Supporting Information

(29 pages, including 16 Figures and 1 Table)

CoS₂ Nanoparticles-Embedded N-Doped Carbon Nanobox Derived from ZIF-67 for Electrocatalytic N₂-to-NH₃ Fixation under Ambient Conditions

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Experimental section

Materials: Hydrochloric acid (HCl), ammonium chloride (NH₄Cl), methanol (CH₃OH) and ethanol (C₂H₅OH) were purchased from Chengdu Kelong Chemical Reagent Factory. Salicylic acid $(C_7H_5O_3),$ sodium citrate dihydrate (C₆H₅Na₃O₇·2H₂O), sodium hypochlorite (NaClO), and Nafion (5wt%) sodium were purchased from Aladdin Ltd. in Shanghai. Nitroferricyanide (III) dihydrate (Na₂Fe(CN)₅NO·2H₂O), Para-(dimethylamino) benzaldehyde (C₉H₁₁NO), salicylic acid (C₇H₅O₃), sodium hydroxide (NaOH), Co(Ac)₂·4H₂O, 2-methylimidazole, sulfur, CoS₂, and hydrazine monohydrate (N₂H₄·H₂O), carbon paper, sodium sulfate (Na_2SO_4) , sodium salicylate $(C_7H_5O_3Na)$ and sodium hydroxide (NaOH) were bought from Beijing Chemical Corporation. The water used throughout all experiments was purified through a Millipore system. All chemicals were used as received without further purification.

Preparation of ZIF-67: 18 mmol of $Co(Ac)_2 \cdot 4H_2O$ and 72 mmol of 2-methylimidazole were dissolved in 450 mL CH₃OH to form the clear solution, respectively. The two solutions were mixed at room temperature under magnetic stirring for 10 min to obtain the homogenous system. Then the solution was aged for 24 h. Precipitates were separated by centrifugation and washed with CH₃OH and C₂H₅OH 3 times, respectively, dried at 60 °C for one night.

Synthesis of Co@NC and NC: ZIF-67 was carbonized at 500 °C. The carbonization process was kept for 2 h under gas mixture atmosphere of 95% argon gas (Ar) and 5% hydrogen (H₂) with a heating rate of 5 °C min⁻¹ and cooled down to room temperature naturally. NC was prepared via 0.1 M HCl etching and stirring overnight.

Synthesis of $CoS_2@NC$ composites: The obtained products of Co@NC composites were uniformly mixed with sulfur powder with a mass ratio of $M_{Co@NC}:M_S = 2:1$. The mixture sealed in a glass tube and heated to 300 °C for 2 h with a ramping rate of 10 °C/min in the Ar atmosphere to get $CoS_2@NC$.

Preparation of $CoS_2@NC/CP$, CoS_2/CP , Co@NC/CP, and NC/CP electrode: $CoS_2@NC/CP$ as prepared as following: First, 10 mg of $CoS_2@NC$ and 20 µL of Nafion solution (5 wt%) were dispersed in 980 μ L mixed solution containing ethanol and H₂O (V:V=2:1) by 30 min sonication to form a homogeneous ink. Then 10 μ L of the CoS₂@NC ink was loaded on a carbon paper (1 cm × 1 cm) (CoS₂@NC/CP) and dried under ambient condition for measurement. The CoS₂/CP, Co@NC/CP, and NC/CP were prepared by following the same method.

Characterization: Powder XRD data were acquired on a RigakuD/MAX 2550 diffractometer with Cu K α radiation (λ =1.5418 Å). SEM measurements were carried out on an XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. TEM measurements were performed on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) with an accelerating voltage of 200 kV. XPS data were acquired on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the excitation source. The absorbance data of spectrophotometer was measured on the UV-Vis spectrophotometer.

Electrochemical measurement: Before NRR measures, the Nafion membrane was pretreated by heating in H₂O₂ solution (3 wt%) and 0.5 M H₂SO₄ at 80 °C for 2 h, respectively. Then it was dipped in ultrapure water at 80 °C for overnight. The H-shape electrochemical cell was also cleaned via heating in the water at 80 °C for overnight. All the electrochemical measurements were tested with a CHI660E workstation (CH Instruments, China) in a typical three-electrode setup using a graphite rod as the counter electrode, Ag/AgCl as the reference electrode, and CoS₂@NC/CP as the working electrode. All experiments were performed at ambient conditions. Before the NRR measurements, the electrolyte was bubbled with high-purity N₂ (99.999%) for 30 min. The potentials reported in this work were converted to RHE scale via calibration with the following equation: E (vs RHE) =E (vs Ag/AgCl) + 0.197 + 0.059 × pH.

Determination of NH₃: Concentration of produced NH₃ in 0.1M HCl was determined by spectrophotometry measurement with salicylic acid.¹ In detail, 2 ml post-tested solution was removed from the cathodic chamber, and then added into 2 ml 1.0 M NaOH solution containing $C_7H_6O_3$ and $C_6H_5Na_3O_7 \cdot 2H_2O$ (5 wt%), then added 1 ml NaClO (0.05 M) and 0.2 ml Na₂[Fe(NO)(CN)₅] $\cdot 2H_2O$ (1 wt%) aqueous solution in turn. After standing at room temperature for 2 h, the UV-Vis absorption spectrum was measured. The concentration of indophenol blue was determined by using the absorbance at a wavelength of 655 nm. The concentration-absorbance curves were calibrated using standard NH₄Cl solution (0.1 M HCl as mother solution) with a serious of concentrations. Typically, 100 µg mL⁻¹ NH₄Cl solution was prepared and diluted to 2 µg mL⁻¹. The concentration-absorbance curves were calibrated using standard NH₄Cl solution of concentrations. The fitting curve (y = 0.370 x + 0.075, R² = 0.997) shows good linear relation of absorbance value with NH₃ concentration by three times independent calibrations.

NH₃ concentration in 0.1 M Na₂SO₄ was determined by the indophenol blue method.² In detail, 4 mL of post-NRR solution was removed from the cathodic chamber. Then, 50 µL oxidizing solution (NaClO (ρ_{Cl} =4~4.9) and 0.75 M NaOH), 500 µL coloring solution (0.4 M C₇H₅O₃Na and 0.32 M NaOH), and 50 µL catalyst solution (0.1 g Na₂[Fe(CN)₅NO]·2H₂O diluted to 10 mL with deionized water) were added to the sample solution, sequentially. After standing the mixture solution at room temperature for 1 h, UV-Vis absorption spectra were measured at a wavelength of 655 nm. The concentration-absorbance curve was calibrated using standard ammonia solutions with a series of concentrations. The fitting curve (y = 0.581x + 0.018, R² = 0.998) shows good linear relation of absorbance value with NH₃ concentration by three times independent calibrations.

Determination of N₂H₄: The N₂H₄ presented in the electrolyte was estimated by Watt and Chrisp method.³ A mixed solution of C₉H₁₁NO (5.99 g), HCl (concentrated, 30 mL) and ethanol (300 mL) was used as a color reagent. Typically, 1 mL electrolyte from the cathodic chamber was added into 1 mL above prepared color reagent and stirring 15 min at room temperature. The absorbance measurement of the resulting solution was performed at 455 nm. The concentration absorbance curves were calibrated using standard N₂H₄ solution with a series of concentrations. The fitting curve shows good linear relation of absorbance with N_2H_4 · H_2O concentration in 0.1 M HCl (y = 0.738 x + 0.1, R² = 0.999) by three times independent calibrations.

Calculations of NH₃ yield and FE: The Faradic efficiency (FE) for N_2 reduction was defined as the amount of electric charge used for synthesizing NH₃ divided the total charge passed through the electrodes during the electrolysis. The total amount of NH₃ produced was measured using colorimetric methods. NH₃ yield was calculated using the following equation:

$$NH_3$$
 yield = $[NH_3] \times V / (m_{cat.} \times t)$ S1

We hypothesis that the production of one NH_3 molecule needed three electrons. The FE in 0.1 M HCl could be calculated according to following equation:

$$FE = 3 \times F \times [NH_3] \times V / (17 \times Q) \times 100\%$$
 S2

Where F is the Faraday constant (96500 C mol⁻¹); Q (C) is the quantity of applied electricity; [NH₃] (μ g/ml) is the measured NH₃ concentration. V (mL) is the volume of electrolyte (in our work 35 mL), t (h) is the reduction reaction time and m_{cat.} (mg) is the mass loading of catalyst on CP.



Figure S1. XRD patterns of (a) ZIF-67 and (b) Co@NC.



Figure S2. SEM images of (a) ZIF-67, (b) Co@NC, and (c) CoS₂@NC.



Figure S3. SAED pattern of CoS₂@NC.



Figure S4. EDS spectrum of CoS₂@NC.



Figure S5. XPS survey spectrum for CoS₂@NC.



Figure S6. (a) UV-Vis absorption spectra of indophenol assays with NH_3 in 0.1 M HCl after incubated for 2 h at room temperature. (b) Calibration curve used for calculation of NH_3 concentration.



Figure S7. (a) UV-Vis absorption spectra of various N_2H_4 concentrations stained with $C_9H_{11}NO$ indicator after incubated for 15 min at room temperature. (b) Calibration curve used for calculation of N_2H_4 concentration.



Figure S8. UV-Vis absorption spectra of the electrolytes stained with $C_9H_{11}NO$ indicator after NRR electrolysis at a series of potentials.



Figure S9. TEM image for CoS₂@NC (inset: particle size distribution histograms).



Figure S10. Cyclic voltammetry curves of (a) $CoS_2@NC/CP$ and (b) CoS_2/CP with various scan rates (10-60 mV s⁻¹) in the region of 0.45 to 0.55 V vs. Ag/AgCl. The capacitive current densities at 0.5 V vs. Ag/AgCl as a function of scan rates for (c) $CoS_2@NC/CP$ and (d) CoS_2/CP .



Figure S11. NH_3 yields and FEs with different electrodes at -0.15 V (vs. RHE) after 2 h electrolysis under ambient conditions.



Figure S12. NH₃ yields and FEs for CoS₂@NC/CP with different catalyst loadings.



Figure S13. (a) UV-Vis spectra of indophenol assays with NH₃ concentrations in 0.1 M Na₂SO₄ after incubated for 1 h at room temperature. (b) Calibration curve used for calculation of NH₃ concentrations. (c) UV-Vis absorption spectra of the electrolytes stained with indophenol indicator after NRR electrolysis at a series of potentials for 2 h. (d) NH₃ yields and FEs of CoS₂@NC/CP for NRR at different potentials.



Figure S14. Time-dependent generation of NH_3 at -0.15 V vs. RHE over $CoS_2@NC/CP$.



Figure S15. Chronoamperometry curves for $CoS_2@NC$ catalyst at the potential of -0.15 V for 24 h.



Figure S16. XPS spectra of post $-NRR CoS_2@NC$ in the (a) Co 2p, (b) S 2p, (c) C 1s and (d) N 1s.

Table S1. Comparison of electrocatalytic NRR performance for CoS_2 @NC with noble-metal-free electrocatalysts under ambient conditions.

Testing method	Catalyst	Electrolyte	NH ₃ yield	FE (%)	Ref.
indophenol	CoS ₂ @NC/CP	0.1 M HCl	17.45 μg h ⁻¹ mg ⁻¹ _{cat.}	4.6	This work
blue method	VN	0.1 M HCl	$8.40 \times 10^{-11} \text{ mol s}^{-1}$ cm ⁻²	2.25	4
	TiC/C nanofiber	0.1 M HCl	14.1 μg h ⁻¹ mg ⁻¹ _{cat.}	5.8	5
	N-doped carbon	0.1 M HCl	15.7 μg h ⁻¹ mg ⁻¹ _{cat.}	1.45	6
	PTCA-rGO	0.1 M HCl	24.7 $\mu g h^{-1} m g^{-1}{}_{cat.}$	6.9	7
		0.1 M 8.08 × 10 ⁻¹¹ mol s ⁻¹	$8.08 \times 10^{-11} \text{ mol s}^{-1}$	1.17	8
	MOS ₂	Na ₂ SO ₄	cm ⁻²		
	0.1 M		2		
	V ₂ O ₃ /C	Na ₂ SO ₄	12.3 μ g h ⁻¹ mg ⁻¹ _{cat.}	7.28	9
	Dimensilari	0.1 M	12.22 1-1 -2	10.46	10
	Bi nanosneet	Bi nanosheet $13.23 \ \mu g \ h^{-1} \ cm^{-2}$ $Na_2 SO_4$	13.23 μg n ⁻¹ cm ⁻²		
	boron-doped	0.1 M	14.4 1-1 -1	2.4	11
	TiO ₂	Na ₂ SO ₄	14.4 μ g n ' mg ' _{cat.}	3.4	11
	T:O -CO	0.1 M	15.13 μ g h ⁻¹ mg ⁻¹ _{cat.}	3.3	12
	Na ₂ SO ₄	Na ₂ SO ₄			
		0.1 M	$17.4 \ \mu g \ h^{-1} \ m g^{-1}_{cat.}$	3.52	13
	MIn ₃ U ₄ @rGU	Na ₂ SO ₄			
	Fe ₂ O ₃ /Cu	0.1 M KOH	$15.56 \ \mu g \ h^{-1} \ m g^{-1}_{cat.}$	24.4	14

	black phosphorus	0.1 M HCl	$31.37 \ \mu g \ h^{-1} \ m g^{-1}_{cat.}$	5.07	15
	nanosheets		(-0.6 V)	(-0.7 V)	15
	MoO ₂ with rich				
	oxygen	0.1 M HCl	$12.2 \ \mu g \ h^{-1} \ m g^{-1}_{cat.}$	8.2	16
	vacancies				
	VN nanowire		$2.48 \times 10^{-10} \text{ mol s}^{-1}$	2.59	17
	array	0.1 M HCI	cm^{-2}	3.58	17
	W/ NI	W ₂ N ₃ 0.1 M KOH	$11.66 \pm 0.98 \ \mu g \ h^{-1}$	11.67 ±	18
	W ₂ N ₃		$\mathrm{mg}^{-1}_{\mathrm{cat.}}$	0.93	
	Bi ₄ V ₂ O ₁₁ /CeO ₂	0.1 M HCl	23.21 µg h ⁻¹ mg ⁻¹ _{cat.}	10.16	19
	DEVO	0.2 M	0.2 M 8.6 μ g h ⁻¹ mg ⁻¹ _{cat.} Va ₂ SO ₄	10.04	20
	B1VO ₄	Na ₂ SO ₄			20
Nessler's reagent	MXene	0.5 M			
	$(Ti_3C_2T_x)$	Li ₂ SO ₄	4.72 μ g h ⁻¹ cm ⁻²	5.78	21
	nanosheets	(PH=2)			
N-doped porous	N-doped porous	0.05 M	23.8 μ g h ⁻¹ mg ⁻¹ _{cat.}	1.40	22
	carbon	H_2SO_4		1.42	22

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