Cooperative interaction between Cu and sulfur vacancies in SnS$_2$ nanoflower for highly efficient nitrate electroreduction to ammonia

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Supporting information

Characterizations.

The microtopography of the prepared samples was characterized by transmission electron microscopy (TEM, JEOL 2100 plus + ARM 200 F). Energy dispersive X-ray spectroscopy attached to the transmission electron microscope was used to obtain elemental composition. Raman spectroscopy (WITec, alpha300R, excited by a 512 nm laser) was also performed. The crystalline phases were performed by X-ray diffraction (XRD) using an Rigaku D/MAX-2500 powder diffractometer. The chemical states of the prepared sample were conducted using a Thermo Scientific ESCALAB 250Xi photoelectron spectrometer. The absorbance data of spectrophotometer were collected on a SHIMADZU UV-2550 ultravioletvisible (UV-vis) spectrophotometer. Electron spin resonance (ESR) measurements were performed using the Bruker ER 200D spectrometer at room temperature.

Quantification of ammonia

When tested in alkaline solution, we used spectrophotometry method to detect the quantification of ammonia. Briefly, after 1h electrocatalysis, 0.2ml electrolyte was removed from cathode and diluted to 2 mL to detection range and following 2mL of 1M NaOH solution containing 5% salicylic acid and 5% sodium citrate was added into the solution. Subsequently, 1 mL of 0.05M NaClO and 0.2 mL of 1% C₅FeN₆Na₂O·2H₂O were add into the above solution. Then the solution was incubated under dark conditions at for 2h before UV-vis absorption spectrum was measured at a wavelength of 655 nm (Shimadzu, UV-2550). NH₄⁺ calibration curve was calculated by using a series of different concentrations standard NH₃ Solution (0μg/mL,0.25μg/mL,0.5μg/mL,0.75μg/mL,1μg/mL).NH₄Cl was dried in oven before used. Calibration curve showed good linear relationship (y=0.275x+0.02 R²=0.9994).

Quantification of nitrite
The color developer was configured as follows: 20 g of p-aminobenzenesulfonamide was added to a mixed solution of 250 ml of water and 50 ml of phosphoric acid, and then 1 g of N-(1-naphthyl)-ethylenediamine dihydrochloride was dissolved in the above solution. Finally, the above solution was transferred to a 500 mL volumetric flask and diluted to the mark. 1.0 mL electrolyte was taken out from the electrolytic cell and diluted to 5 mL to detection range. Next, 0.1 mL color reagent was added into the aforementioned 5 mL solution. After shaking and standing for 20 minutes, the absorbance was tested by UV-Vis spectrophotometry at a wavelength of 540 nm. The calibration curve can be obtained through different concentrations of NaNO₂ solutions and the corresponding absorbance. It showed an excellent linear relationship between the absorbance value and the NaNO₂ concentration from the fitting curve ($y = 0.768x + 0.034 \ R^2 = 0.9989$).

**Calculation of the Faradaic efficiency and yield.**

The Faradaic efficiency of NO₃RR was calculated as follows

$$FE = \frac{3F \times c \times V}{17 \times Q}$$

where $F$ is the Faraday constant, $c$ is the measured NH₃ concentration, $V$ is the volume of the electrolyte, and $Q$ is the quantity of electric charge for one electron of NO₃RR testing.

The NH₃ formation rate was determined using the following equation:

$$r(\text{NH}_3) = \frac{(c \times V)}{(t \times m)}$$

where $c$ is the measured NH₃ concentration, $V$ is the volume of the electrolyte , $t$ is the reduction reaction time, and $m$ is the loading mass of sample (loading mass: 0.25mg).
**K^{15}NO_3 isotope labelling experiments**

Isotopically labeled nitrate reduction experiments were conducted to elucidate the ammonia source and quantify the concentration of ammonia nitrogen using K\(^{15}\)NO\(_3\) (99\%) as the feed N source. After electrolyzing a 0.1 M KOH solution containing K\(^{15}\)NO\(_3\) (0.1M KOH) for 2 h, electrolyte with \(^{15}\)NH\(_4^+\) was extracted and the pH was further adjusted to weak acid by adding 4M H\(_2\)SO\(_4\). Next, a 50 μL deuterium oxide (D\(_2\)O) was blended with 1mL of acidified electrolyte and the further \(^1\)H NMR spectra was acquired via NMR analysis.

**Calculation details**

All calculations in this work were performed using the Vienna ab initio simulation package (VASP) based on the density functional theory (DFT). The projected augmented wave (PAW) method with PBE functional was employed for the generation of pseudopotential. The kinetic energy cutoff for the plane-wave expansion was set to 400 eV. The 3×3×1 k-point mesh set was used for pristine-SnS\(_2\), SnS\(_{2-x}\) and Cu-SnS\(_{2-x}\) slab models. All the structural models were fully relaxed to the ground state with the convergence of energy and forces setting to 10-5 eV and 0.01 eV Å\(^{-1}\), respectively. SnS\(_2\) (001) was modeled by a 4×4 supercell and a vacuum space of around 20 Å was set along the z-direction.

Here, the chemical reaction considered can be summarized with the reaction equations below.

\[ \text{N} + \text{NO}_3^- \rightarrow \text{NO}_3^- + e^- \]

\[ \text{NO}_3^- + 2\text{H}^+ + 2e^- \rightarrow \text{NO}_2^- + \text{H}_2\text{O} \]

\[ \text{NO}_2^- + 2\text{H}^+ + 2e^- \rightarrow \text{NO}^- + \text{H}_2\text{O} \]
\[ \text{NO} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{N} + \text{H}_2\text{O} \]

\[ \text{N} + \text{H}^+ + \text{e}^- \rightarrow \text{NH} \]

\[ \text{NH} + \text{H}^+ + \text{e}^- \rightarrow \text{NH}_2 \]

\[ \text{NH}_2 + \text{H}^+ + \text{e}^- \rightarrow \text{NH}_3 \]

\[ \text{NH}_3 \rightarrow \text{NH}_3 + * \]

where * represents the active site. Then, the reaction free energy change can be obtained with the equation below:

\[ \Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S \]

where \( \Delta E \) is the total energy difference before and after intermediate adsorbed, \( \Delta E_{ZPE} \) and \( \Delta S \) are, respectively, the differences of zero point energy and entropy. The zero point energy and entropy of free molecules and adsorbents were obtained from the vibrational frequency calculations.
Fig. S1 AFM image of Cu-SnS$_{2-x}$
Fig. S2 AFM image of pristine-SnS$_2$
Fig. S3 Chronoamperometry curves of Cu-SnS$_{2-x}$ at different potentials.
Fig. S4 (a) UV-Vis spectra of various NH₃ concentrations after incubated for 1 h at room temperature. (b) Calibration curve used for calculation of NH₃ concentrations.
Fig. S5 UV-vis spectra of Cu-SnS$_{2-x}$ at different NO$_3^-$ concentrations.
Fig. S6 Chronoamperometry curves of Cu-SnS$_2$ at different NO$_3^-$ concentrations.
Fig. S7 NH\(_3\) yields and FEs of Cu-SnS\(_{2-x}\) at different NO\(_3^-\) concentrations.
Fig. S8(a) UV-Vis spectra of various nitrite concentrations. (b) Calibration curve used for calculation of nitrite concentrations

\[ y = 0.768x + 0.034 \]

\[ R^2 = 0.9989 \]
Fig. S9 Chronoamperometry curves of SnS$_2$ at different potentials.
Fig. S10. UV-vis spectra of SnS$_2$ at different potentials
Fig. S11. CV curves of Cu-SnS$_{2-x}$
Fig. S12. CV curves of SnS₂
Fig. S13. UV-vis spectra of Cu-SnS$_{2-x}$ tested in 0.1KOH and in 0.1MKOH + 0.1MKNO$_3$
Fig. S14. NH$_3$ yields and FEs of three independent samples.
Fig. S15. UV-vis spectra of eight-times cycle test
Fig. S16. SEM image of Cu-SnS$_{2-x}$ after the cycle test
Fig. S17. TEM image of Cu-SnS$_2$ after the cycle test
Fig. S18 XPS of Cu 2p after the cycle tests.
Fig. S19 XPS of Sn 3d after the cycle tests.
Fig. S20 XPS of S 2p after the cycle tests.
Fig.S21 Model of pristine-SnS$_2$ (Grey: Sn, yellow: S).
Fig.S22 Model of SnS$_2$(Grey: Sn, yellow: S).
Fig.S23 Model of Cu-SnS$_{2-x}$(Grey: Sn, yellow: S, orange: Cu).
Fig. S24 Bader charge of pristine-SnS$_2$ (Grey: Sn, yellow: S).
Fig.S25 Bader charge of SnS$_{2-x}$ (Grey: Sn, yellow: S).
Fig.S26 Model of Cu-SnS$_{2-x}$ (Grey: Sn, yellow: S, orange: Cu).
Table S1. Comparison with various electrocatalysts for NO$_3$RR.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>NH$_3$ yield</th>
<th>FE(%)</th>
<th>Electrolyte</th>
<th>Ref.</th>
</tr>
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<tbody>
<tr>
<td>Cu-SnS$_{2-x}$</td>
<td>0.63 mmol/h/mg$_{cat}$</td>
<td>93.8%</td>
<td>0.1MKOH+0.1M KNO$_3$</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>(0.196 mmol/h/cm$^2$)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Cu/Cu-Mn$_3$O$_4$ NSAs/CF</td>
<td>0.21 mmol/h/cm$^2$</td>
<td>92.4%</td>
<td>0.1MKOH+200 ppm KNO$_3$</td>
<td>1</td>
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<tr>
<td>BCN@Cu</td>
<td>0.57 mmol/h/mg$_{cat}$</td>
<td>89.3%</td>
<td>0.1MKOH+0.1M KNO$_3$</td>
<td>2</td>
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<tr>
<td>10Cu/TiO$_{2-x}$</td>
<td>0.1143 mmol/h/mg$_{cat}$</td>
<td>81.34%</td>
<td>0.1MKOH+200 ppm KNO$_3$</td>
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<tr>
<td>TiO$_{2-x}$</td>
<td>0.045 mmol/h/mg$_{cat}$</td>
<td>85%</td>
<td>0.5Na$_2$SO$_4$+50 ppm KNO$_3$</td>
<td>4</td>
</tr>
<tr>
<td>Fe SAC</td>
<td>0.46 mmol/h/cm$^2$</td>
<td>75%</td>
<td>0.1MK$_2$SO$_4$+0.1M KNO$_3$</td>
<td>5</td>
</tr>
<tr>
<td>Cu/Pd/CuO$_x$</td>
<td>0.088 mmol/h/mg$_{cat}$</td>
<td>84.04%</td>
<td>0.5MK$_2$SO$_4$+50 ppm KNO$_3$</td>
<td>6</td>
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<tr>
<td>CuO@MnO$_2$/CF</td>
<td>0.24 mmol/h/cm$^2$</td>
<td>94.92%</td>
<td>0.5MK$_2$SO$_4$+200 ppm KNO$_3$</td>
<td>7</td>
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<tr>
<td>NiCo$_2$O$_4$/CC</td>
<td>0.97 mmol/h/cm$^2$</td>
<td>99%</td>
<td>0.1MNaOH+0.1M NaNO$_3$</td>
<td>8</td>
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</table>
References


