

## Design of polymetallic sulfide NiS<sub>2</sub>@Co<sub>4</sub>S<sub>3</sub>@FeS as bifunctional catalyst for high efficiency seawater splitting

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### Materials and chemicals

Nickel nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, analytical grade, 99.0%), ammonia fluoride (NH<sub>4</sub>F, analytical grade, 96.0%), cobalt nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, analytical grade, 98.5%) were purchased from Tianjin Damao Chemical Reagent Factory. Urea (CH<sub>4</sub>N<sub>2</sub>O, analytical grade, 99.0%), Ferric chloride hexahydrate (FeCl<sub>3</sub>·6H<sub>2</sub>O, analytical grade, 99.0%) were obtained from Sinopharm Chemical Reagent Co., Ltd. Sublimed sulfur (S, analytical grade) from Tianjin Fengchuan Chemical Reagent Technology Co., LTD. Nickel foam (NF) (200\*300\* 0.5mm) was purchased from Kunshan Guangjiayu New Material Co., LTD.

### Electrochemical measurements

All electrochemical tests in this work were carried out by Shanghai Chenhua CHI760E electrochemical workstation. In order to ensure the accuracy of the working electrode potential in the measurement process, the OER performance test was carried out using a standard three-electrode system. Among them, the prepared sample was used as the working electrode, the counter electrode was graphite rod, the reference electrode was Hg/HgO electrode, and the electrolyte solution was seawater solution including 1M KOH. Prior to the electrochemical test, several cyclic voltammetry (CV) scans (0.2~1.0 V vs. Hg/HgO) were used to remove the bubbles covering the catalyst. Linear sweep voltammetry (LSV) records were performed from 0.2 to 1.0 V vs. Hg/HgO at a scan rate of 5 mV s<sup>-1</sup>. Electrochemical impedance spectroscopy (EIS) was performed at 1.676V vs. RHE with a frequency range of 10<sup>6</sup> to 0.01 Hz. Equation:  $\eta = E_{\text{RHE}} - 1.23\text{V}$  was used to calculate the overpotential ( $\eta$ ) of the working electrode, and Tafel equation:  $\eta = b \log j + a$  was adapted to work out Tafel slopes,  $\eta$  is overpotential,  $j$  represents the current density,  $b$  is the Tafel slope. The electrochemical active surface area (ECSA =  $C_{\text{dl}}/C_s$ ) was evaluated by

measuring the dual-layer capacitance ( $C_{dl}$ ) of CV at different sweep rates.  $C_S$  represents the specific capacitance of 1.0 M KOH (0.04 mF/cm<sup>2</sup>).  $C_{dl}$ , which is positively correlated with ECSA, is evaluated by  $C_{dl} = jc/V$ , where  $jc$  stands for current density and  $V$  is the voltage measured by CV. All data were compensated with 70% iR. The stability of the catalyst was tested by continuous LSV and CV scanning.

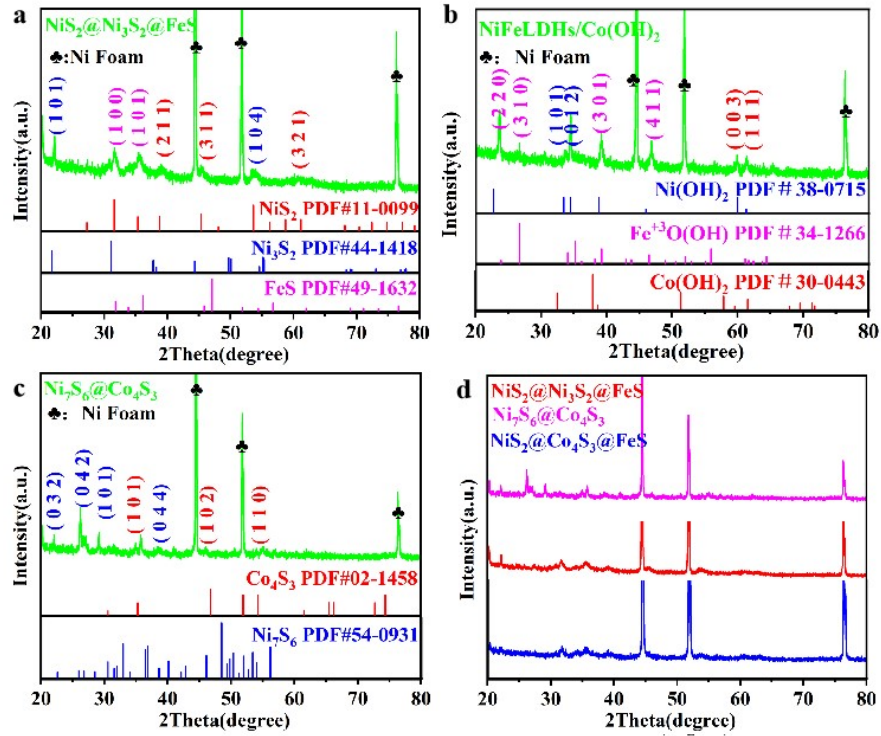
**DFT computation details:**

The DFT calculations were performed using the Cambridge Sequential Total Energy Package (CASTEP) with the plane-wave pseudo-potential method. The geometrical structures of the (100) and (111) plane of FeS and NiS<sub>2</sub> was optimized by the generalized gradient approximation (GGA) methods. The Revised Perdew-Burke-Ernzerh of (RPBE) functional was used to treat the electron exchange correlation interactions. A Monkhorst Pack grid k-points of 5\*5\*1 and 5\*6\*1 of FeS and NiS<sub>2</sub>, a plane-wave basis set cut-off energy of 400 eV were used for integration of the Brillouin zone. The structures were optimized for energy and force convergence set at 0.05 eV/Å and 2.0×10<sup>-5</sup> eV, respectively. The Gibbs free energy of H adsorption was calculated as follows:

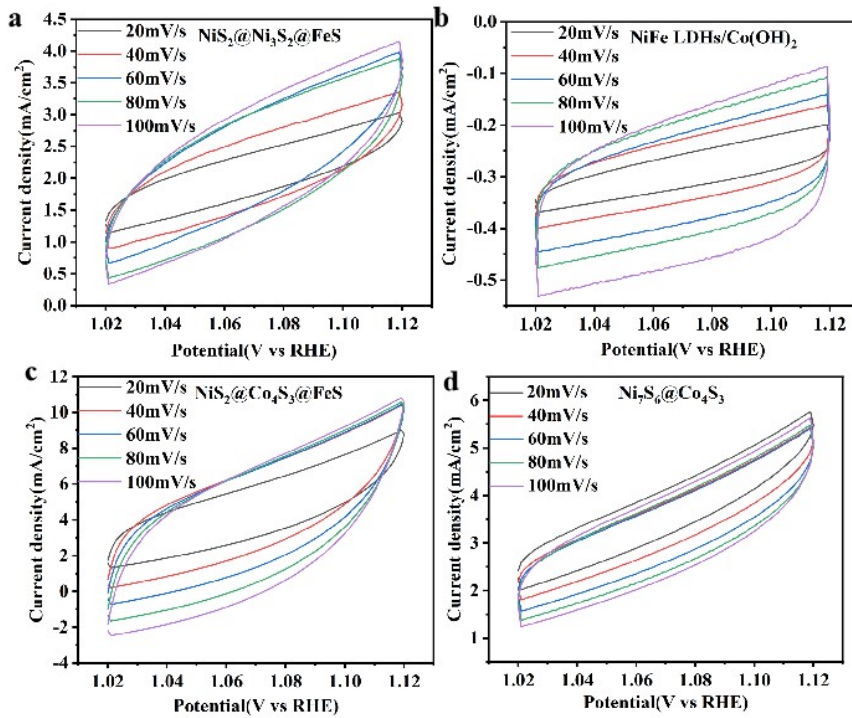
$$\Delta G_{H^*} = \Delta E_{H^*} + \Delta ZPE - T\Delta S$$

Where  $\Delta ZPE$  is the zero-point energy and  $T\Delta S$  stands for the entropy corrections. According to the previous report by Norskov et al., we used the 0.24 eV for the  $\Delta ZPE - T\Delta S$  of hydrogen adsorption in this work.

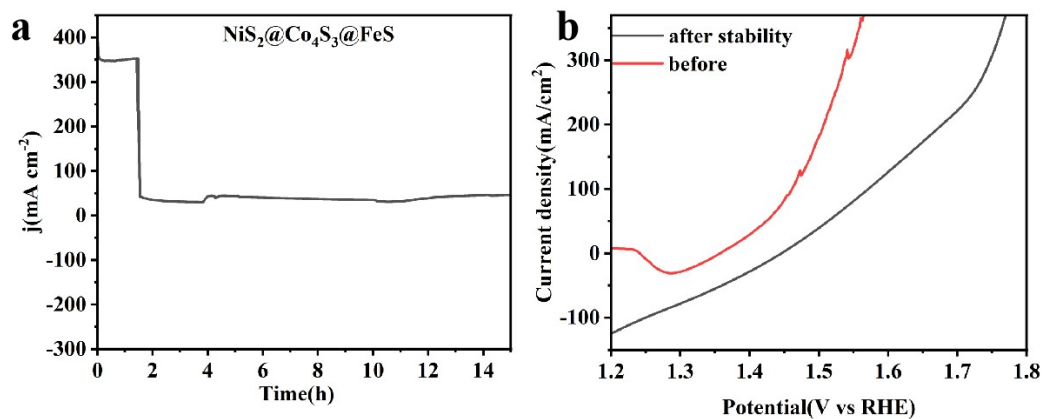
Res: J. Electrochem. Soc., **2005**, 152, J23.



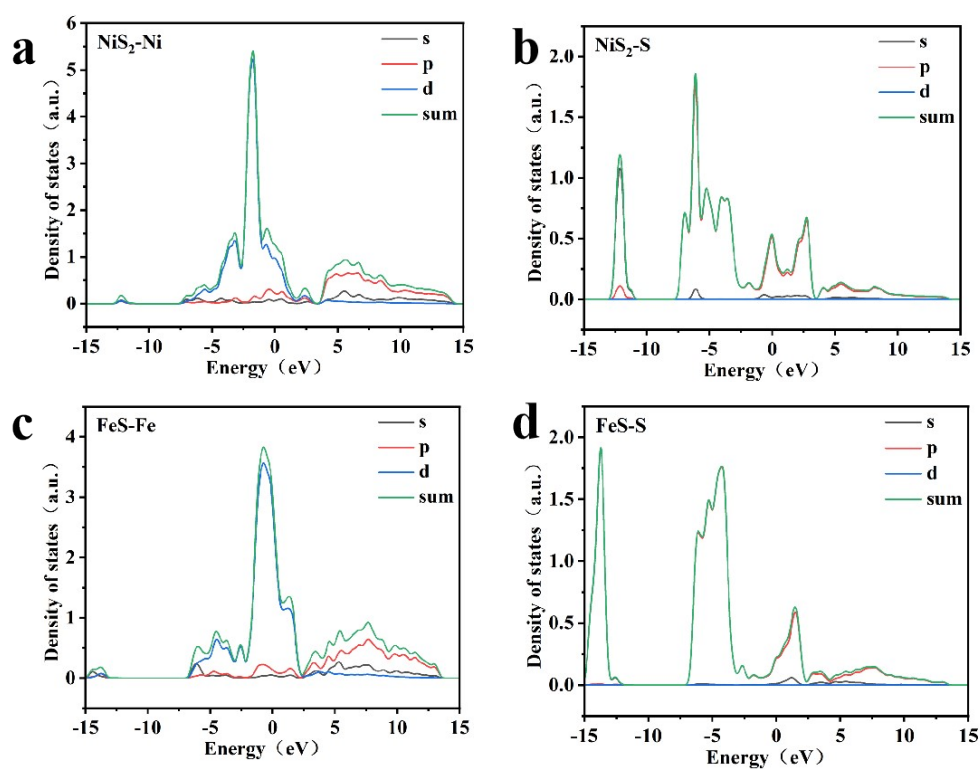
**Fig.S1** XRD curves of  $\text{NiS}_2@Ni_3S_2@FeS$ (a),  $NiFe\ LDHs/Co(OH)_2$ (b),  $Ni_7S_6@Co_4S_3$  (c) and  $NiS_2@Ni_3S_2@FeS$  ,  $Ni_7S_6@Co_4S_3$  and  $NiS_2@Co_4S_3@FeS$  (d).



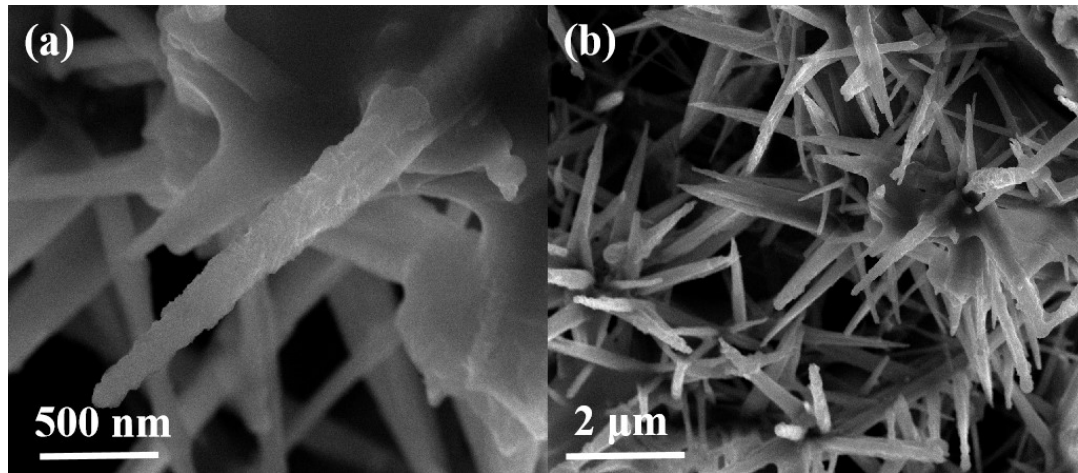
**Fig.S2** CV curves of (a) $\text{NiS}_2@Ni_3S_2@FeS$ , (b) $NiFe\ LDHs/Co(OH)_2$ , (c) $NiS_2@Co_4S_3@FeS$  and (d) $Ni_7S_6@Co_4S_3$ .



**Fig. S3** NiS<sub>2</sub>@Co<sub>4</sub>S<sub>3</sub>@FeS (a) chronoamperometric current curve, (b) LSV curves comparison before and after i-t test in OER.



**Fig.S4** The calculated state densities of (a)NiS<sub>2</sub>-Ni, (b) NiS<sub>2</sub>-S, (c) FeS-Fe and (d) FeS-S.



**Fig.S5** SEM image of NiS<sub>2</sub>@Co<sub>4</sub>S<sub>3</sub>@FeS after it test (a-b).

**Table S1.** Comparison of the OER performance for the obtained materials in this work with other state-of-the-art OER electrocatalysts.

Catalyst	Electrolyte	$\eta_{j=10}$ (mV)	Reference
NiS <sub>2</sub> @Co <sub>4</sub> S <sub>3</sub> @FeS	1 M KOH+seawater	122	This work
(FeCoNi)OH-S	1 M KOH+seawater	157	[1]
CoSe <sub>2</sub>	1 M KOH+seawater	245	[2]
Mo-Ni <sub>3</sub> S <sub>2</sub>	1 M KOH+seawater	212	[3]
Na <sub>2</sub> Co <sub>0.75</sub> Fe <sub>0.25</sub> P <sub>2</sub> O <sub>7</sub> /C =NPs	1 M KOH+seawater	300	[4]
CoS <sub>x</sub> /CuS <sub>x</sub>	1 M KOH+seawater	230	[5]
MnFeCr-LTHs	1 M KOH+seawater	242	[6]
Cu-NiCoP	1 M KOH+seawater	250	[7]
Ni@CNTs- Mo <sub>x</sub> C/Ni <sub>2</sub> P	1 M KOH+seawater	228	[8]
Er-MoO <sub>2</sub>	1 M KOH+seawater	312	[9]

**Table S2.** The atomic percent of metal ions in the samples by XPS analysis and the results.

	C 1s	Co 2p	Fe 2p	Ni 2p	O 1s	S 2p
Atomic (%)	31.44	3.96	3.32	4.78	39.82	16.68

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