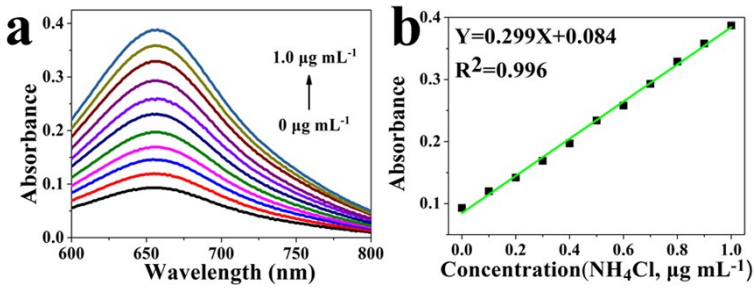

Fig. S4. (a) UV-Vis spectra of indophenol assays with NH_4Cl after incubated for 2 h at room temperature. (b) Calibration curve used for estimation of NH_4Cl.

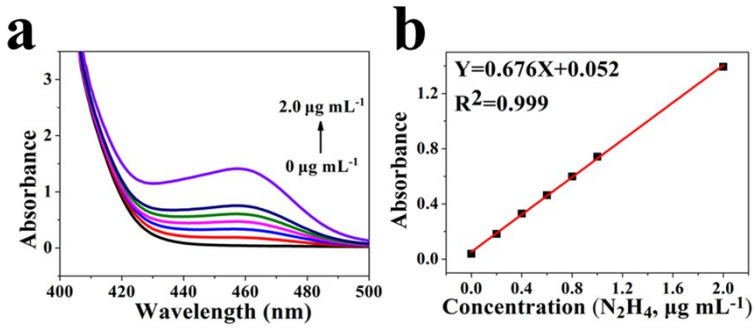

Fig. S5. (a) UV-Vis spectra of various N_2H_4 concentration after incubated for 20 min at room temperature. (b) Calibration curve used for calculation of N_2H_4.

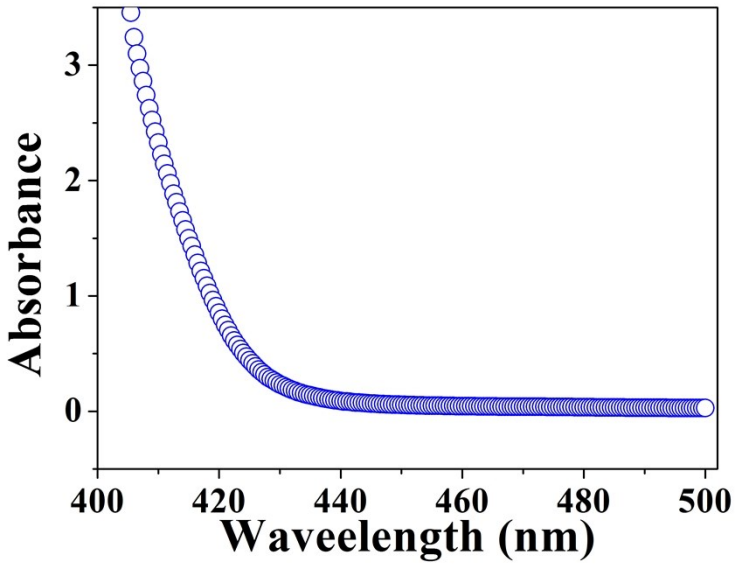

Fig. S6. UV-Vis absorption spectrum of ReS_2/CC catalyst after charging at –0.4 V vs. RHE after incubated with N_2H_4 color agent for 15 min at room temperature.

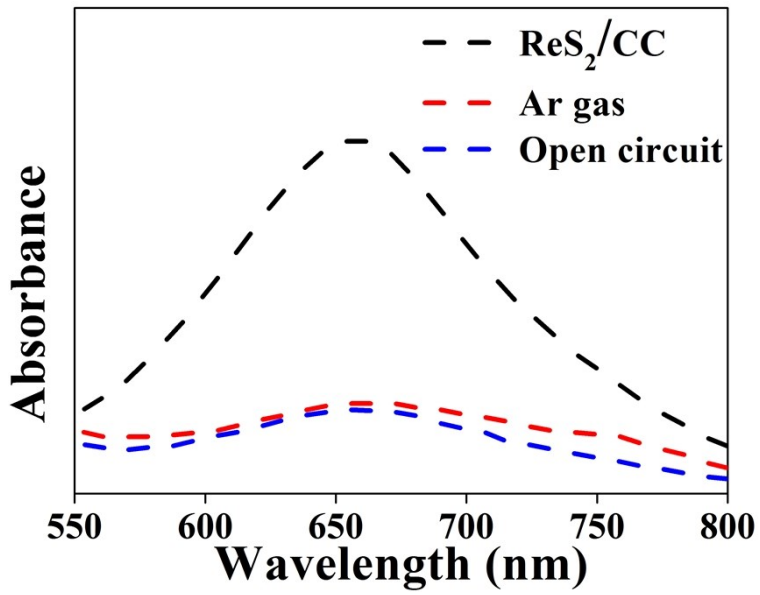

Fig. S7. UV-Vis absorption spectra of the electrolyte stained with indophenol indicator after charging at –0.4 V vs. RHE for 2 h under different electrochemical conditions.

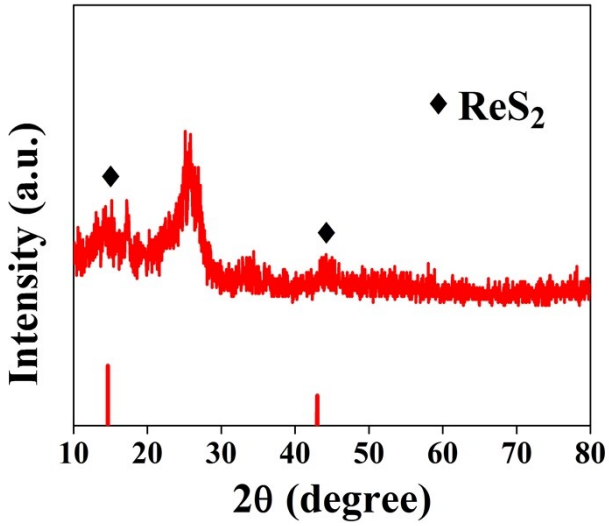

Fig. S8. XRD pattern for ReS_2/CC after NRR process.

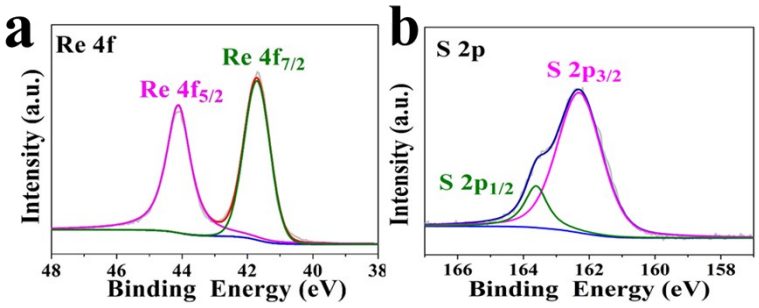

Fig. S9. XPS spectra for ReS_2 in (a) Re 4f and (b) S 2p regions after NRR process.

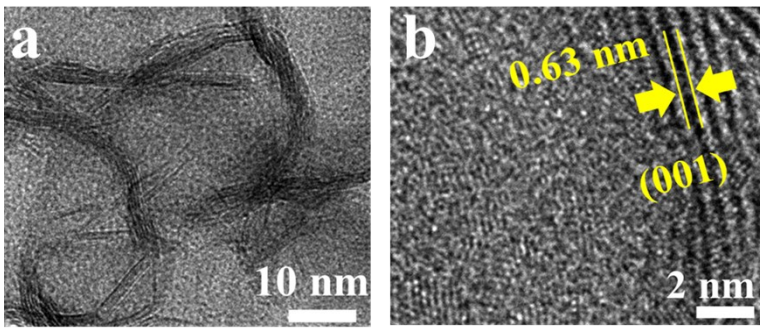

Fig. S10. (a) TEM and (b) HRTEM images for ReS_2 nanosheet after NRR process.

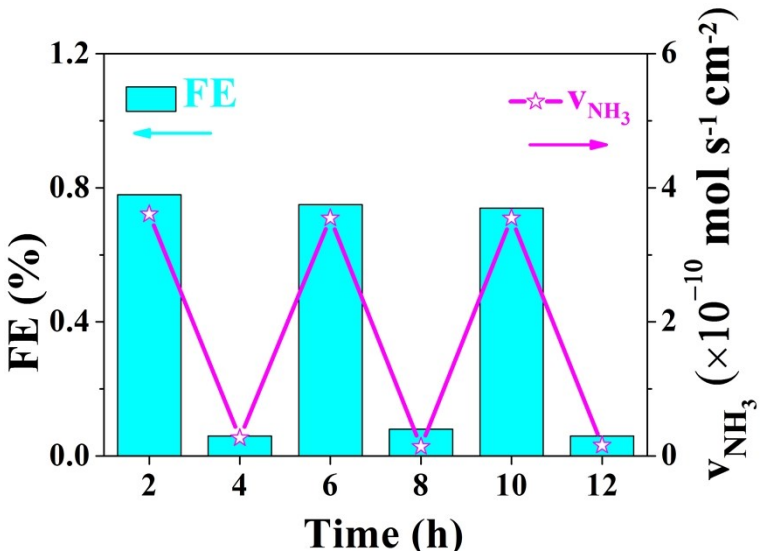

Fig. S11. v_{NH3} and FEs at potential of –0.4 V vs. RHE of ReS_2/CC in N_2 and Ar-saturated electrolytes.

Table S1. Comparison of the electrocatalytic N_2 reduction performance for ReS_2/CC with other NRR catalysts under ambient conditions.

Catalyst	NH_3 yield rate (v_{NH_3})	FE (%)	Ref.
ReS_2/CC	**3.61×10^{-10} mol s^{-1} cm^{-2}**	**0.78 %**	**This work**
Fe_2O_3/CNTs	4.7×10^{-10} mol s^{-1} cm^{-2}	0.15 %	1
Fe_3O_4/Ti	0.56×10^{-10} mol s^{-1} cm^{-2}	2.6 %	2
γ−Fe_2O_3	2.08×10^{-10} mol s^{-1} mg^{-1}	1.9 %	3
Ru/C	2.06×10^{-10} mol s^{-1} cm^{-2}	0.28 %	4
Mo nanofilm	0.31×10^{-10} mol s^{-1} cm^{-2}	0.72 %	5
MoN	3.01×10^{-10} mo1 s^{-1} cm^{-2}	1.15 %	6
MoO_3	2.88×10^{-8} mol s^{-1} mg^{-1}	1.9 %	7
MoS_2	0.81×10^{-10} mol s^{-1} cm^{-2}	1.17 %	8
Mo_2N	7.68×10^{-8} mol s^{-1} mg^{-1}	4.5 %	9
Ag	0.46×10^{-10} mol s^{-1} cm^{-2}	4.8 %	10
VN/CC	2.48×10^{-10} mol^{-1} s^{-1} cm^{-2}	3.58 %	11
CoS/NS-G	2.56×10^{-10} mol s^{-1} mg^{-1}	15.6 %	12
CoS_2/NS-G	4.08×10^{-10} mol s^{-1} mg^{-1}	25.9 %	12
3R MoS_2	1.43×10^{-10} mol s^{-1} mg^{-1}	8.8 %	13
Sn/SnS_2	3.87×10^{-10} mol s^{-1} mg^{-1}	6.5 %	14
FeS_2	6.08×10^{-10} mol s^{-1} mg^{-1}	11.2 %	15

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