Supporting Information for

## Boosting Oxygen Reaction Activity by Coupled Sulfides for High-Performance Rechargeable Metal-Air Battery

## **Experimental Section**

*Chemicals*. NiCl<sub>2</sub>·6H<sub>2</sub>O and FeCl<sub>3</sub>·9H<sub>2</sub>O were purchased from Sinopharm Chemical Reagent Co, Ltd. (SCRC). Graphite powder, sulfur powder, NaOH, Na<sub>2</sub>CO<sub>3</sub>, Pt/C-20 wt.% and Ir/C-20 wt.% were purchased from Beijing Chemical Reagents Company. 18 M $\Omega$  deionized water was used to prepare all aqueous solutions. All reagents were of analytical grade and were used without further purification.

*Characterizations:* The morphologies of the as-prepared samples were characterized by transmission electron microscope (TEM; FEI Tecnai G<sup>2</sup> 20), high-resolution TEM (HRTEM) (JEOL JEM-2100) and scanning electron microscope (SEM; Zeiss SUPRA 55). X-ray diffraction (XRD) patterns were collected on a Shimadzu XRD-6000 with Cu K $\alpha$  radiation (40 kV, 30 mA,  $\lambda$  = 1.5418Å), recorded with 20 in the range from 5° to 90°. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a PHI Quantera II XPS Scanning Microprobe. N<sub>2</sub> adsorption-desorption isotherms were examined by a micromeritics ASAP 2460. Raman spectra were recorded on a Lab RAM ARAMIS Raman Spectrometer (HORIBA JobinYvon) and a 514 nm laser was applied as an excitation source. UV visible absorption spectrum (UV-vis) was recorded on a UV-vis 2450 Spectrometer, Shimadzu. Electron paramagnetic resonance (EPR) measurement was conducted on ELEXSYS-II, Bruker. The ICP emission spectrum was conducted on a Perkin Elmer Optima 7300DV ICP emission spectroscope.

*Preparation of GO, NiFe-LDH/GO and NiFeS2/S-GO composite.* GO was prepared from graphite powder according to a reported method.<sup>11</sup> NiFe-LDH/GO was prepared by a co-precipitation process described below. Firstly, 3 mmol of NiCl<sub>2</sub>·6H<sub>2</sub>O and 1 mmol of FeCl<sub>3</sub>·9H<sub>2</sub>O were dissolved in 40 ml of deionized water to form a homogeneous solution (solution A). Meanwhile, 6 mmol of NaOH and 2 mmol of Na<sub>2</sub>CO<sub>3</sub> were dissolved in 40 ml of deionized water to form solution B. GO was dispersed in water with a concentration of 2 mg/ml, denoted as solution C. Subsequently, solution A and B were added dropwisely to solution C until pH of the final solution was adjusted to 8.5. After stirred for another 24 h, the dark-brown precipitants were formed and collected by centrifugation, and then washed three times by deionized water and ethanol. Finally, the cleaned samples were dried in an oven at 60 °C for 12 h.

To prepare NiFeS<sub>2</sub>/S-GO, NiFe-LDH/GO precursor and 500 mg sulfur powder were put in a porcelain boat. Following, the sample was heated at 300 °C for 1 h in Ar at a heating rate of 5 °C/min.

*Electrochemical measurements*. The OER and ORR electrocatalytic performance were studied with a three-electrode system in 1.0 M aqueous KOH solution using a PINE electrochemical workstation. A saturated calomel electrode (SCE) and a platinum plate were used as the reference and the counter electrode, respectively. To prepare the working electrode, 5 mg of the as-prepared catalyst and 10  $\mu$ L of Nafion solution were dispersed in ethanol (1 mL) under ultrasonication for at least 1 h to form a homogeneous catalyst ink. Afterwards, 7  $\mu$ L of catalyst ink was loaded on a glassy carbon electrode (5 mm in diameter). The electrochemical performance was studied on a rotating disk electrode at a rotating speed of 1600 r/min. After twenty cyclic voltammetric (CV) scans, the polarization data were collected using linear sweep voltammetry (LSV) at a scan rate of 5 mV/s. The durability of the electrode was studied by chronoamperometry and CV method, respectively. For chronoamperometry method, a constant potential was applied to achieve an initial current density of 50 mA/cm<sup>2</sup> for each catalyst. For CV method, the catalyst was characterized by CV for 200 cycles at a scan rate at 1 mV/s.

*Laviron equation.*  $\text{Ec} = \text{E}_{1/2} - (\text{RT}/\alpha nF) \times \ln (\alpha nF/\text{RTk}_s) - (\text{RT}/\alpha nF) \times \ln (v)$ , where Ec is the reduction potential of metal redox,  $\text{E}_{1/2}$  is the formal potential of metal redox, R is the universal gas constant, T is the temperature in Kelvin, n is the number of electrons transferred,  $\alpha$  is the transfer coefficient, k<sub>s</sub> is the rate constant of metal redox, and v is the scan rate in the CV measurement.



Figure S1 XRD pattern of NiFe-LDH.



**Figure S2** Mott-Schottky plots of NiFe-LDH/GO and NiFeS<sub>2</sub>/S-GO on glassy carbon electrode at a frequency of 1000 Hz.



Figure S3 SEM and HRTEM image of NiFe-LDH/GO.



**Figure S4** EDS mapping of NiFeS<sub>2</sub>/S-GO, showing uniform distribution of Ni, Fe, C, O and S.



**Figure S5** Nitrogen adsorption/desorption isotherms for NiFeS<sub>2</sub>/S-GO and physically mixed NiFeS<sub>2</sub> and S-GO.



Figure S6 A: Survey XPS spectrum. B & C: C 1s and S 2p spectrum of NiFeS<sub>2</sub>/S-GO.



**Figure S7** CV curves of (A) NiFe-LDH/GO and (B) NiFeS<sub>2</sub>/S-GO collected at different scan rates. (The catalysts ink was prepared without adding active carbon, which may lead to the poor conductivity of catalysts)



**Figure S8** Electron paramagnetic resonance spectra of NiFe-LDH/GO and NiFeS<sub>2</sub>/S-GO.



**Figure S9** Polarization curves (iR-corrected) of NiFe-LDH/GO, NiFeS<sub>2</sub>/S-GO NiFeS<sub>2</sub>+S-GO (mixture of NiFeS<sub>2</sub> and S-GO). Ir/C-20 wt.% and Pt/C-20 wt.% were set as references.



**Figure S10** Determination of electrochemically active surface area for (A) NiFe-LDH/GO, (B) NiFeS<sub>2</sub>+S-GO and (C) NiFeS<sub>2</sub>/S-GO.



**Figure S11** Polarization curves (ECSA&iR-corrected) of NiFe-LDH/GO, NiFeS<sub>2</sub>/S-GO NiFeS<sub>2</sub>+S-GO (mixture of NiFeS<sub>2</sub> and S-GO). Ir/C-20 wt.% and Pt/C-20 wt.% were set as references.



Figure S12 Electrochemical stability of NiFeS<sub>2</sub>/S-GO by CV method.



Figure S13 (a) OER (b) ORR electrochemical stability of  $NiFeS_2/S-GO$  by chronoamperometry method.



Figure S14 SEM image of NiFeS<sub>2</sub>/S-GO after stability test, the scale bar is 200 nm.



**Figure S15** Electronic structure of (A) Fe and (B) Ni in NiFeS<sub>2</sub>/S-GO before and after stability test, NiCl<sub>2</sub> and FeCl<sub>3</sub> were set as references.



**Figure S16** Voltage efficiency of a Zn-air battery adopting NiFeS<sub>2</sub>/S-GO as the cathode at 10 mA/cm<sup>2</sup>.

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Catalyst	Eorr/V (-3 mA cm <sup>-2</sup> )	EOER/V (10 mA cm-2)	ΔE/V (Eoer- Eorr)	Ref.
Co/N-C-800	0.74	1.599	0.859	22
MnOx	0.73	1.77	1.04	23
NiFe-LDH /Fe-N-C	0.728	1.512	0.786	24
NBSCF/N-rGO	0.869	1.635	0.766	25
NixCoyO4/Co–NG	0.796	1.629	0.833	26
NiCo <sub>2</sub> O <sub>4</sub>	0.78	1.62	0.84	27
Co-N/C 800	0.78	1.74	0.96	28
LDO/CNTs	0.64	1.64	0.99	29
NiFe-LDH/GO	0.42	1.60	1.18	This work
NiFeS <sub>2</sub> /S-GO	0.75	1.48	0.73	This work

Table S1 Comparison of bifunctional performance.

## Table S2 Comparison of Zn-air batteries performances.

Sample	Working current density (mA/cm <sup>2</sup> )	Working period (h)	Initial charging/discharging plateau (V)	Final charging/discharg plateau (V)	Ref.
(N, P)-doped	10	133	0.82	0.87	1
CoS2@TiO2					
rGO/CB2/	10	124	0.86	1.15	2
Co-Bi					
FeNx/C-700-	5	84	1.0	1.02	3
20					
NiFe@NBCNT	10	120	0.6	0.8	4
B,N-carbon	5	33	0.74	0.80	5
Fe0.33-	20	200	0.74	0.68	6
CoP/NF					
NiFeS <sub>2</sub> /S-GO	10	60	0.78	0.81	This work
NiFeS <sub>2</sub> /S-GO	50	30	1.12	1.17	This work

## Reference

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