Supplementary Figures

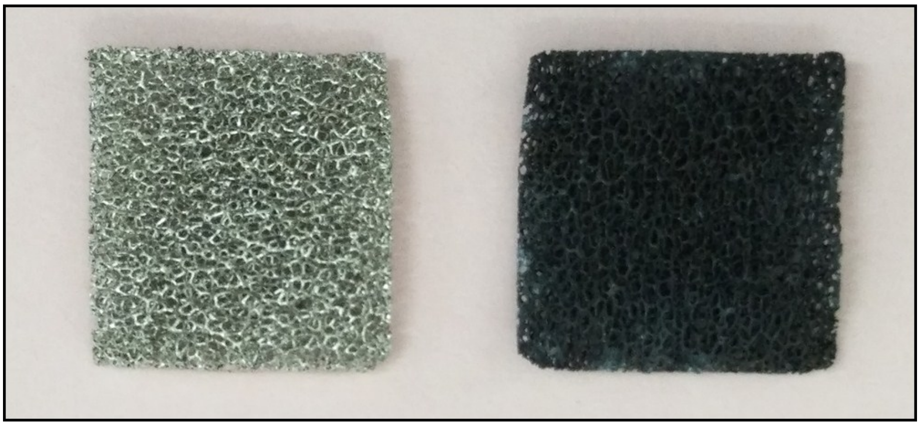

Figure S1. Digital image of bare Ni foam (left) and SnS_2@Ni foam (right).

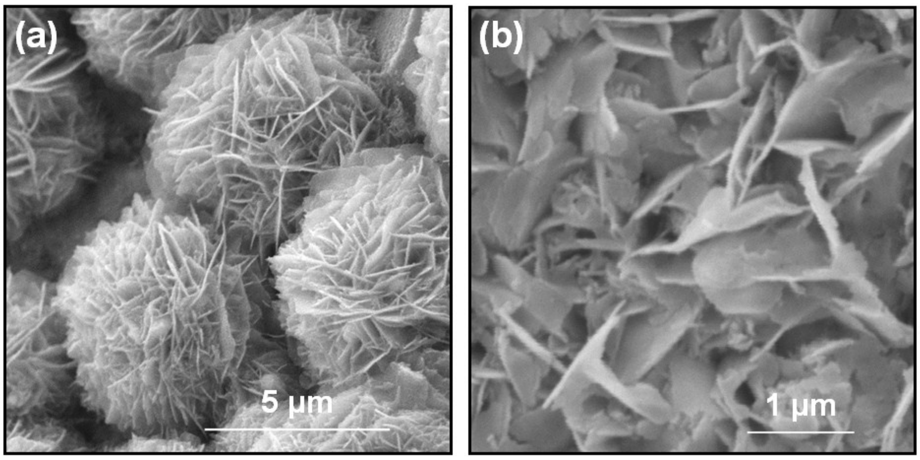

Figure S2. SEM images of (a) self-organized growth of SnS_2 nanoflowers in the presence of Ni foam, and (b) random growth of SnS_2 nanopetals in the absence of Ni foam.

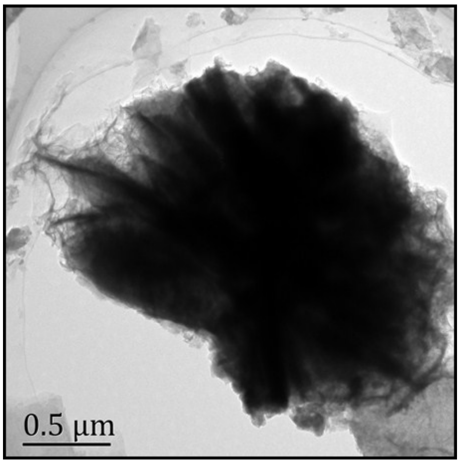

Figure S3. TEM image of a SnS_2 nanoflower which is constructed from numerous nanopetals interconnected to each other at the center.

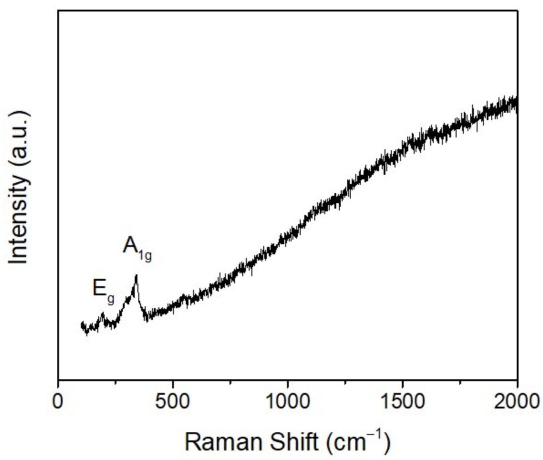

Figure S4. Raman spectrum of SnS_2@Ni foam.[1]

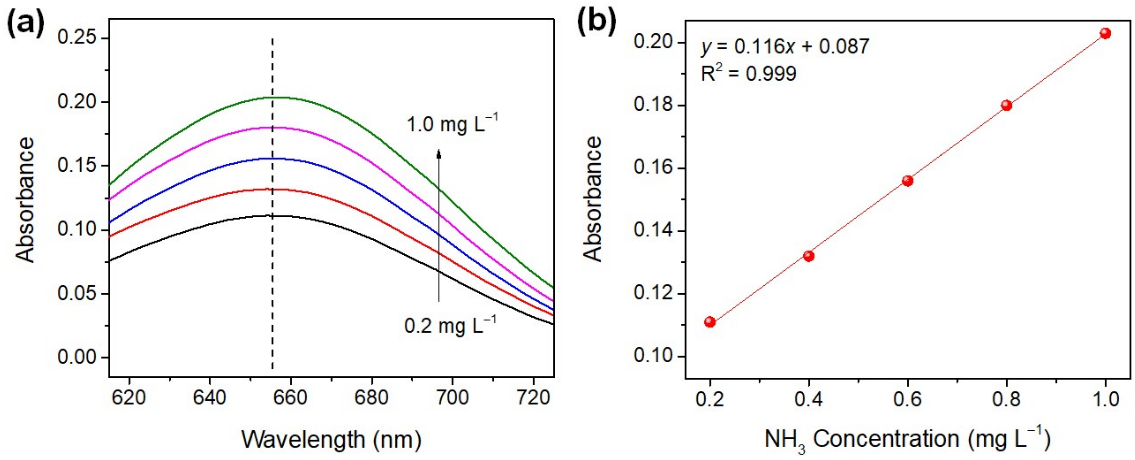

Figure S5. (a) UV-vis spectra at various NH_3 concentrations after being incubated for 2 h at room temperature, and (b) the corresponding calibration curve.[2]

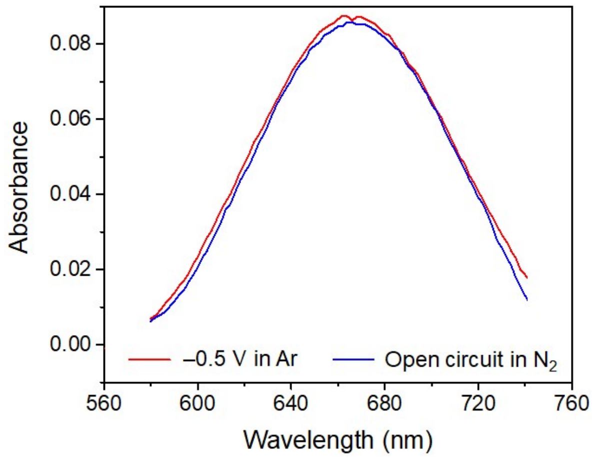

Figure S6. UV-vis absorption spectra of the electrolytes (stained by Nessler's reagent) after 2 h electrolysis in Ar at –0.5 V *vs.* RHE, and in N_2 at open circuit.

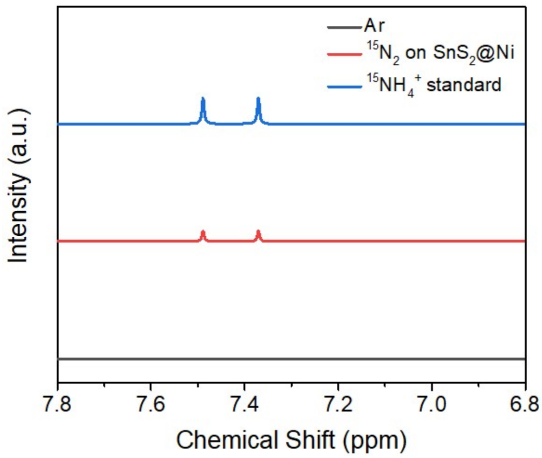

Figure S7. ^{1}H NMR spectra for $^{15}NH_4Cl$, as well as the electrolytes after being electrolyzed in $^{15}N_2$ and argon, respectively.

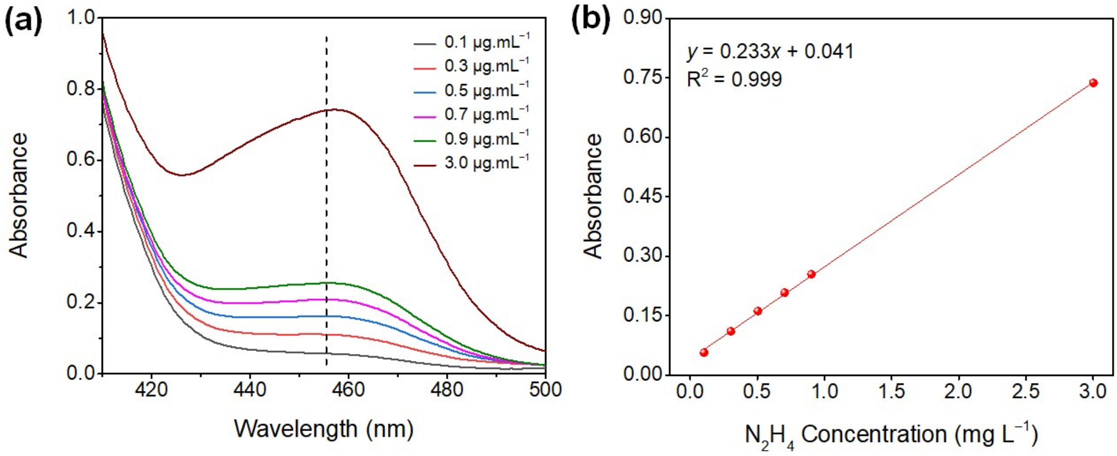

Figure S8. (a) UV-vis spectra at various N_2H_4 concentrations after being incubated for 2 h at room temperature, and (b) the corresponding calibration curve.[3]

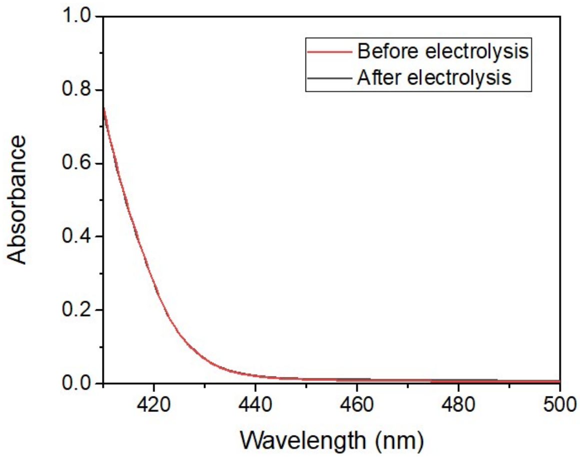

Figure S9. UV-vis absorption spectra of the electrolytes (stained by Watt and Chrisp method) before and after 2 h electrolysis in N_2 at –0.5 V *vs.* RHE.

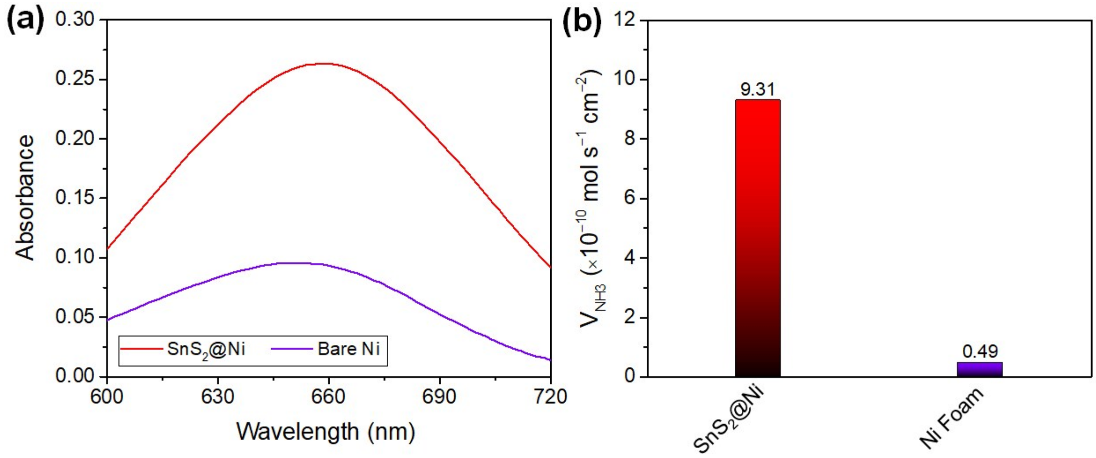

Figure S10. (a) UV-vis absorption spectra of the electrolytes (stained by Nessler's reagent) after electrolysis at –0.5 V *vs.* RHE for 2 h and (b) the corresponding NH_3 yields of SnS_2@Ni foam and bare Ni foam, respectively.

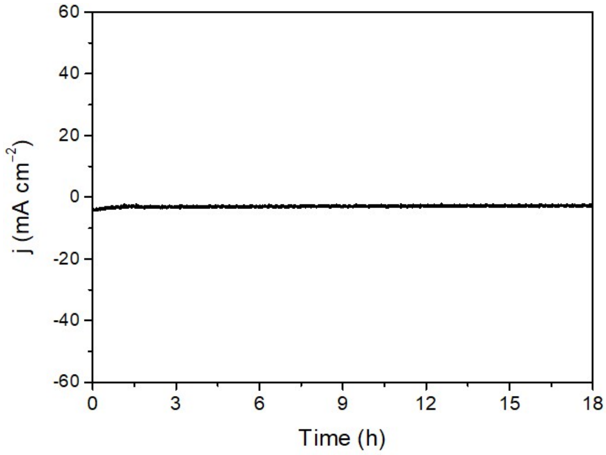

Figure S11. Long-term durability test of SnS_2@Ni foam for NRR at –0.5 V *vs.* RHE for 18 h.

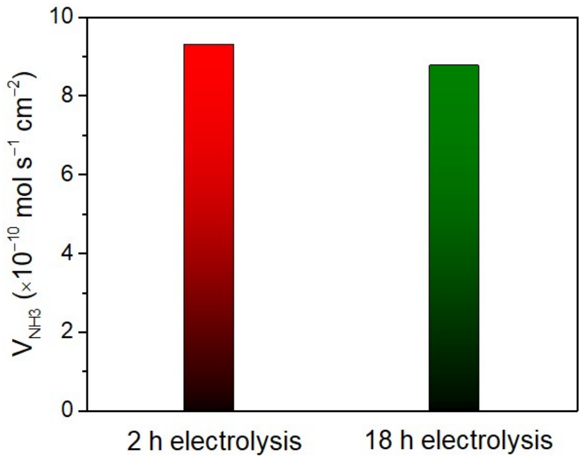

Figure S12. Comparison of NH_3 yields of SnS_2@Ni foam after electrolysis at –0.5 V *vs*. RHE for 2 and 18 h, respectively.

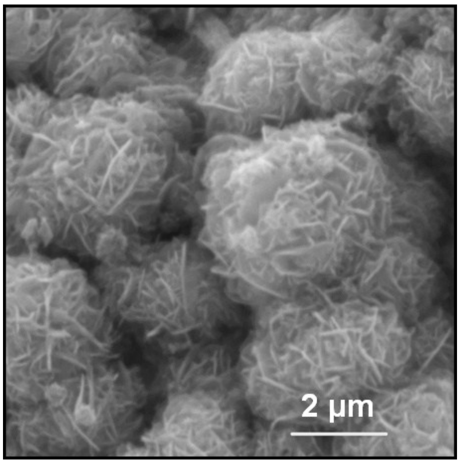

Figure S13. SEM image of flower-like SnS_2 nanoarrays after the electrocatalytic test.

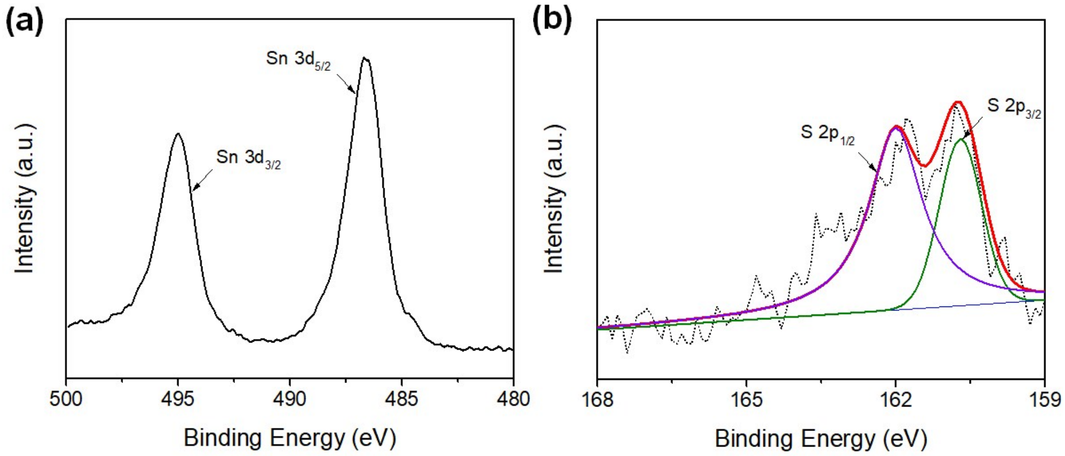

Figure S14. High-resolution (a) Sn 3d and (b) S 2p XPS spectra of SnS_2 nanoflowers after the electrocatalytic test. The two isolated peaks of the Sn 3d spectrum are located at 495.2 and 486.6 eV, corresponding to the Sn $3d_{3/2}$ and $3d_{5/2}$ orbitals of the Sn(IV) state. The two deconvoluted peaks of the S 2p spectrum are located at 162.0 and 160.7 eV, corresponding to the S $2p_{1/2}$ and $2p_{3/2}$ orbitals. These data are nearly identical to those of SnS_2 nanoflowers before the electrocatalytic test without obvious changes.

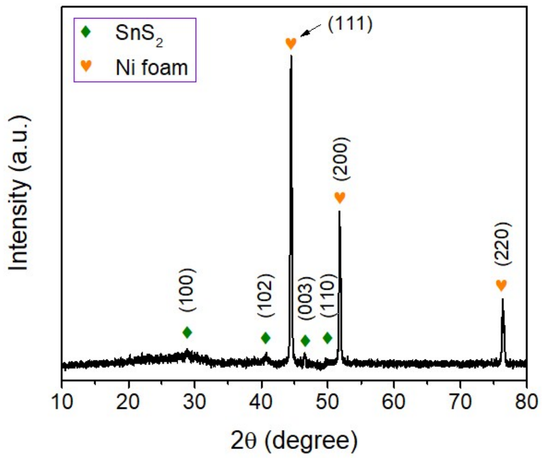

Figure S15. XRD pattern of SnS_2@Ni foam after the electrocatalytic test, in which the (100), (102), (003), and (110) planes of hexagonal SnS_2 can also be seen without obvious changes.

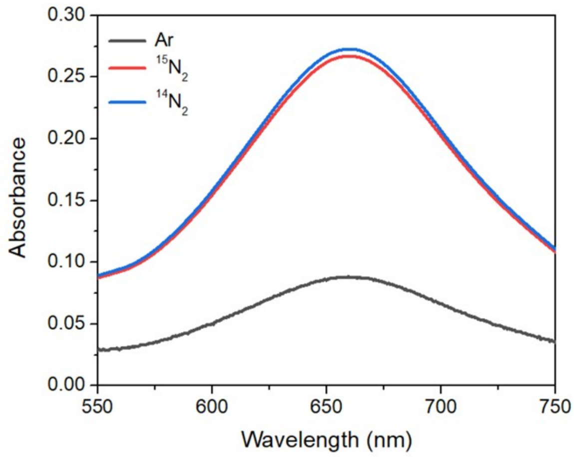

Figure S16. UV-vis absorption spectra of the electrolytes (stained by Nessler's reagent) after 2 h electrolysis in $^{14}N_2$, $^{15}N_2$ and Ar at –0.5 V *vs.* RHE.

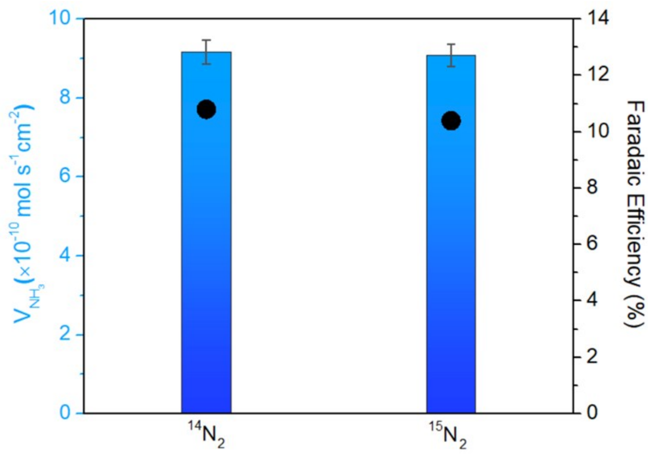

Figure S17. Ammonia yields and Faradaic efficiencies of SnS_2@Ni foam electrolyzed in $^{14}N_2$ and $^{15}N_2$ at –0.5 V *vs.* RHE for 2 h, respectively.

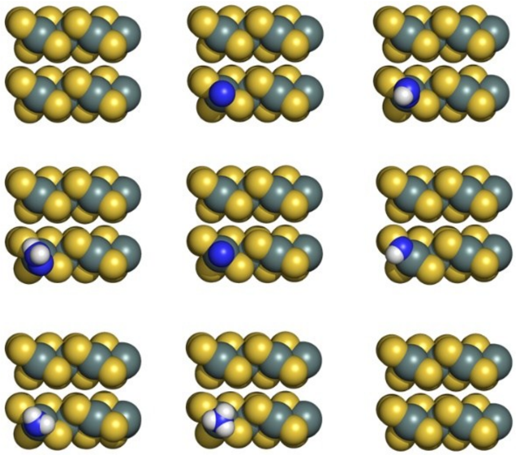

Figure S18. Top-view optimized structures of SnS_2 corresponding to each free energy profile as determined by DFT calculations.

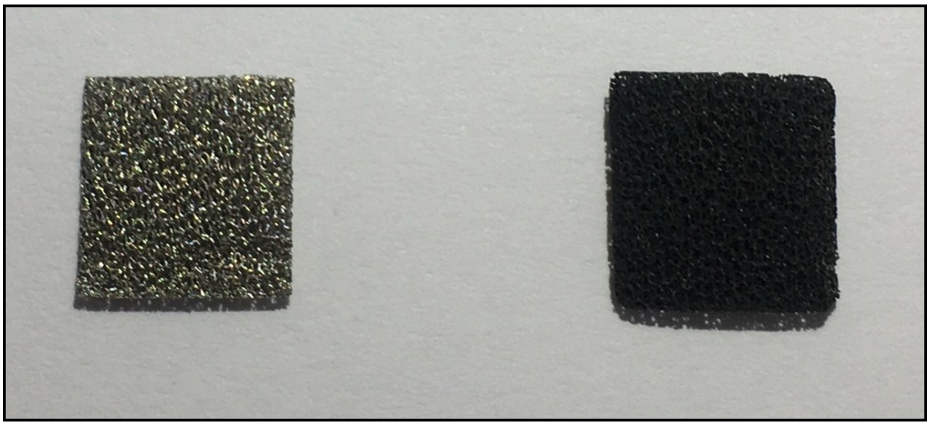

Figure S19. Digital image of bare Ni foam (left) and ZnS@Ni foam (right).

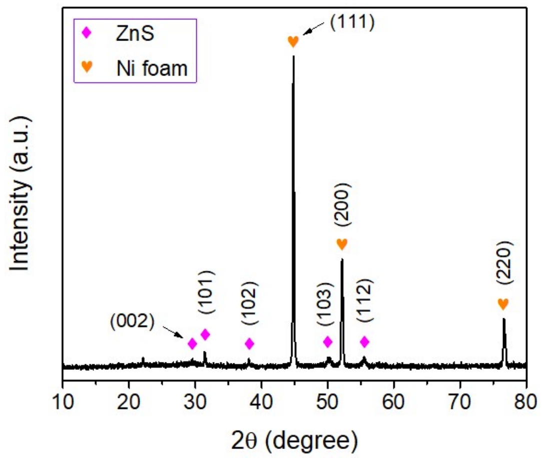

Figure S20. XRD pattern of ZnS@Ni foam, in which three sharp peaks are attributed to the (111), (200), and (220) planes of highly crystalline Ni,[4] while the other peaks are attributed to the (002), (101), (102), (103), and (112) planes of wurtzite ZnS.[5]

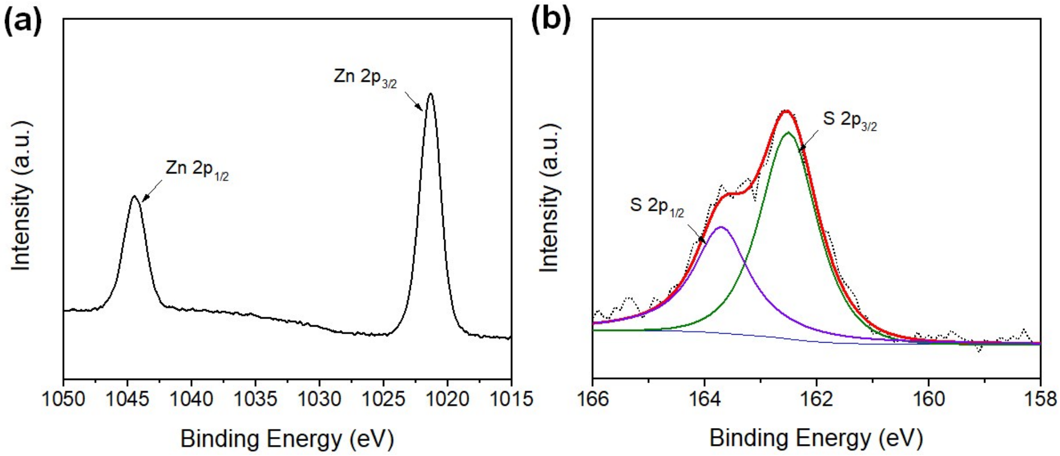

Figure S21. High-resolution (a) Zn 2p and (b) S 2p XPS spectra of ZnS nanowires. The high-resolution Zn 2p spectrum shows a pair of strong peaks centered at 1044.4 and 1021.3 eV corresponding to Zn $2p_{1/2}$ and $2p_{3/2}$ orbitals, and the high-resolution S 2p spectrum shows two deconvoluted peaks at 163.6 and 162.5 eV attributed to S $2p_{1/2}$ and $2p_{3/2}$ orbitals.[6]

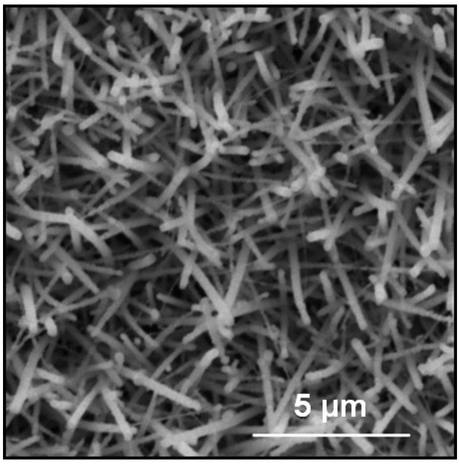

Figure S22. SEM image of forest-like ZnS nanoarrays after the electrocatalytic test.

Table S1. Summary of electrochemical NRR performance of our SnS_2@Ni foam and other transition-metal-based catalysts under ambient conditions.

Catalyst	Electrolyte	Potential (*vs.* RHE)	V_{NH3} ($\times 10^{-11}$)	FE	Reference
SnS_2 nanoflowers on Ni foam	**0.1 M Na_2SO_4**	**−0.5 V**	**93 mol s^{-1} cm^{-2}**	**11.2%**	**This work**
MoS_2 nanosheets on carbon cloth	0.1 M Na_2SO_4	−0.5 V	8.1 mol s^{-1} cm^{-2}	1.17%	*Adv. Mater.* **2018**, *30*, 1800191
Mo_2C@C nanosheets on carbon cloth	0.5 M Li_2SO_4	−0.3 V [a] −0.2 V [b]	18.5 mol s^{-1} mg^{-1} [a]	1.6% [b]	*Adv. Mater.* **2018**, *30*, 1803694
Mo_2C nanorods on glassy carbon electrode	0.1 M HCl	−0.3 V	62 mol s^{-1} cm^{-2}	8.13%	*ACS Cent. Sci.* **2019**, *5*, 116
Ti_3C_2 (MXene) on stainless steel mesh	0.5 M Li_2SO_4	−0.1 V	7.7 mol s^{-1} cm^{-2}	4.62%	*Joule* **2019**, *3*, 279
VN nanoparticles on carbon paper	1 mM H_2SO_4	−0.2 V	50 mol s^{-1} cm^{-2}	6.5%	*J. Am. Chem. Soc.* **2018**, *140*, 13387
VN nanowires on carbon cloth	0.1 M HCl	−0.3 V	25 mol s^{-1} cm^{-2}	3.58%	*Chem. Commun.* **2018**, *54*, 5323
VN nanosheets on Ti mesh	0.1 M HCl	−0.5 V	8.4 mol s^{-1} cm^{-2}	2.25%	*ACS Sustainable Chem. Eng.* **2018**, *6*, 9545
Mo_2N nanorods on glassy carbon electrode	0.1 M HCl	−0.3 V	46 mol s^{-1} cm^{-2}	4.5%	*Chem. Commun.* **2018**, *54*, 8474
MoN nanosheets on carbon cloth	0.1 M HCl	−0.3 V	30.1 mol s^{-1} cm^{-2}	1.15%	*ACS Sustainable Chem. Eng.* **2018**, *6*, 9550
Fe_2O_3@CNT on carbon paper	$KHCO_3$	−2.0 V	0.36 mol s^{-1} cm^{-2}	0.15%	*Angew. Chem. Int. Ed.* **2017**, *56*, 2699
$Bi_4V_2O_{11}/CeO_2$ on carbon paper	0.1 M HCl	−0.2 V	76 mol s^{-1} cm^{-2}	10.16%	*Angew. Chem. Int. Ed.* **2018**, *57*, 6073
Fe_3O_4 nanorods on Ti mesh	0.1 M Na_2SO_4	−0.4 V	5.6 mol s^{-1} cm^{-2}	2.6%	*Nanoscale* **2018**, *10*, 14386
SnO_2 microparticles on carbon cloth	0.1 M Na_2SO_4	−0.8 V [a] −0.7 V [b]	14.7 mol s^{-1} cm^{-2} [a]	2.17% [b]	*Chem. Commun.* **2018**, *54*, 12966
Cr_2O_3 hollow microspheres on carbon paper	0.1 M Na_2SO_4	−0.9 V	5.0 mol s^{-1} cm^{-2}	6.78%	*ACS Catal.* **2018**, *8*, 8540
Mn_3O_4 nanocubes on carbon paper	0.1 M Na_2SO_4	−0.8 V	3.8 mol s^{-1} cm^{-2}	3.0%	*Small* **2018**, *14*, 1803111
Y_2O_3 nanosheets on carbon paper	0.1 M Na_2SO_4	−0.9 V	10.6 mol s^{-1} cm^{-2}	2.53%	*Ind. Eng. Chem. Res.* **2018**, *57*, 16622
Cr_2O_3@RGO on carbon paper	0.1 M HCl	−0.7 V [a] −0.6 V [b]	2.7 mol s^{-1} cm^{-2} [a]	7.33% [b]	*Inorg. Chem.* **2019**, *58*, 2257
CeO_2 nanorods on carbon paper	0.1 M Na_2SO_4	−0.5 V [a] −0.6 V [b]	2.68 mol s^{-1} cm^{-2} [a]	3.7% [b]	*ACS Sustainable Chem. Eng.* **2019**, *7*, 2889
MoO_3 nanosheets on glassy carbon electrode	0.1 M HCl	−0.5 V [a] −0.3 V [b]	48 mol s^{-1} cm^{-2} [a]	1.9% [b]	*J. Mater. Chem. A* **2018**, *6*, 12974
CuO@RGO on carbon paper	0.1 M Na_2SO_4	−0.75 V	18 mol s^{-1} cm^{-2}	3.9%	*ChemCatChem* **2019**, *11*, 1441
NbO_2 nanoparticles on carbon paper	0.05 M H_2SO_4	−0.65 V [a] −0.6 V [b]	19 mol s^{-1} cm^{-2} [a]	32% [b]	*Small Methods* **2019**, *3*, 1800386

Nb_2O_5 nanofibers on carbon paper	0.1 M HCl	–0.55 V	71.2 mol s^{-1} mg^{-1}	9.26%	*Nano Energy* **2018**, *52*, 264
B-TiO_2 microparticles on carbon paper	0.1 M Na_2SO_4	–0.8 V	23.5 mol s^{-1} mg^{-1}	3.4%	*ACS Sustainable Chem. Eng.* **2019**, *7*, 117
Mo@NPC on carbon cloth	0.1 M $KHCO_3$	−0.3 V	22.2 mol s^{-1} cm^{-2}	14.6%	*Angew. Chem. Int. Ed.* **2019**, *58*, 2321

Supporting References

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[2] L. Zhang, X. Ji, X. Ren, Y. Ma, X. Shi, Z. Tian, A. M. Asiri, L. Chen, B. Tang, X. Sun, *Adv. Mater.* **2018**, *30*, 1800191.

[3] W. Qiu, X.-Y. Xie, J. Qiu, W.-H. Fang, R. Liang, X. Ren, X. Ji, G. Cui, A. M. Asiri, G. Cui, B. Tang, X. Sun, *Nat. Commun.* **2018**, *9*, 3485.

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