Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2022

### **Supporting Information:**

### Laser Synthesis of Amorphous CoS<sub>x</sub> Nanospheres for Efficient Hydrogen Evolution and Nitrogen Reduction Reaction

Lili Zhao<sup>a#</sup>, Bin Chang<sup>a,d#</sup>, Tianjiao Dong<sup>a#</sup>, Haifeng Yuan<sup>a</sup>, Yue Li<sup>a</sup>, Zhenfei Tang<sup>a</sup>, Zhen Liu<sup>a</sup>, Hong Liu<sup>a,b</sup>, Xiaoli Zhang<sup>c</sup>, Weijia Zhou<sup>a\*</sup>

a Institute for Advanced Interdisciplinary Research (iAIR), School of Chemistry and Chemical Engineering, University of Jinan, Jinan, 250022, P. R. China

b State Key Laboratory of Crystal Materials, Shandong University, Jinan, 250100, P.

R. China

c School of Materials Science and Engineering, Zhengzhou University, Zhengzhou, 450001, P. R. China.

d State Key Laboratory of Photocatalysis on Energy and Environment, Fuzhou University, Fuzhou, 350116, P. R. China.

<sup>#</sup> These authors contributed equally to this work.

\* Corresponding author. E-mail: ifc\_zhouwj@ujn.edu.cn (W. Zhou)

#### **Experimental section**

#### Chemicals

All chemicals in this work were of analytical grade without further purification. Cobalt nitrate  $(Co(NO_3)_2 \cdot 6H_2O)$ , iron chloride hexahydrate  $(FeCl_3 \cdot 6H_2O)$ , 2aminoterephthalic acid (H<sub>2</sub>BDC-NH<sub>2</sub>), acetic acid, 2-Methylimidazole (C<sub>4</sub>H<sub>6</sub>N<sub>2</sub>), thioacetamide (CH<sub>3</sub>CSNH<sub>2</sub>), absolute ethanol (C<sub>2</sub>H<sub>5</sub>OH), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), sodium sulphate  $(Na_2SO_4),$ sodium hydroxide (NaOH), sodium citrate (Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O), sodium hypochlorite (NaClO), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) and 20 wt.% Pt/C were purchased from Sinopharm Chemical Reagents Beijing Co., Ltd. in China. Salicylic acid ( $C_7H_6O_3$ ), sodium nitroferricyanide ( $C_5FeN_6Na_2O$ ), copper (II) acetate monohydrate, L-glutamic acid and 1,3,5-benzenetricarboxylic acid were purchased from Aladdin Chemical Reagent Co., Ltd., Shanghai. The carbon fiber cloth (CC) was purchased from CeTech Co., Ltd., China. Mixed gases of argon and hydrogen sulfide (H<sub>2</sub>S-Ar, 10 vol% H<sub>2</sub>S) and nitrogen (N<sub>2</sub>) were obtained from Jinan Xuchao Gases CO., LTD.

# Synthesis of $CoS_x$ nanospheres anchored on carbon fiber cloths by laser under $H_2S$ atmosphere

Carbon fiber cloths (CC) were firstly cleaned in 1 M H<sub>2</sub>SO<sub>4</sub>, ethanol and distilled water by ultrasonic treatment for 15 min, respectively. Then the oxygen plasma (ZEPTO ONE, Diener electronic) was applied to convert the carbon fiber cloths from hydrophobic to superhydrophilic. The Co-MOF (ZIF-67) was grown on carbon fiber cloths (denoted as Co-MOF/CC) as reported previously<sup>20</sup>. Typically, 2-Methylimidazole (1.3 g) dissolved in 40 mL deionized water was poured into a 100 mL beaker containing 40 mL Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.58 g) solution and a CC (4 × 4 cm<sup>2</sup>), and then mixed together under continuous vigorous stirring for 10 min. The final purple solution and Co-MOF/CC were obtained by keeping this mixed solution at room temperature for 24 h without interrupt. Finally, the as-prepared Co-MOF/CC was washed with deionized water for three times and dried at 80 °C overnight.

A laser synthesis was adopted to prepare  $CoS_x$  nanospheres anchored on CC

(denoted as CoS<sub>x</sub>/CC-L) under H<sub>2</sub>S atmosphere. Firstly, the above obtained Co-MOF/CC was placed in the bottom of a sealed chamber with a light transmittable quartz window. In a typical laser process, the exposed H<sub>2</sub>S/Ar atmosphere was maintained during the laser-scribing process. The central wavelength, repetition rate and maximum (100%) power of the laser pulse were 1064 nm, 20 kHz and 20 W, respectively. Unless stated differently, the  $CoS_x/CC-L$  sample discussed in the main text was prepared with a laser power of 18 W. The scanning trajectory of the laser beam was programmable, and the scanning speed was 500 mm/s. In order to regulate the S vacancies and investigate the effect of S vacancies on the performance of asprepared CoS<sub>x</sub>, different laser powers (6 W, 12 W and 18 W) were utilized during laser synthesis, which were denoted as CoSx/CC-L-6W, CoSx/CC-L-12W and CoS<sub>x</sub>/CC-L-18W, respectively. For comparison, CoS<sub>2</sub>/CC synthesized by calcination of Co-MOF/CC under H<sub>2</sub>S atmosphere at 600 °C for 1h was prepared to confirm the preponderance of laser processing. For further study the influence of N-doping on the achieved HER and NRR activity of CoS<sub>x</sub>/CC-L, we prepared control samples by laser processing Co-MOF/CC under the mix gases of H<sub>2</sub>S and NH<sub>3</sub> with different ratio (10% NH<sub>3</sub>/H<sub>2</sub>S, 20% NH<sub>3</sub>/H<sub>2</sub>S and 50% NH<sub>3</sub>/H<sub>2</sub>S), to obtain the different N doped CoS<sub>x</sub>/CC-L (denoted as CoS<sub>x</sub>/CC-10% NH<sub>3</sub>-L, CoS<sub>x</sub>/CC-20% NH<sub>3</sub>-L and CoS<sub>x</sub>/CC-50% NH<sub>3</sub>-L). In addition, the carbon cloth processed by laser under NH<sub>3</sub> atmosphere to obtain the N doped carbon cloth (CC-NH<sub>3</sub>-L) were also prepared.

## Synthesis of CuS<sub>x</sub> and FeS<sub>x</sub> anchored on carbon fiber cloths by laser under H<sub>2</sub>S atmosphere

Carbon fiber cloths (CC) were also firstly treated as that in the synthesis of  $CoS_x/CC-L$ . Then the Cu-MOF was grown on carbon fiber cloths (denoted as Cu-MOF/CC) as reported<sup>1</sup>. Typically, 1 mmol of copper (II) acetate monohydrate and 0.5 mmol of L-glutamic acid were dissolved in 40 ml of deionized water. Afterwards, the carbon cloth was added and stirred at ambient condition for 20 min. After that, 0.67 mmol of 1,3,5-benzenetricarboxylic acid completely dissolved in 40 ml of ethanol was poured into the above solution under continuous stirring. The solution

immediately turned turbid. After stirring for 14 h at ambient condition, the green precipitate was collected by centrifugation and washed twice with ethanol. The product was dried at 70 °C for overnight. The Cu-MOF/CC was obtained.

The Fe-MOF was also grown on carbon fiber cloths (denoted as Fe-MOF/CC) as reported<sup>2</sup>. Typically, a reaction mixture containing 1 mmol of FeCl<sub>3</sub>·6H<sub>2</sub>O, 1.5 mmol of 2-aminoterephthalic acid (H<sub>2</sub>BDC-NH<sub>2</sub>), 35 mL of ethanol, 0.5 mL of acetic acid, and carbon cloth in a Teflon hydrothermal vessel, was placed in an oven at 130 °C for 7 h. The resulting Fe-MOF/CC was washed with ethanol and dried at 70 °C for later use.

Then the same laser synthesis process was adopted to prepare  $CuS_x/CC-L$  and  $FeS_x/CC-L$  under  $H_2S$  atmosphere with a laser power of 18W as for  $CoS_x/CC-L$ .

#### Characterization

The morphology and crystal structure were determined by the field emission scanning electron microscope (FESEM, HITACHI regulus 8100) and high resolution transmission electron microscopy (HRTEM, JEM-2100F instrument at an acceleration voltage of 200 kV). The crystalline phase of the prepared samples were detected by a D8 Advance (ThermoFisher, ARL Equinox 3000X) X-ray diffractometer (XRD) with Cu K $\alpha$  radiation ( $\lambda$ = 0.15406 nm). X-ray photoelectron spectra (XPS, Shimadzu, AXIS Ultra Supra) and Raman spectra (HORIBA LabRAM HR Evolution) measurements were recorded to characterize the elementary composition. Electron paramagnetic resonance (EPR) characterizations were carried out on a Bruker ESP-300 spectrometer. The Thermal Imaging Camera (Fotric 226) was used for detecting the temperature of the sealed chamber during the laser processing. X-ray absorption fine structure (XAFS) measurements at the Co K-edge in transmission mode for Co foil or fluorescence mode for samples were performed at Beijing Synchrotron Radiation Facility (beamline 1W1B station), China. Data reduction, data analysis, and EXAFS fitting were performed and analyzed with the Athena and Artemis programs of the Demeter data analysis packages<sup>21</sup> that utilizes the FEFF6 program<sup>22</sup> to fit the EXAFS data. The energy calibration of the sample was conducted through a standard Co foil, which as a reference was simultaneously measured. A linear function was subtracted from the pre-edge region, then the edge jump was normalized using Athena software. The  $\chi(k)$  data were isolated by subtracting a smooth, two-stage polynomial approximating the absorption background of an isolated atom. The k<sup>2</sup>-weighted  $\chi(k)$  data were Fourier transformed after applying a Hanning window function ( $\Delta k = 1.0$ ). For EXAFS modeling, the global amplitude EXAFS (*CN*, *R*,  $\sigma^2$  and  $\Delta E_0$ ) were obtained by nonlinear fitting of the EXAFS equation to the Fourier-transformed data in R-space. The Artemis software and least-squares refinement were used. In order to determine the coordination numbers (CNs) in the Co-S scattering path in sample, the EXAFS of the Co foil is fitted and the obtained amplitude reduction factor  $S_0^2$  value (0.718) was set in the EXAFS analysis.

#### **Electrochemical HER measurements**

Electrochemical measurements were performed on an electrochemical workstation (CHI 760C, CH Instruments Inc.) with a three-electrode configuration and 0.5 M H<sub>2</sub>SO<sub>4</sub> electrolyte, where the as-prepared CoS<sub>x</sub>/CC-L with the effective geometric area of 0.5 \* 0.5 cm<sup>2</sup>, carbon rod and Hg/Hg<sub>2</sub>Cl<sub>2</sub> electrode (SCE, saturated KCl) were used as the working electrode, reference and counter electrode, respectively. Before HER tests, the 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions were saturated with argon for 0.5 h to remove oxygen from the electrolyte. The HER potentials were converted to the reversible hydrogen electrode (RHE) potential using the equation given by  $E_{RHE} = E_{SCE} + 0.0591 \times pH + 0.242$ , resulting in a shift of +0.2597 V versus RHE (0.5 M H<sub>2</sub>SO<sub>4</sub>, pH~0.3).The polarization curves with a sweep rate of 5 mV/s were determined at the potential range from 0 to -0.5 V vs. RHE. Cyclic voltammetry (CV) curves at nonfaradaic potentials were measured to calculate the electrochemical double layer capacitance, which could be used for estimating the effective electrochemical double layer following:

 $C_{dl} = (j_a - j_c)/(2 \cdot v) = (j_a + |j_c|)/(2 \cdot v) = \Delta j/(2 \cdot v)$ 

in which ja and jc is the anodic and cathodic current density, respectively, recorded at

the middle of the select potential range, and v is the scan rate. The chronoamperometric i-t curves were detected at different overpotentials to characterize the catalytic stability of samples. Electrochemical impedance spectroscopy (EIS) was recorded by applying an ac potential amplitude of 10 mV within the frequency range of 100 kHz to 0.01 Hz. The fitting equivalent circuit was composed of the series resistance (Rs), charge transfer resistance (Rct) and a constant phase element (CPE): Rs–(Rct||CPE). The series resistance (Rs) obtained from EIS measurements in the high frequency zone was used to correct the polarization curves for the IR-drop. The amount of final hydrogen gas production was quantified by Gas chromatographic measurements (GC-7900, CEAULIGHT). The 20 wt.% Pt/C electrode as comparison was prepared by dropping the Pt/C inks onto the glassy carbon electrode with a catalyst loading of 0.42 mg cm<sup>-2</sup>.

#### **Electrochemical NRR measurements**

The electrocatalytic NRR tests were measured by using a two-compartment Htype like electrolytic cell, which was separated by a Nafion 117 membrane (DuPont). The Nafion membrane was pretreated by boiling it in  $H_2O_2$  (5%) at 80 °C for 1 h and deionized water for another 1 h, sequentially. The electrochemical experiments were conducted with an electrochemical workstation (CHI 1000C) by using a threeelectrode configuration (working electrode of as-synthesized materials, counter electrode of Pt plate, and reference electrode of Ag/AgCl/saturated KCl). The working electrode had the effective geometric area of  $0.5 * 0.5 \text{ cm}^2$ . Before NRR tests, the cathode electrolyte was purged with high purity nitrogen (99.999%, 40 mL min<sup>-1</sup>) for 0.5 h and then the flow rate was adjusted to 15 mL/min and maintained stable during the constant potential test for 2 h. The ammonia formation rate presented in the manuscript was the average data for the reaction of 2 h. The NRR potentials were converted to the reversible hydrogen electrode (RHE) potential using the equation given by  $E_{RHE}$  =  $E_{Ag/AgCl}$  + 0.0591  $\times$  pH + 0.194, resulting in a shift of +0.6077 V versus RHE (0.05 M Na<sub>2</sub>SO<sub>4</sub>, pH~7.1). Polarization curves were obtained using linear sweep voltammetry (LSV) with scan rate of 2 mV·s<sup>-1</sup> at 25 °C in 0.05 M Na<sub>2</sub>SO<sub>4</sub>

aqueous solution with constant  $N_2$  (g) or Ar (g) continually purging for 30 min prior to the measurements. The polarization curves were the steady-state ones after several cycles. The long-term stability test was carried out using chronoamperometry measurements.

Isotope labeling static experiments using  ${}^{15}N_2$  (from Anzete, Zibo) as feeding gas were conducted to clarify the source of ammonia. The reactor was previously encapsulated and degassed with argon for several times, and subsequently filled with  ${}^{15}N_2$ . After NRR process, the obtained  ${}^{15}NH_4^+$  electrolyte (0.1 mL, concentrated electrolyte) was thoroughly mixed with 0.5 mL dimethyl sulphoxide-D6 and 0.1 mL D<sub>2</sub>O for the 1H nuclear magnetic resonance (NMR) test on a Bruker Avance spectrometer (500 MHz). For comparison,  ${}^{14}N_2$  experiment was also operated in the same way.

#### **Determination of ammonia**

The concentration of produced ammonia was spectrophotometrically detected by the indophenol blue method same as previous reports<sup>23</sup>. In detail, 2 mL aliquot of the solution was removed from the post-electrolysis electrolyte after reaction. Then 2 mL NaOH solution (1 M) containing 5 wt% salicylic acid and 5 wt% sodium citrate was added, followed by 1 mL 0.05 M NaClO and 0.2 mL 1 wt% sodium nitroferricyanide (C<sub>5</sub>FeN<sub>6</sub>Na<sub>2</sub>O) solution. After 1 h, the absorption spectra of the mixed solution were measured with an ultraviolet-visible spectrophotometer. The concentration of NH<sub>3</sub> was determined by absorbance at a wavelength of ~675 nm (**Fig. S1a**). Absolute calibration was achieved using NH<sub>4</sub><sup>+</sup> of known concentration in 0.01 M HCl solutions as standards. The concentration of ammonia was determined by a standard curve (Absorbance =  $0.08677 \times C_{NH3} - 0.04769$ , R<sup>2</sup> = 0.994) (**Fig. S1b**).

The ammonia yield was calculated using the following equation:

$$Yield(NH_3) = \frac{c_{NH_3} \times V}{17 \times t \times A}$$

where  $c_{\text{NH3}}$  is the measured ammonia concentration (µg mL<sup>-1</sup>), V is the volume of the electrolyte solution (10 mL), t is the reaction time (2 h), A is the area of the working electrode (2 cm<sup>2</sup>). The Faradaic efficiency for NRR is defined as the quantity of

electric charge used for synthesizing ammonia. The production of  $NH_3$  molecule theoretically needs three electrons. The Faradaic efficiency (FE) was calculated by the following equation:

$$FE = \frac{3F \times c_{NH_3} \times V}{17 \times \int I dt} \times 100\%$$

Where F is Faraday constant (96485 C mol<sup>-1</sup>),  $c_{\text{NH3}}$  is the measured ammonia concentration (µg mL<sup>-1</sup>), V is the volume of the electrolyte solution (10 mL), I is the current (A), t is the reaction time (2 h). The "17" in the equations for the ammonia yield and faradaic efficiency refers to the NH<sub>3</sub> molar mass (17 g mol<sup>-1</sup>).



**Fig. S1**. Calibration of the indophenol blue method using a series of  $NH_4Cl$  standard solutions. (a) UV-vis absorbance curves of indophenol assays with  $NH_4^+$  ions, (b) calibration curve used for estimation of  $NH_3$  from the  $NH_4^+$  ion concentration.



Fig. S2. The good flexibility of as-prepared  $CoS_x/CC-L$ .



Fig. S3. The as-prepared  $CoS_x/CC-L$  with the large size of  $10 \times 10$  cm<sup>2</sup>.



**Fig. S4**. The photograph (a) and infrared thermal images (b) of laser synthesis equipment.



Fig. S5. The SEM image of Co-MOF/CC.



Fig. S6. (a) XRD pattern of Co-MOF/CC and CoS<sub>x</sub>/CC-L. (b) Energy dispersive-X-ray analysis of  $CoS_x/CC$ -L.



Fig. S7. The SEM image of holes on the surface of the carbon fiber for  $CoS_x/CC-L$ .



Fig. S8. EDS mapping of C element, Co element, S element, N element and O element for  $CoS_x/CC-L$ .



Fig. S9. High-resolution XPS spectra of the survey spectra (a), C 1s (b), N 1s (c) and O 1s (d) for Co-MOF/CC,  $CoS_x/CC-L$  and  $CoS_2/CC$ .



Fig. S10. XRD pattern of  $CoS_2/CC$ .



Fig. S11. SEM images of CoS<sub>2</sub>/CC.



Fig. S12. The SEM images of CC-L.



Fig. S13. Polarization curves of CC-NH<sub>3</sub>-L,  $CoS_x/CC-L$ ,  $CoS_x/CC-10\%$  NH<sub>3</sub>-L,  $CoS_x/CC-20\%$  NH<sub>3</sub>-L and  $CoS_x/CC-50\%$  NH<sub>3</sub>-L in 0.5 M H<sub>2</sub>SO<sub>4</sub> without iR-compensation.



Fig. S14. HER polarization curves for  $CoS_x/CC-L-6W$ ,  $CoS_x/CC-L-12W$  and  $CoS_x/CC-L-18W$  without iR-compensation.



Fig. S15. Nyquist plots of  $CoS_x/CC-L$  with different overpotentials.

Nyquist plots of  $CoS_x/CC-L$  with different overpotentials were shown in **Fig. S15.** The charge transfer resistance (Rct) is related to the electrocatalytic kinetics and its lower value corresponds to the faster reaction rate, which can be obtained from the semicircle in the low frequency zone. Rct value of  $CoS_x/CC-L$  was found to decrease significantly with increasing overpotentials, from ~45  $\Omega$  at 100 mV to ~15  $\Omega$  at 200 mV. The results signified the quick electron transfer and the advantageous HER kinetics towards the electrolyte interface for  $\text{CoS}_x/\text{CC-L}$ .



Fig. S16. Cyclic voltammograms of  $CoS_x/CC-L$  (a),  $CoS_2/CC$  (b) and CC-L (c) within no faradaic reactions ranges.



Fig. S17. TEM (a) and HRTEM (b) images of  $CoS_x/CC-L$  after HER measurements.



Fig. S18. Electrocatalytic NRR performances with  $NH_3$  yield (a) and Faradaic efficiency (b) for samples synthesized with different laser powers at different potentials.

As shown in **Fig. S18**, the NH<sub>3</sub> yield and Faradaic efficiency were increased linearly from  $CoS_x/CC-L-6W$  to  $CoS_x/CC-L-18W$ . At the optimal polarization potential of -0.2 V vs. RHE, the highest electrocatalytic NRR activity of  $CoS_x/CC-L-18W$  was obtained with the NH<sub>3</sub> yield and the corresponding Faradaic efficiency as high as ~12.2 µg h<sup>-1</sup> mg<sup>-1</sup><sub>cat.</sub> and 10.1%, respectively, which were much higher than those of the  $CoS_x/CC-L-6W$  (~3.8 µg h<sup>-1</sup> mg<sup>-1</sup><sub>cat.</sub> and 2.5%) and  $CoS_x/CC-L-12W$  (~7.1 µg h<sup>-1</sup> mg<sup>-1</sup><sub>cat.</sub> and 5.1%). This may be associated with the increasing amount of S vacancies with the applied laser power, providing more adsorption sites for N<sub>2</sub>. As the electron-rich sites, S vacancies led to the effective N<sub>2</sub> activation.



Fig. S19. Corresponding i-t curves at different potentials for CoS<sub>x</sub>/CC-L.



Fig. S20. UV-vis absorption spectra of the resultant electrolytes at different potentials for  $CoS_x/CC-L$ .



Fig. S21. The <sup>1</sup>H NMR spectra of commercial <sup>15</sup>NH<sub>4</sub>Cl samples (a, b) were collected as standard spectra and the internal standard method as well as <sup>1</sup>H NMR spectra using  $^{15}N_2$  as the feeding gas with different reactive time (c, d) were utilized to verify the authenticity of the data.



**Fig. S22.** Corresponding UV-vis absorption spectra of the resultant electrolytes at different potentials and corresponding i-t curves at different potentials for CC-L (a, b), Co-MOF/CC (c, d),  $CoS_2/CC$  (e, f).



Fig. S23. Electrocatalytic NRR performances of NH<sub>3</sub> yield for  $CoS_x/CC-L$ ,  $CoS_x/CC-10\%$  NH<sub>3</sub>-L,  $CoS_x/CC-20\%$  NH<sub>3</sub>-L and  $CoS_x/CC-50\%$  NH<sub>3</sub>-L in 0.05 M Na<sub>2</sub>SO<sub>4</sub>.



Fig. S24. Electrocatalytic NRR performances of  $NH_3$  yield for  $FeS_x/CC-L$ ,  $CuS_x/CC-L$  and  $CoS_x/CC-L$  samples.



Fig. S25. SEM images of  $CoS_x/CC-L$  after i-t testing for NRR.

Table	<b>S1</b> .	EXAFS	fitting	parameters	at	the	Co	K-edge	for	various
sample	$s (S_0^2)$	=0.718)								

Sample	Shell	CNa	$R(\text{\AA})^b$	$\sigma^2({ m \AA}^2)^c$	$\Delta E_0(\mathrm{eV})^d$	R factor
Co foil	Co-Co	12*	$2.49{\pm}0.01$	$0.0062 \pm 0.0003$	7.1	0.0021
CoS <sub>2</sub> /CC	Co-S	$6.0 \pm 0.2$	$2.31 \pm 0.01$	$0.0050 \pm 0.0009$	2.9	0.0058
CoS <sub>x</sub> /CC-L	Co-S	$5.8 \pm 0.4$	$2.30{\pm}0.01$	$0.0065{\pm}\ 0.0009$	2.4	0.0039

<sup>*a*</sup>*CN*, coordination number; <sup>*b*</sup>*R*, distance between absorber and backscatter atoms; <sup>*c*</sup> $\sigma^2$ , Debye-Waller factor to account for both thermal and structural disorders; <sup>*d*</sup> $\Delta E_0$ , inner potential correction; *R* factor indicates the goodness of the fit. *S*0<sup>2</sup> was fixed to 0.718, according to the experimental EXAFS fit of Co foil by fixing CN as the known crystallographic value. Fitting range:  $3.0 \le k$  (/Å)  $\le 12.5$  and  $1.0 \le R$  (Å)  $\le 3.0$  (Co foil);  $3.0 \le k$  (/Å)  $\le 12.4$  and  $1.0 \le R$  (Å)  $\le 2.5$  (CoS2);  $3.0 \le k$  (/Å)  $\le 12.4$  and  $1.0 \le R$  (Å)  $\le 2.5$  (CoS2);  $3.0 \le k$  (/Å)  $\le 12.4$  and  $1.0 \le R$  (Å)  $\le 2.5$  (Co2 and Co3). A reasonable range of EXAFS fitting parameters:  $0.700 < S_0^2 < 1.000$ ; CN > 0;  $\sigma^2 > 0$  Å<sup>2</sup>;  $\Delta E_0 < 10$  eV; R factor < 0.02.

**Table S2**. Comparison of the electrocatalytic performance of  $CoS_x/CC-L$  with Cobalt sulfide-based electrocatalysts reported for HER in acidic electrolyte.

Catalyst	Electrolyte	Current	Overpotential	Reference	
	solution	density	at the		
		(j)	corresponding		
			j		
CoS <sub>x</sub> /CC-L	0.5M	-10	87 mV	This work	
	$H_2SO_4$	mA/cm <sup>2</sup>			
CoS <sub>2</sub> /RGO-CNT	0.5M	-10	142 mV	Angew. Chem. Int.	
	$H_2SO_4$	mA/cm <sup>2</sup>		Ea. 2014, 53, 12594 -12599	
$CoS_2 NW$	0.5M	-10	145 mV	J. Am. Chem. Soc.	
	$H_2SO_4$	mA/cm <sup>2</sup>		2014, 136, 10053–10061.	
$Co_{0.9}S_{0.58}P_{0.42}$	0.5M	-10	139 mV	ACS Nano <b>2017</b> , 11,	
	$H_2SO_4$	mA/cm <sup>2</sup>		11031-11040	
surface selenized	0.5M	-10	110 mV	ACS Catal. <b>2019</b> , 9,	
meso-CoS <sub>2</sub>	$H_2SO_4$	mA/cm <sup>2</sup>		456-465	
$Co_9S_8@MoS_x$	0.5M	-10	98 mV	Nano Energy <b>2017</b> ,	
	$H_2SO_4$	mA/cm <sup>2</sup>		32, 4/0-4/8.	
Co <sub>9</sub> S <sub>8</sub> -NDCL	0.5M	-10	96 mV	ACS Appl. Nano	
	$H_2SO_4$	mA/cm <sup>2</sup>		Mater. 2021, 4, 1776–1785	
Mo <sub>2</sub> N/CoS <sub>2</sub>	0.5M	-10	85 mV	ACS Appl. Mater.	
	$H_2SO_4$	mA/cm <sup>2</sup>		Interfaces 2021, 13, 41573–41583	
$Zn_{0.30}Co_{2.70}S_4$	0.5M	-10	80 mV	J. Am. Chem. Soc.	
	$H_2SO_4$	mA/cm <sup>2</sup>		2 <b>016</b> , 138, 1359–1365	

MCNTs@CoS <sub>x</sub> @MoS	0.5M	-10	196 mV	Chemical
2	$H_2SO_4$	mA/cm <sup>2</sup>		Engineering Journal 417 (2021) 129270
$1T-MoS_2/CoS_2$	0.5M	-10	26 mV	Small 2020, 16,
	$H_2SO_4$	mA/cm <sup>2</sup>		2002850.
$MoS_2/CoS_2$	0.5M	-10	90 mV	J. Mater. Chem. A,
	$H_2SO_4$	mA/cm <sup>2</sup>		2019, 7, 13339– 13346
$CoS_x$	0.5M	-10	42 mV	Energy Environ. Sci.,
	$H_2SO_4$	mA/cm <sup>2</sup>		2018, 11, 246/-24/5
NiS-CoS	0.5M	-10	85 mV	Electrochimica Acta
	$H_2SO_4$	mA/cm <sup>2</sup>		260 (2018) 82-91.
$CoS_2$	0.5M	-10	53 mV	Electrochimica Acta
	$H_2SO_4$	mA/cm <sup>2</sup>		259 (2018) 955-961.
$CoS_x@MoS_2$	0.5M	-10	239 mV	ACS Sustainable
	$H_2SO_4$	mA/cm <sup>2</sup>		Chem. Eng. 2018, 6, 12961–12968.
CoSP	0.5M	-10	58 mV	ACS Sustainable
	$H_2SO_4$	mA/cm <sup>2</sup>		Chem. Eng. 2018, 6, 15618–15623.
$CoS_2$	0.5M	-10	43 mV	ACS Energy Lett.
	$H_2SO_4$	mA/cm <sup>2</sup>		2018, 3, 779–786.
$CoS_2/GF$	0.5M	-20	144 mV	Phys. Chem. Chem.
	$H_2SO_4$	mA/cm <sup>2</sup>		Phys., 2017, 19, 4821 - 4826.
$Co_3O_4$ $@CoS_2$	0.5M	-10	152 mV	Journal of Power
	$H_2SO_4$	mA/cm <sup>2</sup>		<i>Sources</i> 356 (2017) 89-96.
$CoS_2/CoSe_2$	0.5M	-10	80 mV	J. Mater. Chem. A,
	$H_2SO_4$	mA/cm <sup>2</sup>		2017, 5, 2504–2507.
(NSCDs)/CoS	0.5M	-10	165 mV	J. Mater. Chem. A,
	$H_2SO_4$	mA/cm <sup>2</sup>		2017, 5, 2717 - 2723.
CoS <sub>2</sub> NP/Al <sub>2</sub> O <sub>3</sub> NSs	0.5M	-10	53 mV	J. Mater. Chem. A,
	$H_2SO_4$	mA/cm <sup>2</sup>		2017, 5, 2861 - 2869.
Fe-NiS <sub>2</sub>	0.5M	-10	121 mV	J. Mater. Chem. A, 2017, 5, 10173 -

	$\mathrm{H}_2\mathrm{SO}_4$	mA/cm <sup>2</sup>		10181.
CoS <sub>2</sub> /RGO	0.5M	-10	180 mV	International Journal
	$\mathrm{H}_2\mathrm{SO}_4$	mA/cm <sup>2</sup>		of Hydrogen Energy 42 (2017) 6665-6673.
CoS/CC	0.5M	-10	212 mV	International Journal
	$\mathrm{H}_2\mathrm{SO}_4$	mA/cm <sup>2</sup>		of Hydrogen Energy 42 (2017) 9914-9921.
$CoS_2/MoS_2$	0.5M	-10	154 mV	International Journal
	$H_2SO_4$	mA/cm <sup>2</sup>		of Hydrogen Energy 42 (2017) 12246- 12253.
CoS2@MoS2/RGO	0.5M	-10	98 mV	Adv. Funct. Mater.
	$\mathrm{H}_2\mathrm{SO}_4$	mA/cm <sup>2</sup>		2017, 1602699.
CoNi <sub>2</sub> S <sub>4</sub> /WS <sub>2</sub> /Co <sub>9</sub> S <sub>8</sub>	0.5M	-10	61 mV	Applied Catalysis B:
	$\mathrm{H}_2\mathrm{SO}_4$	mA/cm <sup>2</sup>		(2021) 120455.
$Co_9S_8$ - $MoS_2$	0.5M	-10	> 200  mV	Adv. Funct. Mater.
	$\mathrm{H}_2\mathrm{SO}_4$	mA/cm <sup>2</sup>		2020, 30, 2002536.
MoS <sub>2</sub> /Co <sub>9</sub> S <sub>8</sub> /Ni <sub>3</sub> S <sub>2</sub> /Ni	0.5M	-10	103 mV	J. Am. Chem. Soc.
	$H_2SO_4$	mA/cm <sup>2</sup>		10417 <i>-</i> 10430.
Co <sub>9</sub> S <sub>8</sub> /Ni <sub>3</sub> S <sub>2</sub>	0.5M	-10	124 mV	NATURE
	$\mathrm{H}_2\mathrm{SO}_4$	mA/cm <sup>2</sup>		<i>COMMUNICATION</i> <i>S</i>   (2018) 9:3132.
Fe-Co <sub>9</sub> S <sub>8</sub> NSs/CC	0.5M	-10	65 mV	Electrochimica Acta
	$\mathrm{H}_2\mathrm{SO}_4$	mA/cm <sup>2</sup>		264 (2018) 157-165.
$Co_9S_8/MoS_2$	0.5M	-10	97 mV	Adv. Mater. 2018, 30,
	$\mathrm{H}_2\mathrm{SO}_4$	mA/cm <sup>2</sup>		1707301.
$Co_9S_8/NC@MoS_2$	0.5M	-10	117 mV	ACS Appl. Mater. Interfaces 2017, 9,
	$H_2SO_4$	mA/cm <sup>2</sup>		28394 - 28405.
$Co_3S_4@MoS_2$	0.5M	-10	210 mV	Chem. Mater. 2017,
5 7 2	$H_2SO_4$	mA/cm <sup>2</sup>		29, 5566 –5573.

Table S3. Comparison of the neutral NRR performance of  $\text{CoS}_x/\text{CC-L}$  with the other

reported electrocatalysts	rocatalysts.
---------------------------	--------------

Catalyst	Electrolyte NH <sub>3</sub> yield		Faradaic	Reference
	solution	$(\mu g h^{-1} cm^{-2}_{cat.})$	efficiency (%	
			)	
CoS <sub>x</sub> /CC-L	0.05M Na <sub>2</sub> SO <sub>4</sub>	12.2 (-0.2 V)	10.1 (-0.2 V)	This work
CoVP@NiFeV-	0.1M Na <sub>2</sub> SO <sub>4</sub>	27.2 (-	1.17 (-0.5 V)	Appl. Catal. B:
LDHs		0.3V)		Environ., <b>2020</b> , 265, 118559
NiO@TiO <sub>2</sub>	0.05M Na <sub>2</sub> SO <sub>4</sub>	10.75 (-	9.83 (-0.4 V)	J. Mater. Chem. A,
		0.4V)		<b>2022</b> , 10, 2800-2806
CoS <sub>2</sub> -CeO <sub>2</sub> /Ti	0.1M Na <sub>2</sub> SO <sub>4</sub>	22.37 (-	2.52 (-0.5 V)	ACS Sustainable
		0.5V)		Chem. Eng. 2021, 9, 13399
VNiON	0.05M Na <sub>2</sub> SO <sub>4</sub>	6.78 (-	5.57 (-0.2 V)	J. Mater. Chem. A,
		0.4V)		<b>2020</b> , 8, 91
Mo-	0.1M Na <sub>2</sub> SO <sub>4</sub>	16.1 (-0.25 V)	7.1 (-0.25 V)	Adv. Mater. 2020,
Mo <sub>2</sub> C@NCNTs				20021//
MXene/TiFeO <sub>x</sub>	0.1M Na <sub>2</sub> SO <sub>4</sub>	2.19 (-0.2 V)	25.4 (-0.2 V)	ACS Nano <b>2020</b> , 14, 7, 9089–9097
Zr-doped TiO <sub>2</sub>	0.1M Na <sub>2</sub> SO <sub>4</sub>	8.9 (-	17.3 (-0.45 V)	Nature Commun,
		0.45V)		<b>2019</b> ,10, 28/7
$V_2O_3/C$	0.1M Na <sub>2</sub> SO <sub>4</sub>	12.3 (-	7.28 (-0.6 V)	Inorg. Chem. Front.
		0.6V)		<b>2019</b> , 0, 391
TiO <sub>2</sub> /Ti	0.1M Na <sub>2</sub> SO <sub>4</sub>	5.6 (-0.7V)	2.50 (-0.7 V)	ACS Appl. Mater.
				Interfaces <b>2018</b> , 10, 28251
MoS <sub>2</sub> /CC	0.1M Na <sub>2</sub> SO <sub>4</sub>	4.94 (-	1.17 (-0.5 V)	<i>Adv. Mater.</i> 2018,
		0.5V)		30, 1800191
Y <sub>2</sub> O <sub>3</sub> nanosheet	0.1M Na <sub>2</sub> SO <sub>4</sub>	6.49 (-	2.53 (-0.9 V)	Ind. Eng. Chem. Res.
		0.9V)		2018, 57, 16622
SnO <sub>2</sub> /CC	0.1M Na <sub>2</sub> SO <sub>4</sub>	9.0 (-0.8V)	2.17 (-0.7 V)	Chem. Commun. <b>2018,</b> 54, 12966

## Reference

[1] Hao Bin Wu, Bao Yu Xia, Le Yu, Xin-Yao Yu & Xiong Wen (David) Lou, *Nat. Commun.* 2015, 6, 6512.

[2] Duraisamy Senthil Raja, Hao-Wei Lin, Shih-Yuan Lu, Nano Energy 57 (2019) 1–
13.