Supplementary Information (SI) for Inorganic Chemistry Frontiers.

Supporting Information

Fe, Ce Synergistic Doped of Ni_3S_2 to Enhance the Oxygen Evolution Reaction Performance

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Experimental section

materials

Shanghai Macklin Biochemical Technology Co. provided the ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$, AR), cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, AR), and thiourea (CH_4N_2S, AR). Beijing Tongguang Fine Chemical Co. supplied the ethanol (EtOH, AR) and the acetone (C_3H_6O, AR). All reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. The laboratory produced deionized water on-site, which was utilized for every experiment.

Synthesis of Fe, Ce-Ni_3S_2@NF

The 20×30 mm nickel foam was firstly sonicated in 3M HCl for 15 minutes to remove surface oxides, and then immersed in acetone and sonicated for 15 min to clean the surface oil, followed by rinsing with anhydrous ethanol and deionized water for several times, and then placed in a vacuum drying oven at 60°C for drying. 0.5 mmol $FeSO_4 \cdot 7H_2O$ and 0.2 mmol $Ce(NO_3)_3 \cdot 6H_2O$ were dispersed in 35 mL of 0.1M CH_4N_2S solution and stirred magnetically for 30 minutes, they were then transferred to a 50 mL Teflon-lined stainless steel autoclave and placed in a dry nickel foam and held at 140 °C for 8 hours. The resulting Fe, Ce-Ni_3S_2@NF was washed repeatedly with anhydrous ethanol and deionized water, and then dried in a vacuum oven at 60 °C for 12 hours.

Synthesis of Fe-Ni_3S_2@NF, Ce-Ni_3S_2@NF and Ni_3S_2@NF

Fe-Ni_3S_2@NF, Ce-Ni_3S_2@NF and Ni_3S_2@NF were prepared in the same way, except that Fe-Ni_3S_2@NF was synthesized without the addition of the 0.2 mmol $Ce(NO_3)_3 \cdot 6H_2O$ metal precursor. Similarly, Ce-Ni_3S_2@NF comparison samples were synthesized without the addition of the 0.5 mmol $FeSO_4 \cdot 7H_2O$ metal precursor, and Ni_3S_2@NF was synthesized without the addition of the 0.5 mmol $FeSO_4 \cdot 7H_2O$ and 0.2 mmol $Ce(NO_3)_3 \cdot 6H_2O$ metal precursors.

The catalyst loadings on Ni foam for Fe, Ce-Ni_3S_2@NF, Fe-Ni_3S_2@NF, Ce-Ni_3S_2@NF and Ni_3S_2@NF samples were evenly measured as 3.9, 3.3, 4.3 and 2.9 mg cm^{-2}, respectively (**Table S1**). To obtain the RuO_2 catalysts, 4 mg of catalysts was mixed in 1 mL of solution (480 μL anhydrous ethanol + 480 μL deionized water + 40 μL Nafion membrane solution), which was ultrasonicated for 1 h and added dropwise to pure nickel foam with an equivalent loading of about 4 mg cm^{-2}.

Materials characterizations

The morphology of the prepared samples was observed by field emission scanning electron microscopy (FESEM, Hitachi, SU-8010) with an accelerating voltage of 5 kV. Transmission electron microscopy (TEM, Talos F200S, 200 kV) was used to record the structural information and elemental composition of the materials. X-ray powder diffraction of samples recorded under Cu Kα radiation ($\lambda = 1.54056$ Å) using a Phillips X'pert ProMPD diffraction recorder. A microscopic confocal Raman spectrometer (LabRAMAramis, Horiba Jobin Yvon) was used to record Raman spectra from 100 to 800 cm-1 with an excitation wavelength of 532 nm. An ESCALAB 250Xi spectrometer

(Thermo Fishe) was used for x-ray photoelectron spectroscopy (XPS) measurements.

Electrochemical measurements

An electrochemical workstation (CHI 760E, Shanghai Chenhua, China) was used to perform electrochemical tests in a standard three-electrode system. The catalyst (0.5×0.5 cm), Hg/HgO electrode, and graphite electrode were used as the working electrode, reference electrode, and counter electrode, respectively. OER tests were performed in 1 M KOH electrolyte. According to the Nernst equation: $E_{RHE} = E_{Hg/HgO}+0.098+0.059\times PH$, all potentials of the catalyst were converted to the potential of the reversible hydrogen electrode (RHE), and the overpotential at a current density of 10 $mA\cdot cm^{-2}$ was calculated according to the equation: $\eta_{10} = E_{RHE}-1.23V$. Linear scanning voltammetry (LSV) was performed over a potential range of 0.105 to 1.105 V (vs. Hg/HgO) with a scan rate of 5 $mV\cdot s^{-1}$. Measurements of the double layer capacitance (C_{dl}) were carried out by cyclic voltammetry (CV) in a potential window of -0.3~-0.2 V (vs. Hg/HgO) at scan rates of 10, 20, 40, 60, 80, and 100 $mV\cdot s^{-1}$. The electrochemically active surface area (ECSA) of the synthesized electrocatalysts was estimated according to the equation: $ECSA=C_{dl}/C_s$, where C_s is the specific capacitance of the corresponding surface smoothed samples under the same conditions. Electrochemical impedance spectroscopy (EIS) was performed at open-circuit voltage and at frequencies ranging from 0.01 Hz to 1000 kHz with a sinusoidal amplitude of 5 mV. In addition, the long-term stability of the prepared electrocatalyst was measured and recorded at a potential of 20 $mA\cdot cm^{-2}$ (vs. Hg/HgO). All data in this article are not iR corrected.

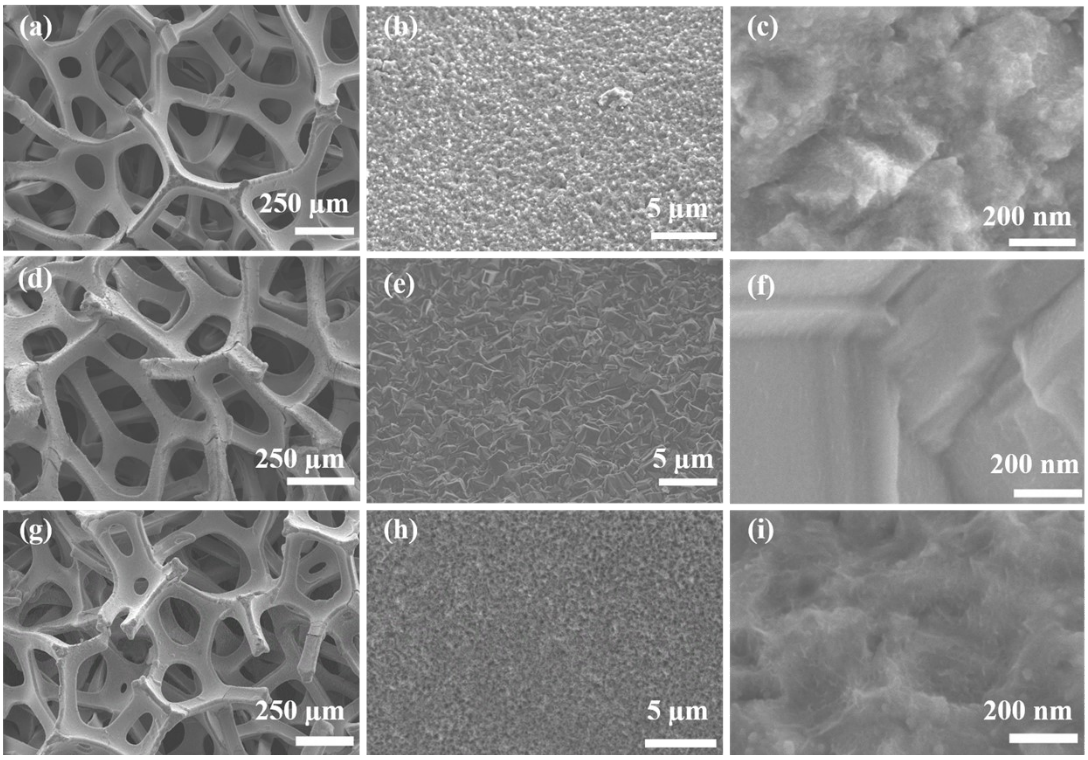

Fig. S1. SEM images of (a-c) Fe -Ni_3S_2@NF, (d-f) Ce-Ni_3S_2@NF and (g-i) Ni_3S_2@NF at different magnifications.

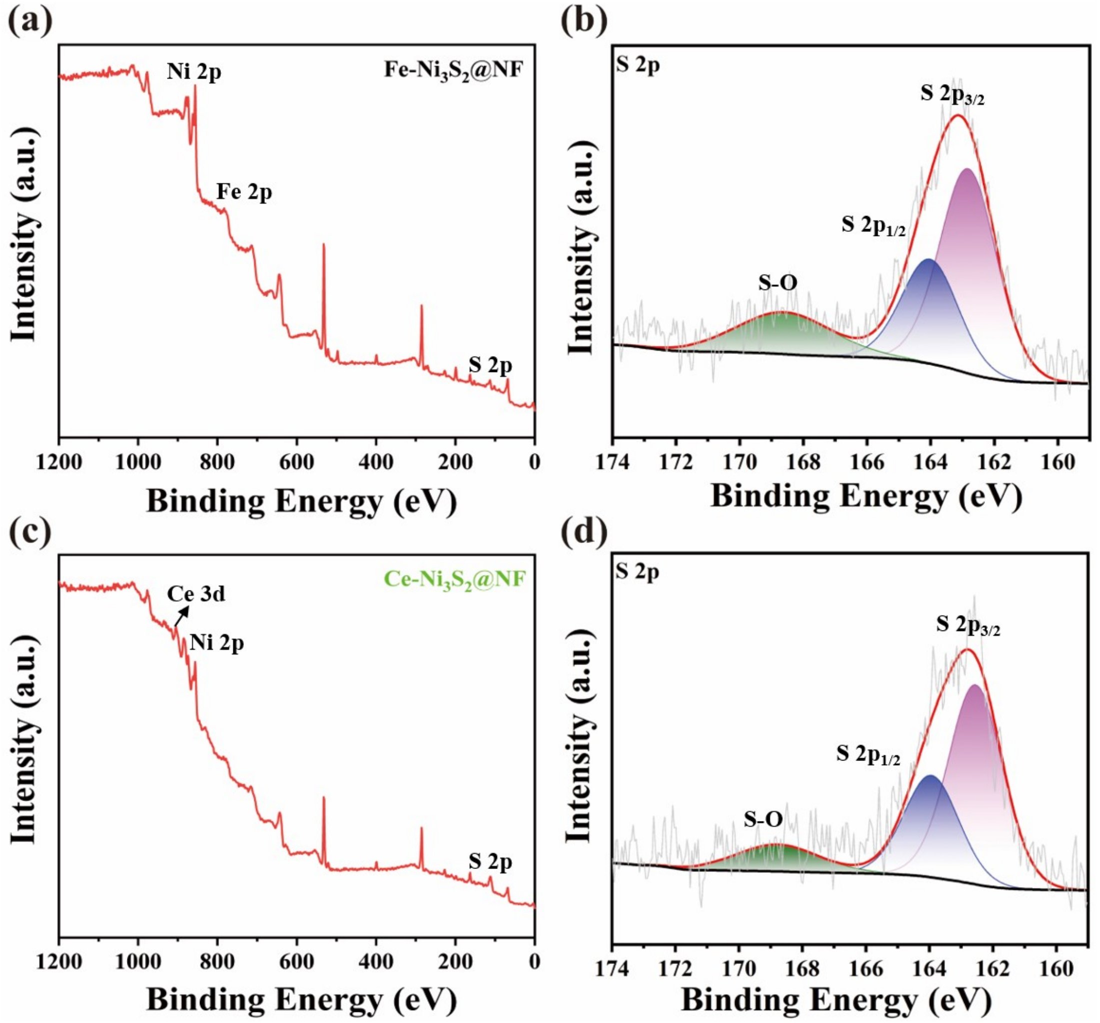

Fig. S2. (a) XPS survey spectrum of Fe-Ni_3S_2@NF. (b) XPS high-resolution spectra of S 2p for Fe-Ni_3S_2@NF. (c) XPS survey spectrum of Ce-Ni_3S_2@NF. (d) XPS high-resolution spectra of S 2p for Ce-Ni_3S_2@NF.

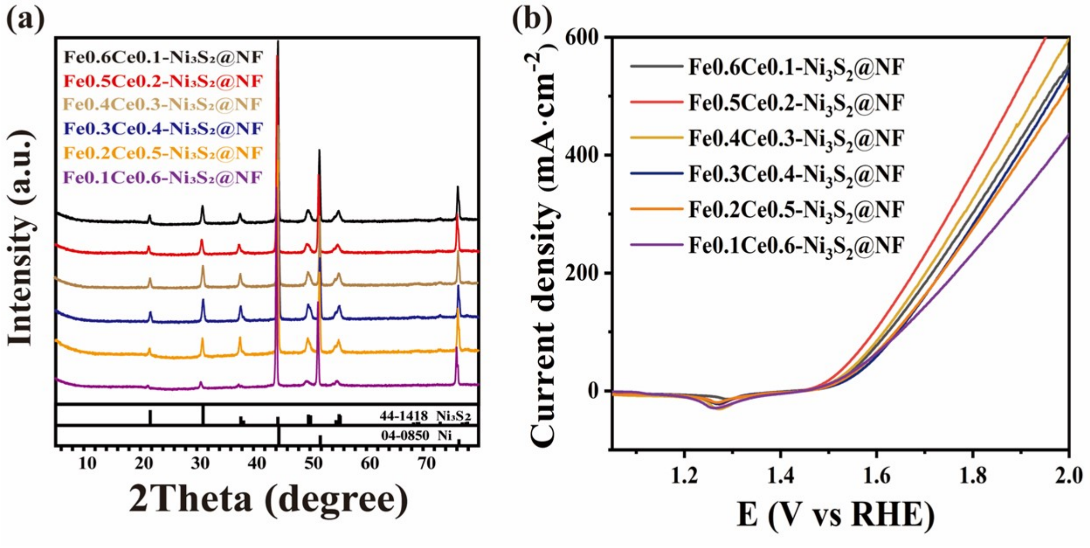

Fig. S3. (a) XRD and (b) LSV of Fe, Ce-Ni_3S_2@NF with different molar ratios (6:1, 5:2, 4:3, 3:4, 2:5, 1:6).

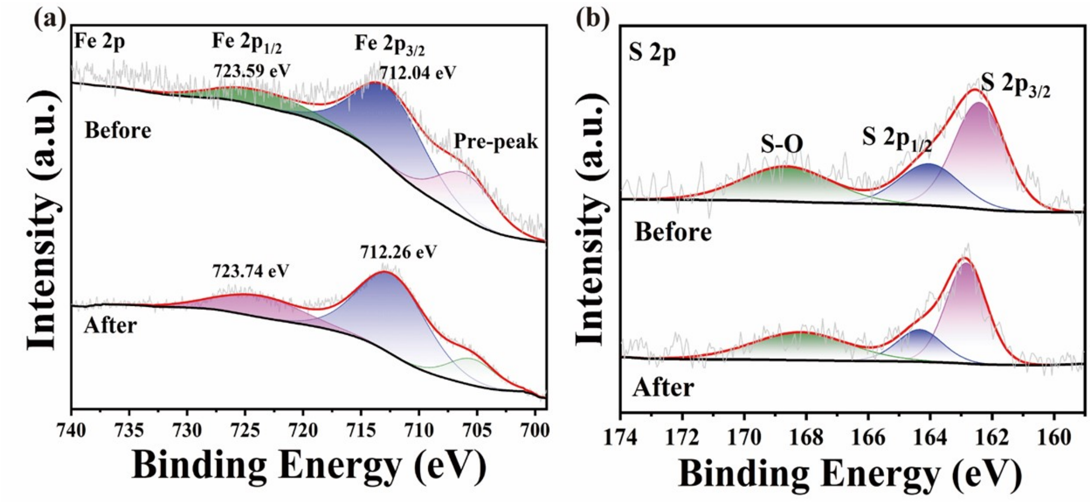

Fig. S4. Fe, Ce-Ni_3S_2@NF tests before and after (a) Fe 2p and (b) S 2p high resolution spectrum.

Table S1. Average mass loading of catalysts on NF substrates.

Samples	Mass loading (mg cm^{-2})
Fe, Ce-Ni_3S_2@NF	3.9
Fe-Ni_3S_2@NF	3.3
Ce-Ni_3S_2@NF	4.3
Ni_3S_2@NF	2.9

Table S2. XPS fitting parameters for the Ce peak area of Fe, Ce-Ni_3S_2@NF and Ce-Ni_3S_2@NF catalysts.

Samples (Ce^{3+}/Ce^{4+} ratio)	Peak area			
	Ce^{3+}		Ce^{4+}	
	$3d_{5/2}$	$3d_{3/2}$	$3d_{5/2}$	$3d_{3/2}$
Fe, Ce-Ni_3S_2@NF (0.60)	6586 6401	3561 3742	5829 3390 3360	4733 4571 2827
Ce-Ni_3S_2@NF (0.32)	5122 5077	2049 2168	7755 5642 1999	4182 5125 3599

* Only Ce $3d_{3/2}$ peaks are included in the calculation for accuracy, as the Ce $3d_{5/2}$ region

is affected by Ni 2p spectra.

Table S3. The simulated series resistance (R_s) and charge transfer (R_{ct}) based on the EIS fitting models.

Samples	R_s (Ω)	R_{ct} (Ω)
Fe, Ce-Ni_3S_2@NF	1.030	1.059
Fe-Ni_3S_2@NF	1.017	1.135
Ce-Ni_3S_2@NF	0.981	1.171
Ni_3S_2@NF	1.042	1.353

Table S4. XPS fitting parameters of Ni peak area before and after OER testing of Fe, Ce-Ni3S2@NF catalyst.

Fe, Ce-Ni_3S_2@NF (Ni^{3+}/Ni^{2+} ratio)	Peak area			
	Ni^{2+}		Ni^{3+}	
	$2p_{3/2}$	$2p_{1/2}$	$2p_{3/2}$	$2p_{1/2}$
Before (0.41)	17927	10923	7280	4301
After (0.70)	63436	28448	44611	18422

*Only Ni $2p_{3/2}$ peaks are taken into the calculation for accuracy as the Ni $2p_{1/2}$ region is influenced by Ce 3d spectra.

Table S5. XPS fitting parameters of Fe peak area before and after OER testing of Fe, Ce-Ni3S2@NF catalyst.

Fe, Ce-Ni_3S_2@NF (Pre-peak/All peak ratio)	Peak area		
	Pre-peak	$2p_{3/2}$	$2p_{1/2}$
Before (0.27)	6719	14584	3900
After (0.14)	12394	54947	18311