Experimental Section

Synthesis of Sb$_2$S$_3$ nanoflowers

All the chemicals are of analytical grade and used as received. Sb$_2$S$_3$ 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 Sb$_2$S$_3$ 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. $^1$H 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 H$_2$SO$_4$) to eliminate the potential NO$_x$ and NH$_3$ 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: \( E_{\text{RHE}} \ (V) = E_{\text{Ag/AgCl}} + 0.197 + 0.059 \times \text{pH} \). The CC substrate was pretreated by soaking it in 0.5 M H\textsubscript{2}SO\textsubscript{4} 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 cm\textsuperscript{2} 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% H\textsubscript{2}O\textsubscript{2} solution for 1 h, 0.5 M H\textsubscript{2}SO\textsubscript{4} for 1 h and deionized water for 1 h in turn. During each electrolysis, ultra-high-purity N\textsubscript{2} gas (99.999%) was continuously purged into the cathodic chamber at a flow rate of 20 mL min\textsuperscript{-1}. After each NRR electrolysis, the produced NH\textsubscript{3} and possible N\textsubscript{2}H\textsubscript{4} were quantitatively determined by the indophenol blue method[3], and approach of Watt and Chrisp[4], respectively.

**Determination of N\textsubscript{2}H\textsubscript{4}**

4 mL of electrolyte was removed from the electrochemical reaction vessel. Then 50 μL of solution containing NaOH (0.75 M) and NaClO (\( \rho_{\text{Cl}} = ~4 \)), 500 μL of solution containing 0.32 M NaOH, 0.4 M C\textsubscript{7}H\textsubscript{6}O\textsubscript{3}, and 50 μL of C\textsubscript{5}FeN\textsubscript{6}Na\textsubscript{2}O 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 NH\textsubscript{4}Cl solution with a series of concentrations.

\[
\text{NH}_3 \text{ yield (μg h}^{-1} \text{ mg}^{-1}) = \frac{c_{\text{NH}_3} \times V}{t \times m} \tag{1}
\]

Faradaic efficiency was calculated by the following equation:

\[
\text{Faradaic efficiency} (\%) = \frac{3 \times F \times c_{\text{NH}_3} \times V}{17 \times Q} \times 100\% \tag{2}
\]

where \( c_{\text{NH}_3} \) (μg mL\textsuperscript{-1}) is the measured NH\textsubscript{3} 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\textsuperscript{-1}) is the Faraday constant, \( Q \) (C) is the quantity of applied
electricity.

**Determination of N\textsubscript{2}H\textsubscript{4}\**

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\textsubscript{9}H\textsubscript{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\textsubscript{2}H\textsubscript{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 × 3 × 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\textsuperscript{-1}, respectively. The Sb\textsubscript{2}S\textsubscript{3} (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]:

\[ ΔG = ΔE + ΔZPE - TΔS \]

(3)

where ΔE is the adsorption energy, ΔZPE is the zero point energy difference and TΔS 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$_2$S$_3$. 
Fig. S2. (a) UV-vis absorption spectra of indophenol assays with NH$_4$Cl 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 N₂H₄ assays after incubated for 20 min at ambient conditions. (b) Calibration curve used for calculation of N₂H₄ 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$_2$S$_3$ at various potentials, and (b) corresponding N$_2$H$_4$ concentrations in the electrolytes.
Fig. S5. Mass of produced NH$_3$ after NRR electrolysis at various times (1-4 h) on Sb$_2$S$_3$ at -0.3 V.
Fig. S6. Morphologies of Sb$_2$S$_3$ after stability test. (a) SEM image. (b) TEM image. (c) HRTEM image.
Fig. S7. XRD pattern of Sb$_2$S$_3$ before and after stability test.
Fig. S8. XPS spectra of Sb$_2$S$_3$ after stability test. (a) Sb2p. (b) S2p.
Fig. S9. Free energy diagrams of distal NRR pathway on Sb$_2$S$_3$ at zero and applied energy of -0.84 V.
Table S1. Comparison of optimum NH$_3$ yield and Faradic efficiency (FE) for recently reported state-of-the-art NRR electrocatalysts at ambient conditions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Electrolyte</th>
<th>Determination method</th>
<th>Optimum Potential (V Vs RHE)</th>
<th>NH$_3$ yield (μg h$^{-1}$ mg$^{-1}$)</th>
<th>FE (%)</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>Bi$_4$V$<em>2$O$</em>{11}$-CeO$_2$ nanofibers</td>
<td>0.1 M HCl</td>
<td>Indophenol blue method</td>
<td>-0.2</td>
<td>23.21</td>
<td>10.16</td>
<td>[7]</td>
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<td>CoP hollow nanocage</td>
<td>1.0 M KOH</td>
<td>Indophenol blue method</td>
<td>-0.4</td>
<td>10.78</td>
<td>7.36</td>
<td>[8]</td>
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<tr>
<td>Fe–N/C hybrid</td>
<td>0.1 M KOH</td>
<td>Indophenol blue method</td>
<td>-0.2</td>
<td>34.83</td>
<td>9.28</td>
<td>[9]</td>
</tr>
<tr>
<td>MoO$_2$ with oxygen vacancies</td>
<td>0.1 M HCl</td>
<td>Indophenol blue method</td>
<td>-0.15</td>
<td>12.2</td>
<td>8.2</td>
<td>[10]</td>
</tr>
<tr>
<td>PC/Sb/SbPO$_4$</td>
<td>0.1 M HCl</td>
<td>Indophenol blue method</td>
<td>-0.15</td>
<td>33.4</td>
<td>31</td>
<td>[11]</td>
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<tr>
<td>Mo$_2$C/C</td>
<td>0.5 M Li$_2$SO$_4$</td>
<td>Indophenol blue method</td>
<td>-0.3</td>
<td>11.3</td>
<td>7.8</td>
<td>[12]</td>
</tr>
<tr>
<td>Mo single atoms</td>
<td>0.1 M KOH</td>
<td>Indophenol blue method</td>
<td>-0.3</td>
<td>34</td>
<td>14.6</td>
<td>[13]</td>
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<tr>
<td>Sulfur-doped graphene</td>
<td>0.1 M HCl</td>
<td>Indophenol blue method</td>
<td>-0.6</td>
<td>27.3</td>
<td>11.5</td>
<td>[14]</td>
</tr>
<tr>
<td>Amorphous Pd$<em>{0.2}$Cu$</em>{0.8}$/RGO</td>
<td>0.1 M KOH</td>
<td>Indophenol blue method</td>
<td>-0.2</td>
<td>2.8</td>
<td>0.6</td>
<td>[15]</td>
</tr>
<tr>
<td>MoS$_2$ with Li-S Interactions</td>
<td>0.1 M Li$_2$SO$_4$</td>
<td>Indophenol blue method</td>
<td>-0.2</td>
<td>43.4</td>
<td>9.81</td>
<td>[16]</td>
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<tr>
<td>Defect-rich MoS$_2$ nanoflower</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>Indophenol blue method</td>
<td>-0.4</td>
<td>29.28</td>
<td>8.34</td>
<td>[17]</td>
</tr>
<tr>
<td>Nb$_2$O$_3$ nanofibers</td>
<td>0.1 M HCl</td>
<td>Indophenol blue method</td>
<td>-0.55</td>
<td>43.6</td>
<td>9.26</td>
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<td>S-doped carbon nanospheres</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>Indophenol blue method</td>
<td>-0.7</td>
<td>19.07</td>
<td>7.47</td>
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<tr>
<td>C-doped TiO$_2$ nanoparticles</td>
<td>0.1 M Na$_2$SO$_4$</td>
<td>Indophenol blue method</td>
<td>-0.7</td>
<td>16.22</td>
<td>1.84</td>
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<tr>
<td>MnO$_2$–Ti$_3$C$_2$T$_x$ MXene nanohybrid</td>
<td>0.1 M HCl</td>
<td>Indophenol blue method</td>
<td>-0.55</td>
<td>34.12</td>
<td>11.39</td>
<td>[21]</td>
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<tr>
<td>MoO$_3$ nanosheets</td>
<td>0.1 M HCl</td>
<td>Indophenol blue method</td>
<td>-0.5</td>
<td>29.43</td>
<td>1.9</td>
<td>[22]</td>
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<tr>
<td>CoP hollow nanocage</td>
<td>1.0 M KOH</td>
<td>Indophenol blue method</td>
<td>-0.4</td>
<td>10.78</td>
<td>7.36</td>
<td>[8]</td>
</tr>
<tr>
<td>Sb$_2$S$_3$ nanoflowers</td>
<td>0.5 M LiClO$_4$</td>
<td>Indophenol blue method</td>
<td>-0.5</td>
<td>33.4</td>
<td>24.1</td>
<td>This work</td>
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Supplementary references
[18]. J. Han, Z. Liu, Y. Ma, G. Cui, F. Xie, F. Wang, Y. Wu, S. Gao, Y. Xu and X. Sun, Nano Energy, 2018, 52, 264-270.
[22]. J. Han, X. Ji, X. Ren, G. Cui, L. Li, F. Xie, H. Wang, B. Li and X. Sun, J. Mater. Chem. A, 2018, 6, 12974-12977.