

Electronic Supplementary Information for

In-situ fabrication of Ni-Fe-S hollow hierarchical sphere: An efficient (pre)catalyst for OER and HER

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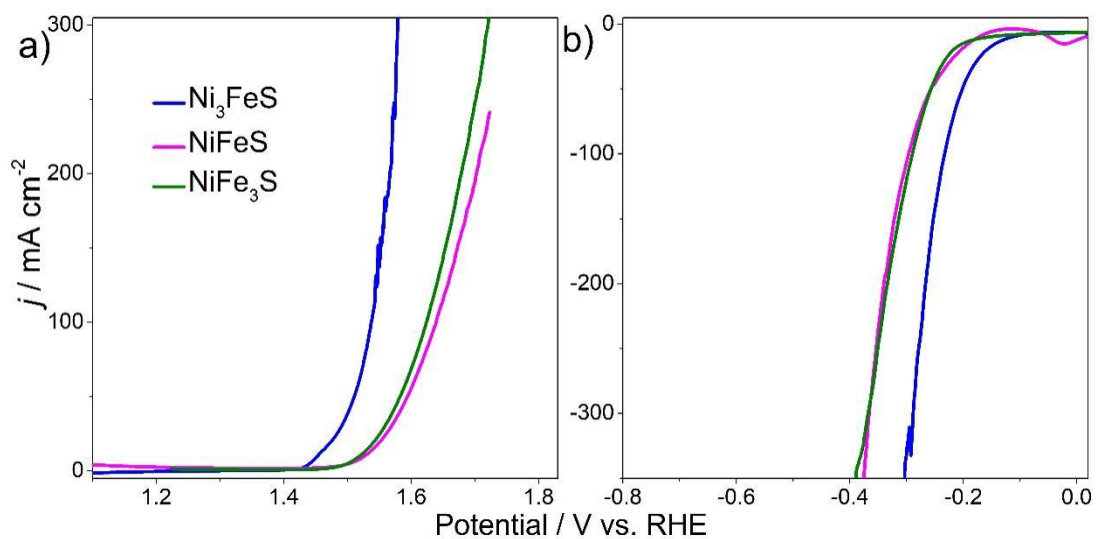


Figure S1 Electrochemical measurements of $\text{Ni}_x\text{Fe}_y\text{S}$, (a) OER in 1.0 M KOH, (b) HER in 1.0 M KOH,

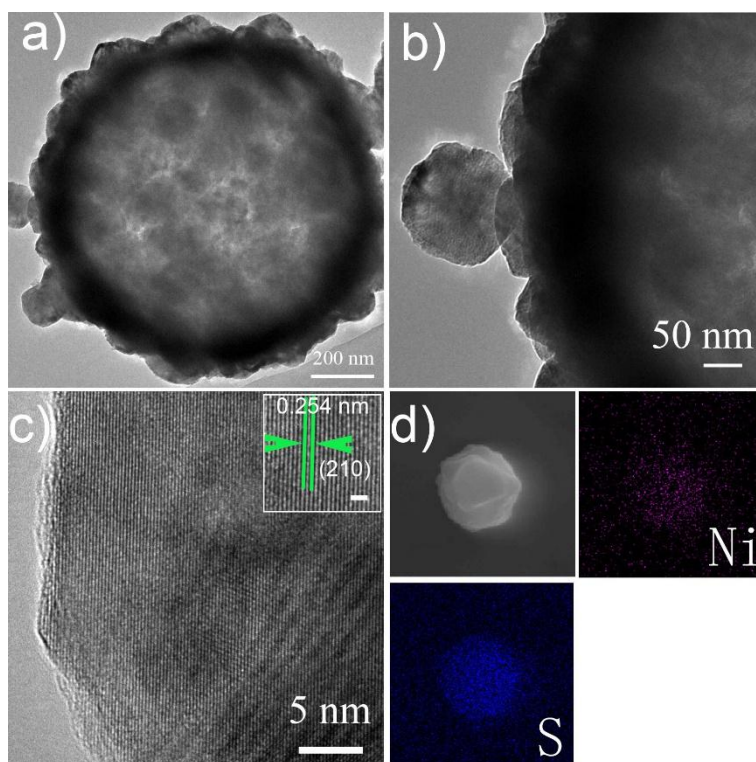


Figure S2 Structural characterization of the Ni-S hierarchical sphere, a) low-resolution TEM image, b) the microcosmic structures of surface, c) HRTEM image and the scale bar in the inset: 1 nm, d) EDX elemental mapping images of Ni, S.

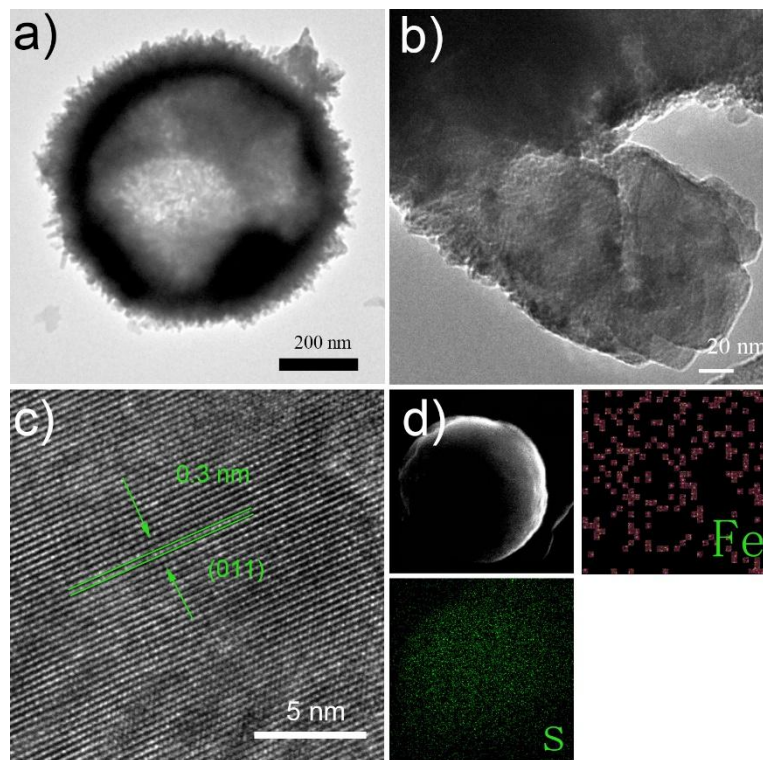


Figure S3 Structural characterization of the Fe-S hierarchical sphere, a) low-resolution TEM image, b) the microscopic structures of surface, c) HRTEM image and the scale bar in the inset: 1 nm, d) EDX elemental mapping images of Fe, S.

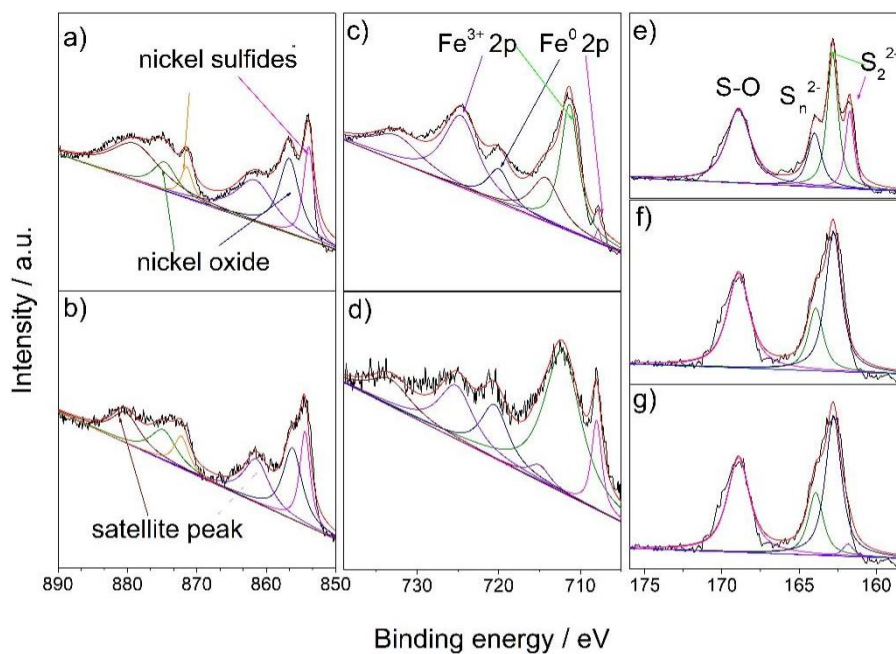


Figure S4 Comparison of XPS spectrum of Ni-S, Fe-S and Ni-Fe-S. a,b)Ni 2p c,d) Fe 2p e,f,g) s 2p

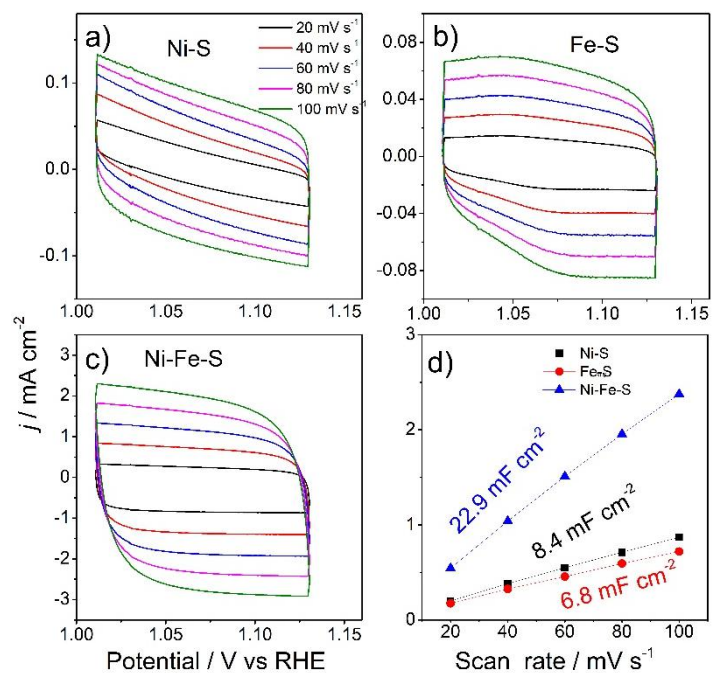


Figure S5 The cyclic voltammograms curves of Microspheres a) Ni-S, b) Fe-S, c) Ni-Fe-S and d) C_{dl} for Ni-S, Fe-S, Ni-Fe-S toward to OER.

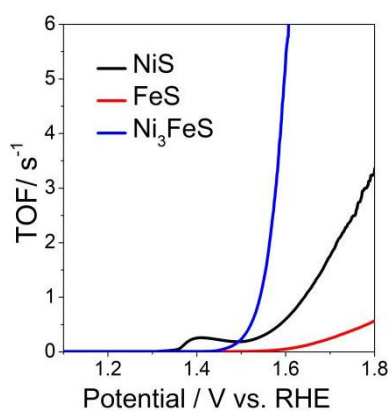


Figure S6 The OER TOFs of the Ni-S, Fe-S, Ni-Fe-S

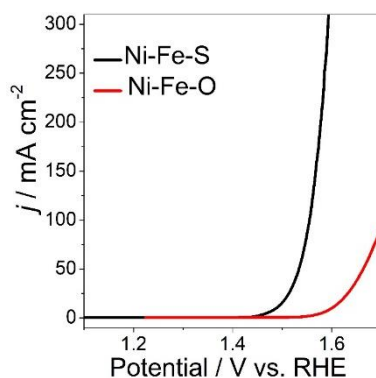


Figure S7 The polarization curves of Ni-Fe-O and Ni-Fe-S toward the OER

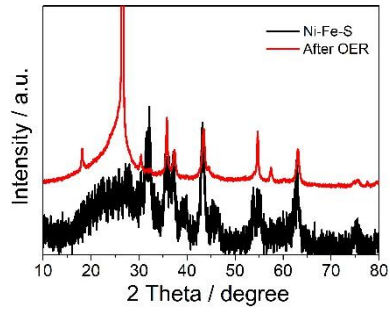


Figure S8 XRD patterns of after the OER process for Ni-Fe-S

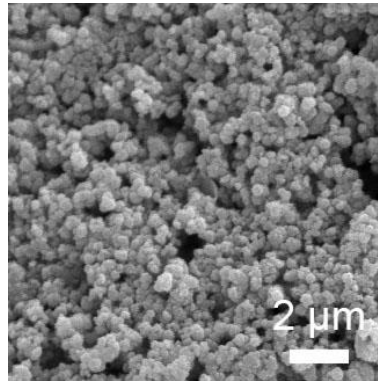


Figure S9 SEM images of Ni-Fe-S catalysts after OER

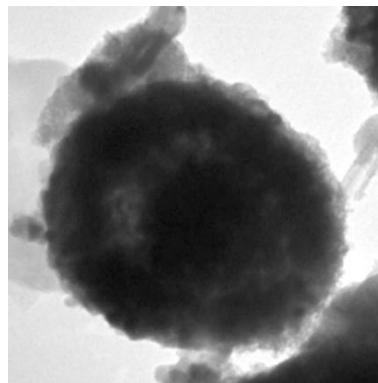


Figure S10 TEM images of Ni-Fe-S catalysts after OER

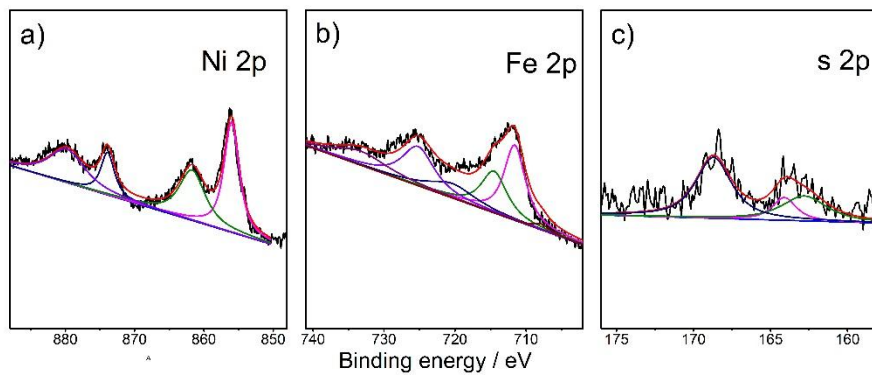


Figure S11 The XPS spectrum of Ni-Fe-S after OER a) Ni 2p b) Fe 2p c) s 2p

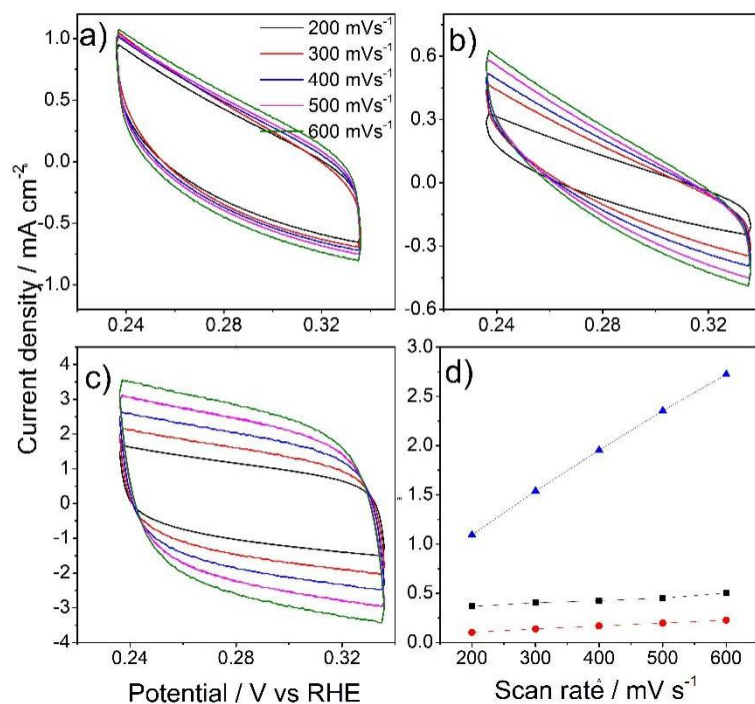


Figure S12 The cyclic voltammograms curves of Microspheres a) Ni-S, b) Fe-S, c) Ni-Fe-S and d) C_{dl} for Ni-S, Fe-S, Ni-Fe-S toward to HER.

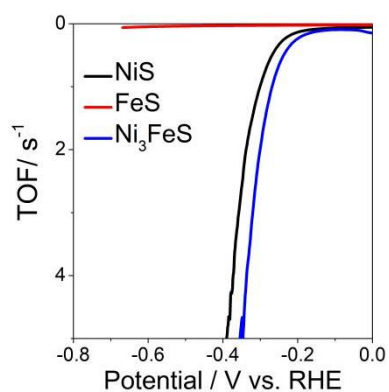


Figure S 13 The HER TOFs of the Ni-S, Fe-S, Ni-Fe-S

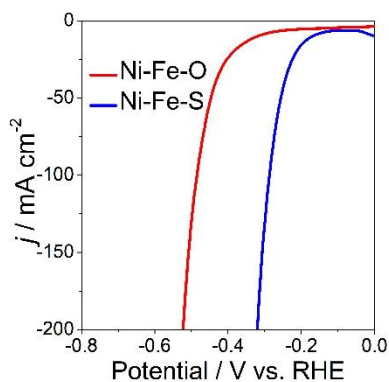


Figure S 14 The polarization curves of Ni-Fe-O and Ni-Fe-S toward the HER

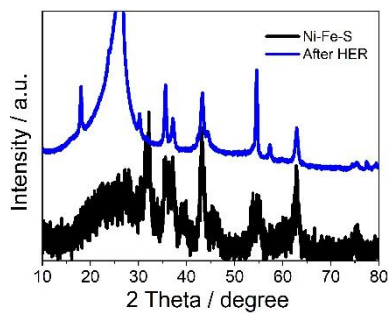


Figure S15 XRD patterns of after the OER process for Ni-Fe-S

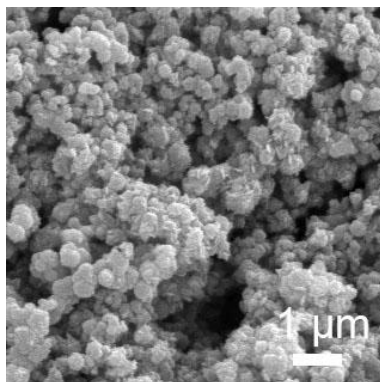


Figure S16 SEM images of Ni-Fe-S catalysts after HER

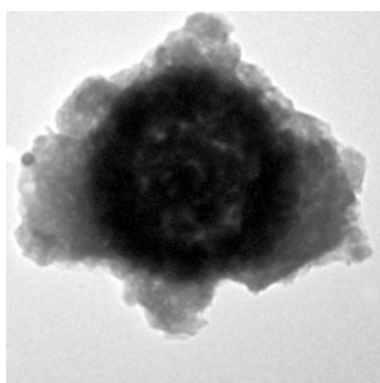


Figure S17 TEM images of Ni-Fe-S catalysts after HER

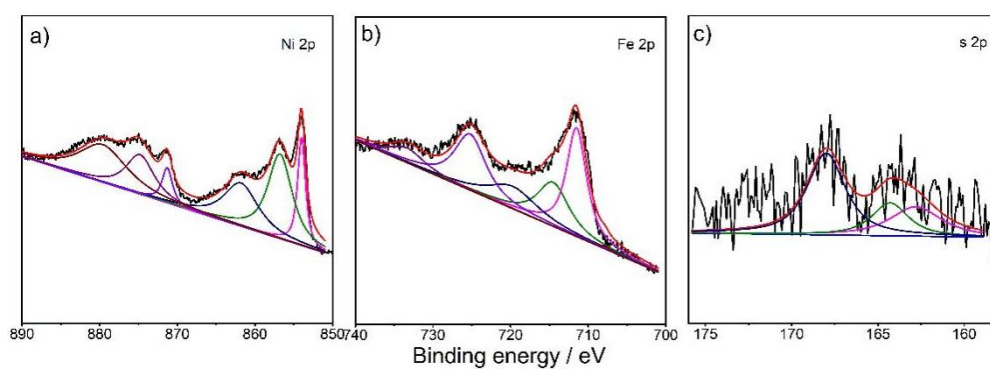


Figure S18 The XPS spectrum of Ni-Fe-S after HER a) Ni 2p b) Fe 2p c) s 2p

Table S1. The detailed parameters of Ni-S、 Fe-S, Ni-Fe-S and IrO₂ toward the OER.

	Ni-S	Fe-S	Ni-Fe-S	IrO₂
Fe/Ni	----	----	1/3	----
Overpotential at 10 mA cm ⁻²	290 mV	400 mV	223 mV	280 mV
anodic peak position	1.41 V vs. RHE	--	--	--
Rct	1.6 Ω cm ²	1.8 Ω cm ²	1.3 Ω cm ²	--
Cdl	8.4 mF cm ⁻²	6.8 mF cm ⁻²	22.9 mF cm ⁻²	--
surface area	105 m ² g ⁻¹	123 m ² g ⁻¹	112 m ² g ⁻¹	131 m ² g ⁻¹
bandgap	1.4 eV	0.8 eV	1.2 eV	0.5 eV

Table S2. Comparison of OER activity of the Ni-Fe-S with recently reported catalyst.

Catalysts	Overpotential at 10 mA cm ⁻² (mV vs RHE)	Electrolyte concentration (pH)	Ref.
Ni-Fe-S	223	14	This work
Ni/NiO@G-SH	270	14	7
Ni/Ni(OH) ₂	310	14	8
CF@NiP _x	200	14	11
NiCo _{0.2} NS/Ni/CF	228	14	12
NCN/CC	247	14	13
C doped Co/Co ₃ O ₄ hollow spheres	352	14	19
CoP	280	14	20
CoS ₂ -MoS ₂	288	14	22
CoM-P-3DHFLMs	292	14	29
CoCu-ZIF@GDY	250	14	30
Ni ₄ Cu ₂ @C	280	14	31
Co/Fe	378	14	32
Ni-Mo-S/CC	300	14	33
ECT-S-Co _{0.37} Ni _{0.26} Fe _{0.37} O	232	14	34
FeNi ₃ N-Ni ₃ S	230	14	35
CoCuNCNT@PC-700-2	340	14	36
H-NiFe oxyphosphide	253	14	37
Co-Fe-P-Se	270	14	38

Table S3. The detailed parameters of Ni-S, Fe-S, Ni-Fe-S and IrO₂ toward the HER.

	Ni-S	Fe-S	Ni-Fe-S	Pt
Fe/Ni	----	----	1/3	----
Overpotential at 10 mA cm ⁻²	228 mV	> 660 mV	115 mV	16 mV
Rct	1.5 Ω cm ²	1.6 Ω cm ²	1.4 Ω cm ²	--
Cdl	8.4 mF cm ⁻²	6.8 mF cm ⁻²	22.9 mF cm ⁻²	--
surface area	105 m ² g ⁻¹	123 m ² g ⁻¹	112 m ² g ⁻¹	--
TOF	1.4 eV	0.8 eV	1.2 eV	0.5 eV

Table S4. Comparison of HER activity of the Ni-Fe-S with recently reported catalyst.

Catalysts	Overpotential at 10 mA cm ⁻² (mV vs RHE)	Electrolyte concentration (pH)	Ref.
Ni-Fe-S	115	14	This work
Ni/Ni(OH) ₂	168	14	8
NiS-NiS ₂ -Ni ₃ S ₂ /NF	137	14	9
NiS/NiS ₂	143	14	10
CF@NiP _x	118	14	11
NiC _{0.2} NS/Ni/CF	121	14	12
β-Mo ₂ C/N	119	0	17
MoO ₂ -G	>150	0	23
Ni ₂ P@MoS ₂	181	14	25
Ni-Mo-S/CC	118	14	33

Table S5. Comparison of the electrochemical performance of Ni-Fe-S|Ni-Fe-S as bifunctional catalysts for overall water splitting in 1.0 M KOH with recently published results.

Catalysts	Voltage at 10 mA cm ⁻² (V)	Electrolyte concentration (pH)	Ref.
Ni-Fe-S	1.57 1.59 (20 mA cm ⁻²)	14	This work
Co-P films	1.65	14	40
Co _{0.9} S _{0.58} P _{0.42}	1.59	14	41
CCF LDH-60	1.68	14	42
NiMoN-550	1.596	14	43
Ni _{0.69} Co _{0.31} -P	1.59	14	44
Co-NiMoN NRs	1.57	14	45
FeNi ₃ N/NG	1.585(20 mA cm ⁻²)	14	46
N, B co-doped Co ₃ C	> 1.7	14	47
Mo ₂ C@NC/Co@NGs	> 1.7	14	48
CoP	1.58	14	49