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Experimental Section

Synthesis of Sb₂S₃ nanoflowers

All the chemicals are of analytical grade and used as received. Sb_2S_3 nanoflowers were synthesized by a solvothermal method[1]. In typical, 1 mmol of $SbCl_3$ was dissolved in 30 mL of ethylene glycol, to which 0.5 g of L-cysteine was added under stirring until completely dissolved. The pH of the suspension was adjusted to 10 with a 10 mol/L NaOH aqueous solution. The resulting precursor solution was transferred into a 50mL Teflon-lined stainless autoclave, sealed and heated in the oven at 160 °C for 24 h. After cooling to room temperature, the precipitate was collected via centrifugation and further washed with de-ionized water and ethanol, and dried at 60 °C for 12 h. The dried precipitates were finally annealed in a tube furnace at 500 °C for 2 h in Ar atmosphere to obtain the Sb₂S₃ nanoflowers.

Characterizations

Scanning electron microscopy (SEM) was performed on a JSM-6701 microscope. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were carried out on a Tecnai G² F20 microscope. X-ray diffraction (XRD) pattern was recorded on a Rigaku D/max 2400 diffractometer. X-ray photoelectron spectroscopy (XPS) analysis was recorded on a PHI 5702 spectrometer. Nitrogen adsorption/desorption isotherms were recorded on an ASAP 2020 instrument. The UV-vis absorbance measurements were performed on a MAPADA P5 spectrophotometer. ¹H nuclear magnetic resonance (NMR) measurements were carried out on a 500 MHz Bruker superconducting-magnet NMR spectrometer. Prior to NMR measurements, all the feeding gases were respectively purified by an acid trap (0.05 M H₂SO₄) to eliminate the potential NO_x and NH₃ contaminants [2].

Electrochemical experiments

The electrochemical measurements were carried out on a CHI-760E electrochemical workstation Shanghai Chenhua Instrument Corp., China) using a three-electrode configuration with each as-prepared electrode, a graphite rod and a

Ag/AgCl electrode as the working, the counter and the reference electrodes, respectively. All potentials were referenced to reversible hydrogen electrode (RHE) by following equation: E_{RHE} (V)= $E_{Ag/AgCl}$ +0.197+0.059×pH. The CC substrate was pretreated by soaking it in 0.5 M H₂SO₄ for 12 h, and then washed with deionized water several times and dried at 60 °C for 24 h. To prepare working electrode, 1 mg catalyst and 5 µL of Nafion (5 wt%) were ultrasonically dispersed in 100 µL of ethyl alcohol to form a homogeneous ink. Then 20 µL of catalyst ink was loaded on a 1×1 cm² CC substrate and dried under ambient condition. The NRR tests were performed using an H-type two-compartment electrochemical cell separated by a Nafion 211 membrane. The Nafion membrane was pretreated by boiling it in 5% H₂O₂ solution for 1 h, 0.5 M H₂SO₄ for 1 h and deionized water for 1 h in turn. During each electrolysis, ultra-high-purity N₂ gas (99.999%) was continuously purged into the cathodic chamber at a flow rate of 20 mL min⁻¹. After each NRR electrolysis, the produced NH₃ and possible N₂H₄ were quantitatively determined by the indophenol blue method[3], and approach of Watt and Chrisp[4], respectively.

Determination of N₂H₄

4 mL of electrolyte was removed from the electrochemical reaction vessel. Then 50 μ L of solution containing NaOH (0.75 M) and NaClO ($\rho_{Cl} = \sim 4$), 500 μ L of solution containing 0.32 M NaOH, 0.4 M C₇H₆O₃, and 50 μ L of C₅FeN₆Na₂O solution (1 wt%) were respectively added into the electrolyte. After standing for 2 h, the UV-Vis absorption spectrum was measured and the concentration-absorbance curves were calibrated by the standard NH₄Cl solution with a series of concentrations.

NH₃ yield (
$$\mu$$
g h⁻¹ mg⁻¹_{cat}) = $\frac{c_{\rm NH_3} \times V}{t \times m}$ (1)

Faradaic efficiency was calculated by the following equation:

Faradaic efficiency (%) =
$$\frac{3 \times F \times c_{_{\rm NH_3}} \times V}{17 \times Q} \times 100\%$$
 (2)

where $c_{\rm NH3}$ (µg mL⁻¹) is the measured NH₃ concentration, V (mL) is the volume of the electrolyte, t (h) is the reduction time and m (mg) is the mass loading of the catalyst on CC. F (96500 C mol⁻¹) is the Faraday constant, Q (C) is the quantity of applied

electricity.

Determination of N₂H₄

5 mL of electrolyte was removed from the electrochemical reaction vessel. The 330 mL of color reagent containing 300 mL of ethyl alcohol, 5.99 g of $C_9H_{11}NO$ and 30 mL of HCl were prepared, and 5 mL of color reagent was added into the electrolyte. After stirring for 10 min, the UV-Vis absorption spectrum was measured and the concentration-absorbance curves were calibrated by the standard N_2H_4 solution with a series of concentrations.

Calculation details

First-principles calculations were carried out by using the Cambridge sequential total energy package (CASTEP), based on the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) functional [5]. DFT-D method was adopted to account for the van der Waals interactions throughout the calculations. The Brillouin zone was sampled by $3 \times 3 \times 1$ Monkhorst–Pack k-point mesh. The electron wave functions were expanded using plane waves with a cutoff energy of 400 eV, and the convergence criteria of energy and force change during all calculations were set to 2×10^{-5} eV and 0.02 eV Å⁻¹, respectively. The Sb₂S₃ (130) was modeled by a 2×2 supercell, and a vacuum space of around 15 Å was set along the z direction to avoid the interaction between periodical images.

The Gibbs free energy (ΔG , 298 K) of reaction steps is calculated by [6]:

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S \tag{3}$$

where ΔE is the adsorption energy, ΔZPE is the zero point energy difference and $T\Delta S$ is the entropy difference between the gas phase and adsorbed state. The entropies of free gases were acquired from the NIST database.



Fig. S1. Lattice line measurement obtained from the noise-filtered HRTEM image of Sb_2S_3 .



Fig. S2. (a) UV-vis absorption spectra of indophenol assays with NH_4Cl after incubated for 2 h at ambient conditions. (b) Calibration curve used for calculation of NH_3 concentrations.



Fig. S3. (a) UV-vis absorption spectra of N_2H_4 assays after incubated for 20 min at ambient conditions. (b) Calibration curve used for calculation of N_2H_4 concentrations.



Fig. S4. (a) UV-vis spectra of the electrolytes (stained with the chemical indicator based on the method of Watt and Chrisp) after 2 h of electrolysis on Sb_2S_3 at various potentials, and (b) corresponding N_2H_4 concentrations in the electrolytes.



Fig. S5. Mass of produced NH_3 after NRR electrolysis at various times (1-4 h) on Sb_2S_3 at -0.3 V.



Fig. S6. Morphologies of Sb_2S_3 after stability test. (a) SEM image. (b) TEM image. (c) HRTEM image.



Fig. S7. XRD pattern of Sb_2S_3 before and after stability test.



Fig. S8. XPS spectra of Sb_2S_3 after stability test. (a) Sb2p. (b) S2p.



Fig. S9. Free energy diagrams of distal NRR pathway on $\mathrm{Sb}_2\mathrm{S}_3$ at zero and applied energy of -0.84 V.

Catalyst	Electrolyte	Determination method	Optimum Potential (V Vs RHE)	NH₃ yield (μg h ⁻¹ mg ⁻¹)	FE (%)	Ref.
Bi ₄ V ₂ O ₁₁ -CeO ₂ nanofibers	0.1 M HCl	Indophenol blue method	-0.2	23.21	10.16	[7]
CoP hollow nanocage	1.0 M KOH	Indophenol blue method	-0.4	10.78	7.36	[8]
Fe-N/C hybrid	0.1 M KOH	Indophenol blue method	-0.2	34.83	9.28	[9]
MoO ₂ with oxygen vacancies	0.1 M HCl	Indophenol blue method	-0.15	12.2	8.2	[10]
PC/Sb/SbPO4	0.1 M HCl	Indophenol blue method	-0.15	33.4	31	[11]
Mo ₂ C/C	0.5 M Li ₂ SO ₄	Nessler's reagent method	-0.3	11.3	7.8	[12]
Mo single atoms	0.1 M KOH	Indophenol blue method	-0.3	34	14.6	[13]
Sulfur-doped graphene	0.1 M HCl	Indophenol blue method	-0.6	27.3	11.5	[14]
Amorphous Pd _{0.2} Cu _{0.8} /RGO	0.1 M KOH	Indophenol blue method	-0.2	2.8	0.6	[15]
MoS ₂ with Li-S Interactions	0.1 M Li ₂ SO ₄	Indophenol blue method	-0.2	43.4	9.81	[16]
Defect-rich MoS ₂ nanoflower	0.1 M Na ₂ SO ₄	Indophenol blue method	-0.4	29.28	8.34	[17]
Nb ₂ O ₅ nanofibers	0.1 M HCl	Indophenol blue method	-0.55	43.6	9.26	[18]
S-doped carbon nanospheres	0.1 M Na ₂ SO ₄	Indophenol blue method	-0.7	19.07	7.47	[19]
C-doped TiO ₂ nanoparticles	0.1 M Na ₂ SO ₄	Indophenol blue method	-0.7	16.22	1.84	[20]
$MnO_2-Ti_3C_2T_x$ MXene nanohybrid	0.1 M HCl	Indophenol blue method	-0.55	34.12	11.39	[21]
MoO ₃ nanosheets	0.1 M HCl	Indophenol blue method	-0.5	29.43	1.9	[22]
CoP hollow nanocage	1.0 M KOH	Indophenol blue method	-0.4	10.78	7.36	[8]
Sb ₂ S ₃ nanoflowers	0.5 M LiClO ₄	Indophenol blue method	-0.5	33.4	24.1	This work

Table S1. Comparison of optimum NH₃ yield and Faradic efficiency (FE) for recently reported state-of-the-art NRR electrocatalysts at ambient conditions.

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