Supporting information

Architecting Flower-like ZnS/CoS Heterojunction for Efficient N_2 Electroreduction to NH_3

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Experimental section

1.1 Materials

Zinc acetate ($(CH_3COO)_2Zn$, 99%), cobalt chloride hexahydrate ($CoCl·6H_2O$, 98%), thiourea (CH_4N_2S, 99%); ethanol (C_2H_5OH, >99.5%), sodium hydroxide (NaOH, 96%), sodium nitroprusside ($Na_2[Fe(NO)(CN)_5]·2H_2O$, 99%), ammonium chloride (NH_4Cl, 99.99%), sodium hypochlorite solution (NaClO, 6-14%), salicylic acid ($C_7H_6O_3$, 99.5%), Nafion solution (5 wt.%), and sodium citrate ($C_6H_5Na_3O_7$, 98%) were purchased from Aladdin.

1.2 Synthesis of CoS electrocatalysts

The CoS electrocatalysts were prepared by the hydrothermal reaction. Firstly, 1.6 mmol of CoCl·6H2O was added to 40 mL of deionized water and stirred until completely dissolved. Then, 1 mmol of CH4N2S was added to the solution and stirred for 60 min. After that, the mixture was transferred to a 50 mL Teflon-lined autoclave and maintained at 180 °C for 10 h in an oven. Finally, the Teflon-lined autoclave was allowed to cool to room temperature. The CoS electrocatalysts were collected, washed with deionized water, and dried at 60 °C overnight.

1.3 Synthesis of ZnS/CoS heterostructure

The ZnS/CoS-101 catalyst was synthesized by hydrothermal synthesis method. Specifically, 200 mg of CoS was added to 40 mL of deionized water and sonicated for 40 min to obtain a dispersion. Then added 482 mg of (CH3COO)2Zn and 167 mg of CH4N2S to the dispersion liquid, stirred until completely dissolved. Afterward, the mixture was transferred into a hydrothermal synthesis reactor (50 mL) and heated in an electric oven at 160 °C for 12 hours. Following cooling to room temperature, the resulting solid was washed twice with deionized water and ethanol. Finally, the material was dried at 60 °C for 12 h. In a similar manner, we prepared a series of catalyst materials by adjusting the molar ratio of Zn and Co (Zn:Co=1:3, 1:5, 1:10), resulting in materials labeled ZnS/CoS-103, ZnS/CoS-105 and ZnS/CoS-110, respectively.

1.4 Electrochemical measurements

The electrochemical measurements were performed using a standard three-electrode

system in a 0.1 M Na_2SO_4 electrolyte solution under ambient temperature and pressure conditions via the CHI-660E electrochemical workstation. The catalysts loaded carbon paper (CP) was used as the working electrode, and a graphite rod and saturated Ag/AgCl electrode were served as counter and reference electrodes, respectively. The working electrode (1×1 cm^2) was fabricated using catalyst ink and air-dried at ambient temperature. The catalyst ink was prepared by sonication, where 5 mg of catalyst was dispersed in 920 μL of ethanol containing 80 μL of Nafion (5 wt%). Subsequently, a volume of 20 μL of the catalyst ink was applied to the CP and dried at room temperature. The NRR tests were conducted using an H-type dual chamber electrochemical cell, which was separated by a Nafion 115 membrane. Before conducting the tests, the Nafion membrane underwent pretreatment involving heating in a 5% H_2O_2 solution for 1 h, followed by immersion in a 0.5 M H_2SO_4 solution for another hour, and finally rinsing with deionized water for 1 h. The potentials were all converted to reversible hydrogen electrodes (RHE), where E (V *vs*. RHE) = E (V *vs*. Ag/AgCl) + 0.197 + 0.059 × pH. Before the NRR test, the electrolyte was purged with N_2 for a duration of 30 min.

1.5 Determination of NH_3

The ammonia concentration in the electrolyte was determined by the indophenol blue method. 4 mL of electrolyte removed from the electrochemical reaction vessel and added 0.2 mL of the catalyst solution (1 wt.% $Na_2[Fe(NO)(CN)_5]\cdot 2H_2O$), 1 mL of the oxidizing solution (0.05 M NaClO), and 2 mL of colouring solution (1.0 M NaOH solution with 5 wt.% salicylic acid and 5 wt.% sodium citrate) into it. After standing at room temperature for 2 h, the UV-Vis absorption spectra were tested using a UV-2700 UV-Vis spectrophotometer at λ=655 nm. The concentration absorbance curves were calibrated using standard NH_4Cl in 0.1 M Na_2SO_4 solution and the obtained calibration curve ($y = 0.382x + 0.03$, $R^2 = 0.999$) was used to calculate the ammonia concentration.

1.6 Calculations of NH_3 yield rate and FE

NH_3 yield rate was calculated using the following equations:

$$NH_3 \text{ yield rate } (\mu g\ h^{-1}\ mg_{cat.}^{-1}) = ([NH_4^+]\times V)/(t\times m_{cat.}) \quad (1)$$

FE was calculated according the following equations:

$$FE = 3 \times F \times [NH_4^+] \times V/18 \times Q \times 100\% \quad (2)$$

where $[NH_4^+]$ (μg/mL) is the concentration of the NH_3 produced; V (mL) is the volume of the electrolyte solution; t (h) is the potential applied time; $m_{cat.}$ (mg) is the mass loading of catalyst on CP; F is the Faraday constant (96485 C mol^{-1}); Q (C) is the quantity of applied electricity during the NRR.

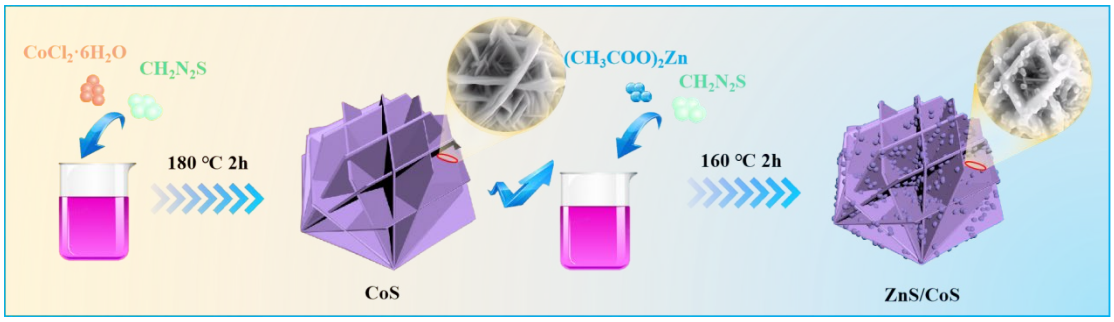

Fig. S1 Schematic illustration of synthesis process for ZnS/CoS.

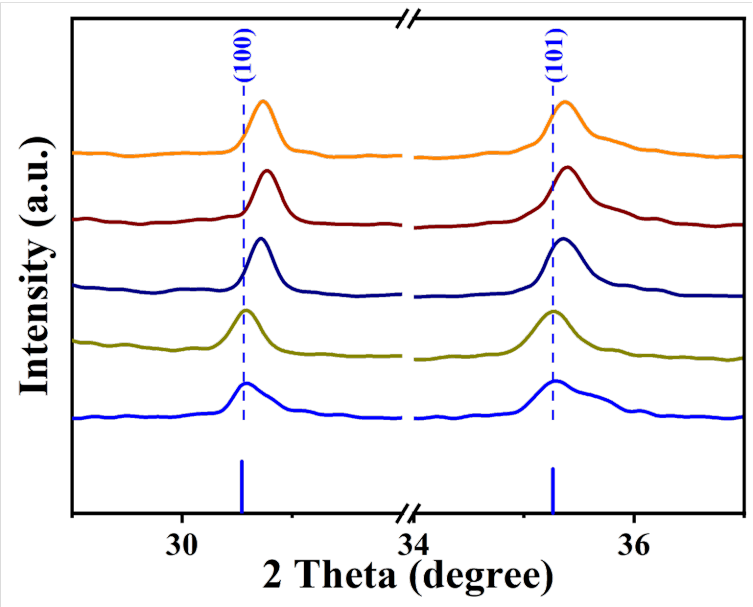

Fig. S2 a partial enlargement of the ZnS/CoS-n and CoS

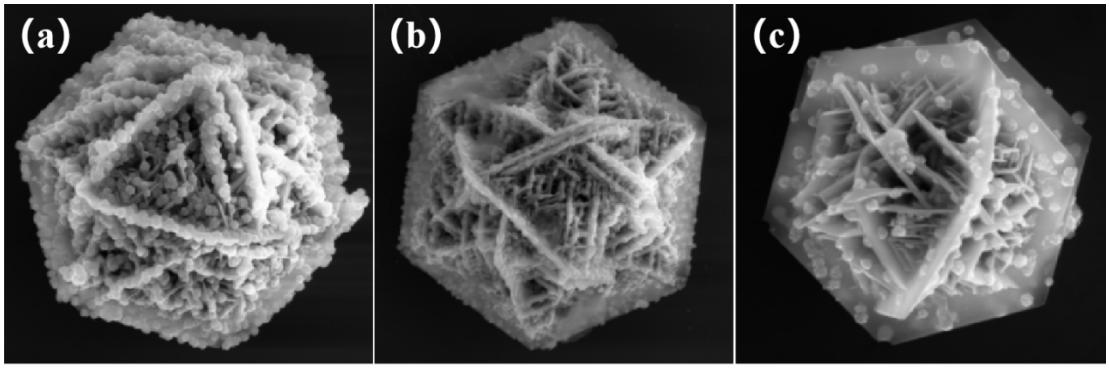

Fig. S3 SEM images of (a) ZnS/CoS-101, (b) ZnS/CoS-103, and (c) ZnS/CoS-110.

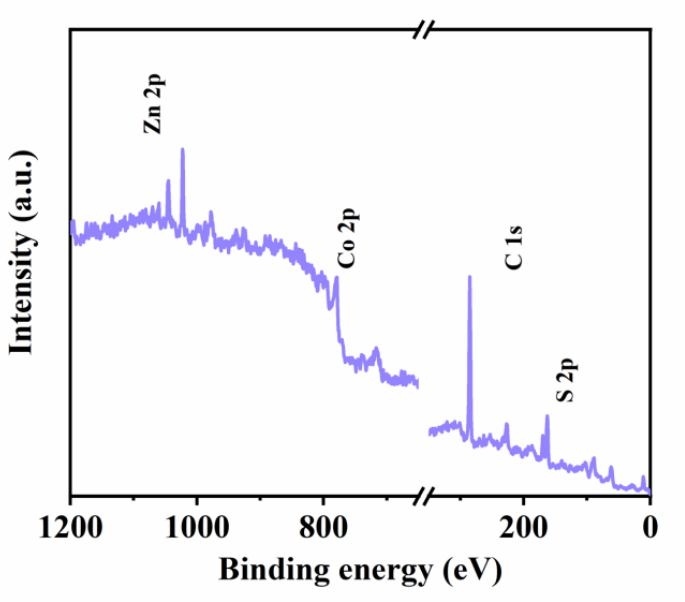

Fig. S4 XPS diffraction patterns of the ZnS/CoS-105 heterostructure.

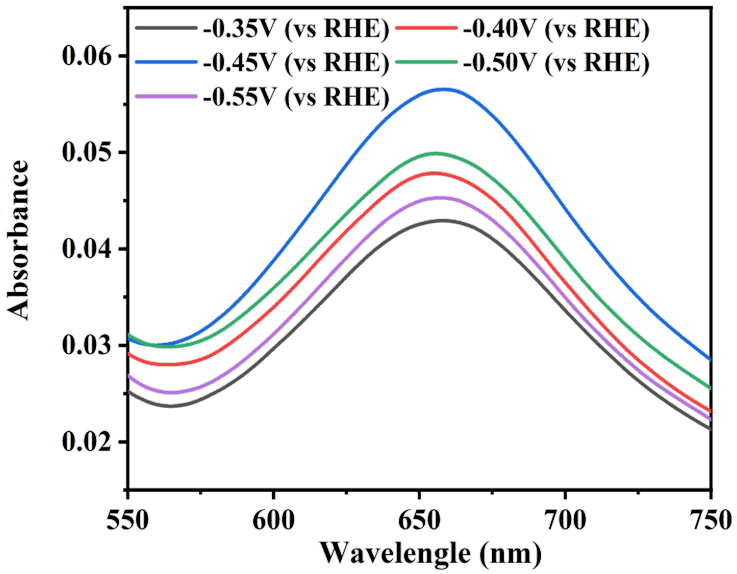

Fig. S5. UV-vis spectra.

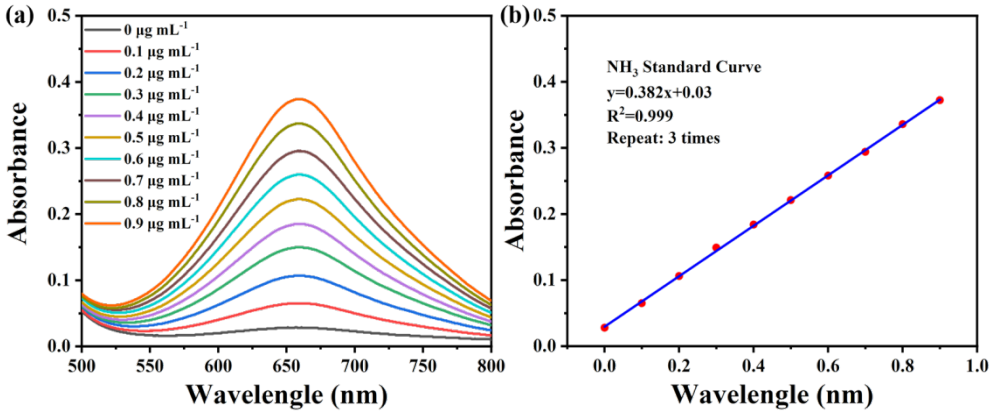

Fig. S6 (a) UV-Vis absorption spectra of indophenol blue method with different NH_3 concentrations. (b) Calibration curve used for calculation of NH_3 concentrations.

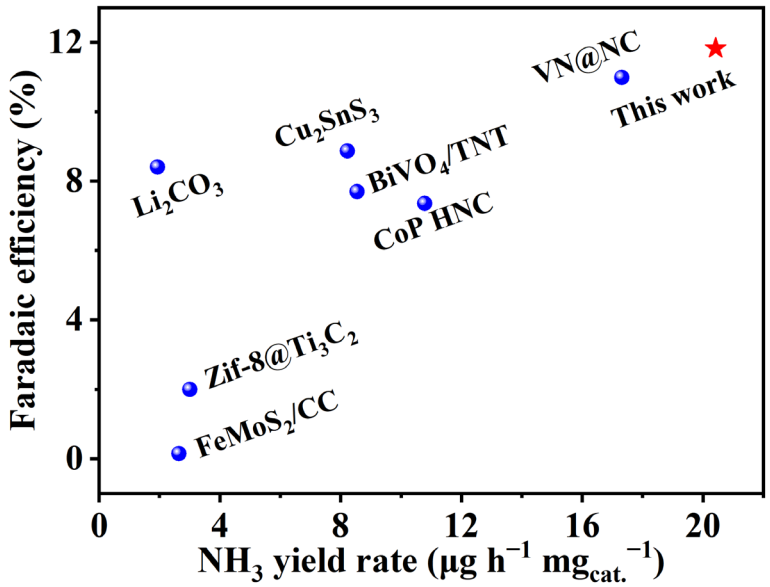

Fig. S7 Comparison of NH_3 yields and FEs with reported electrocatalysts.

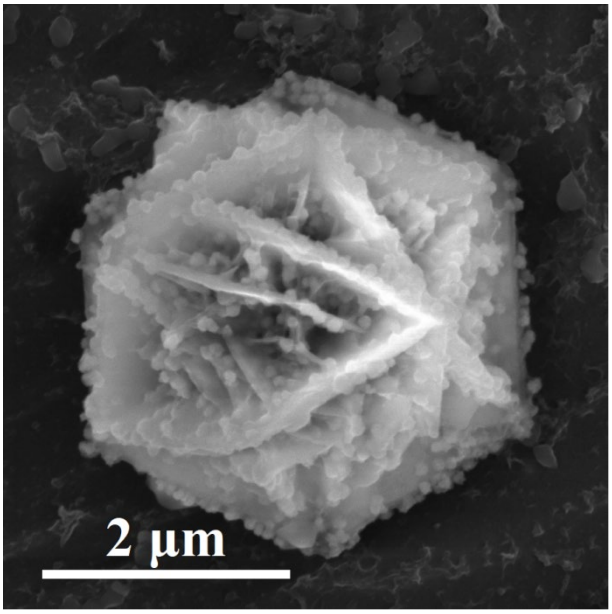

Fig. S8 SEM image of ZnS/CoS-105 after 2 h of nitrogen reduction reaction.

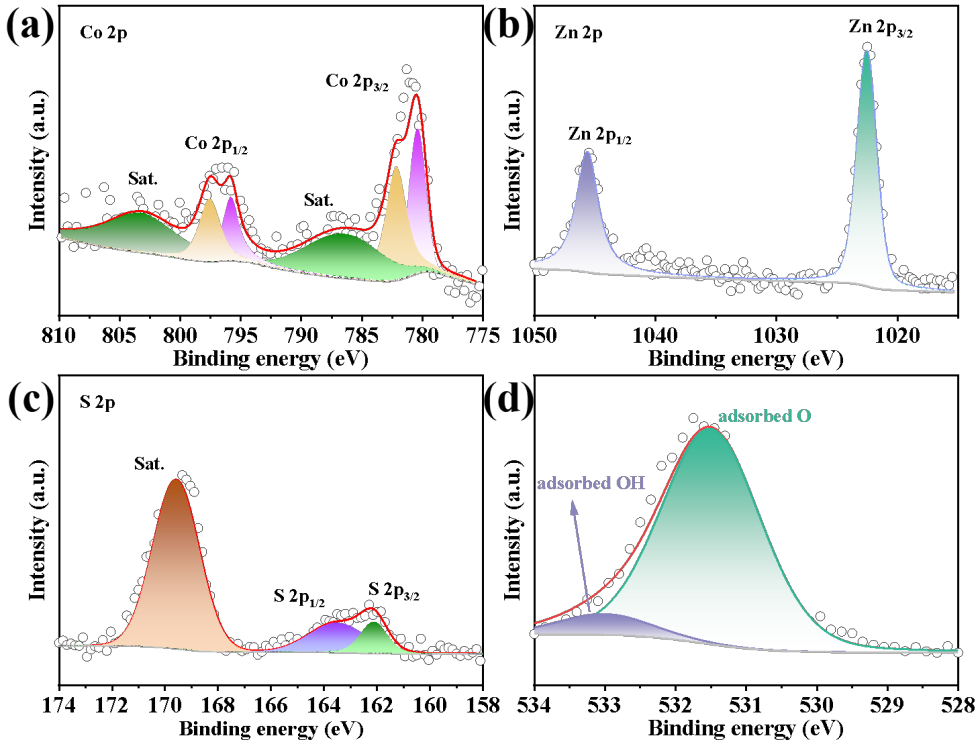

Fig. S9 High-resolution XPS spectra of (a) Co 2p, (b) Zn 2p, (c) S 2p, and (d) O1s of ZnS/CoS-105 after NRR.

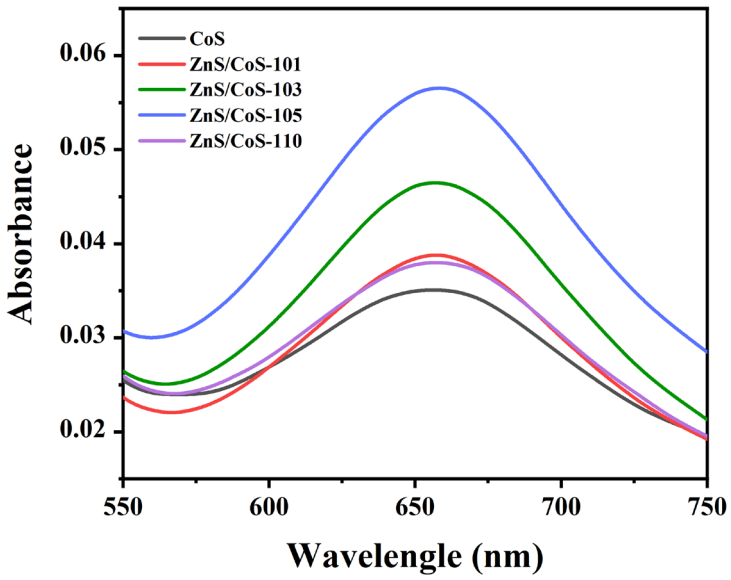

Fig. S10 UV-vis spectra of different samples at -0.45V for 2 h.

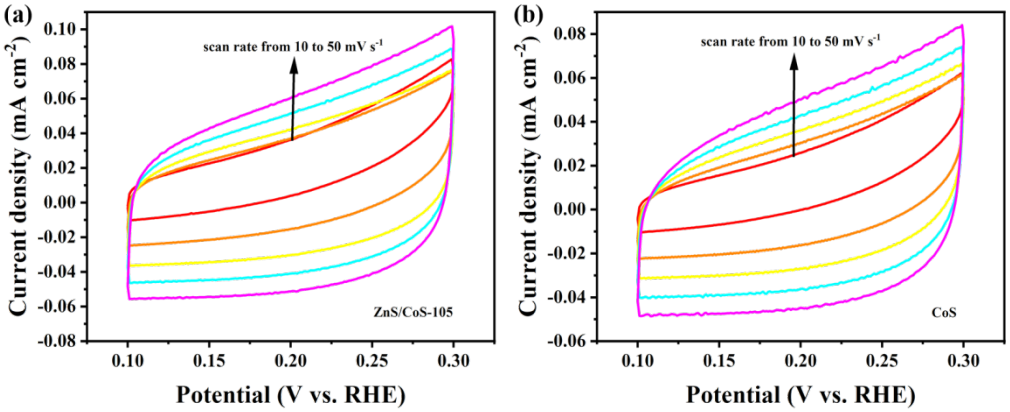

Fig. S11 Cyclic voltammograms (CV) of (a) CoS and (b) ZnS/CoS-105 under different scan rates in 0,1M Na_2SO_4