

Supporting Information

Ternary nickel-iron sulfide microflower as a robust electrocatalyst for bifunctional water splitting

Jiahao Yu,^a Gongzhen Cheng^a and Wei Luo^{a,b*}

^aCollege of Chemistry and Molecular Sciences, Wuhan University, Wuhan, Hubei
430072, P. R. China, Tel.: +86-027-68752366

*Corresponding author. E-mail addresses: wluo@whu.edu.cn.

^bKey laboratory of Advanced Energy Materials Chemistry (Ministry of Education),
Nankai University, Tianjin 300071, P. R. China

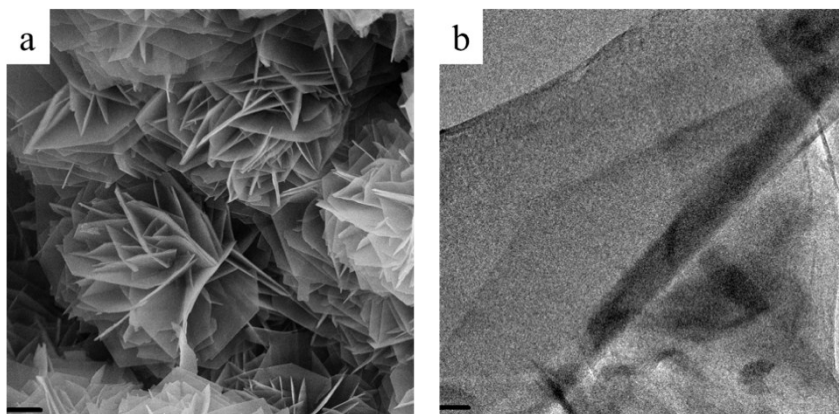


Figure S1. (a) SEM image and (b) TEM image of NiFe LDH. (c) 1 μm ; (d) 100 nm.

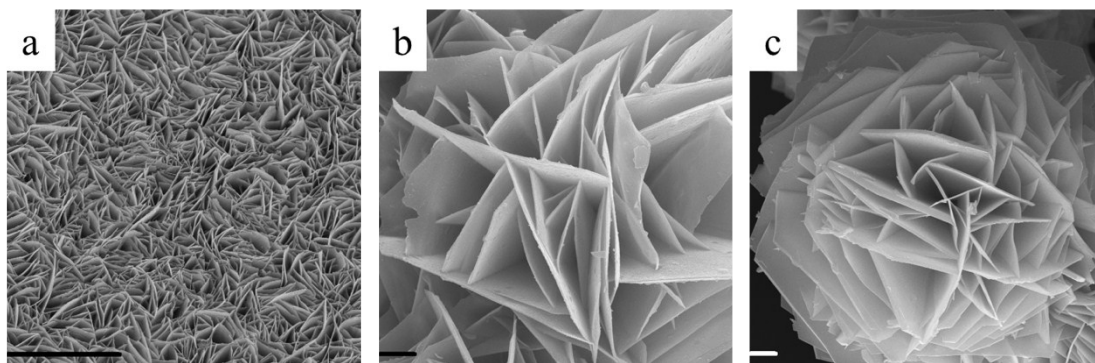


Figure S2. SEM images of (a) NiS_2 , (b) $\text{Ni}_{0.86}\text{Fe}_{0.14}\text{S}_2$ and (c) $\text{Ni}_{0.58}\text{Fe}_{0.42}\text{S}_2$. Scale bars: (a) 10 μm ; (b) and (c) 1 μm .

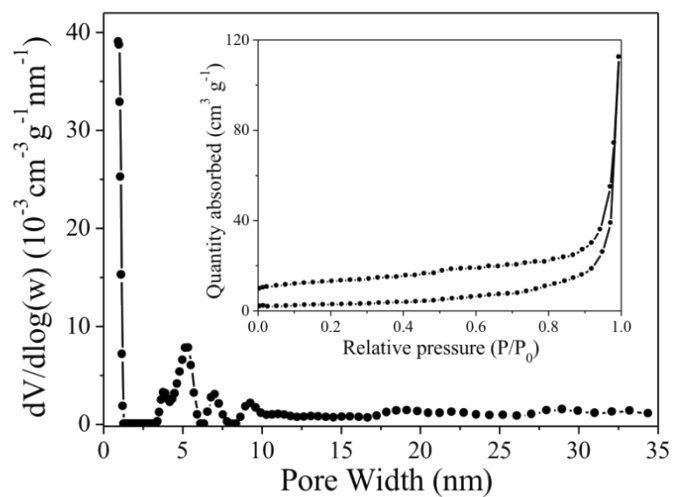


Figure S3. Pore size distribution (DFT model) of $\text{Ni}_{0.7}\text{Fe}_{0.3}\text{S}_2$. Inset shows the N_2 adsorption-desorption isotherm.

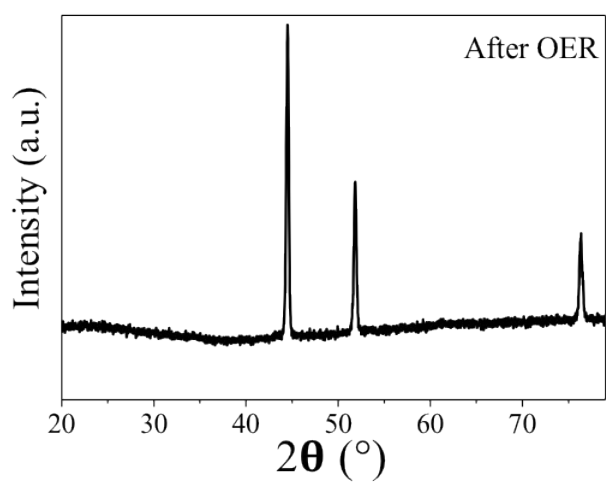


Figure S4. XRD pattern for $\text{Ni}_{0.7}\text{Fe}_{0.3}\text{S}_2$ after OER test.

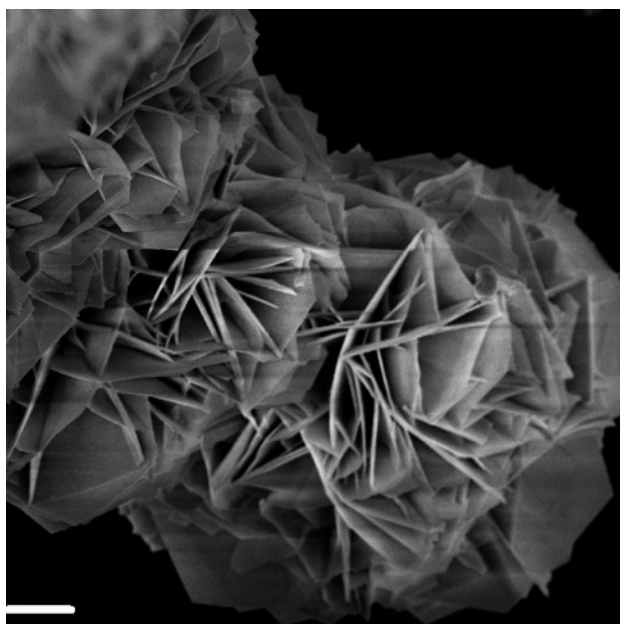


Figure S5. SEM images of $\text{Ni}_{0.7}\text{Fe}_{0.3}\text{S}_2$ after chronopotentiometric measurements of OER. Scale bar: 2 μm .

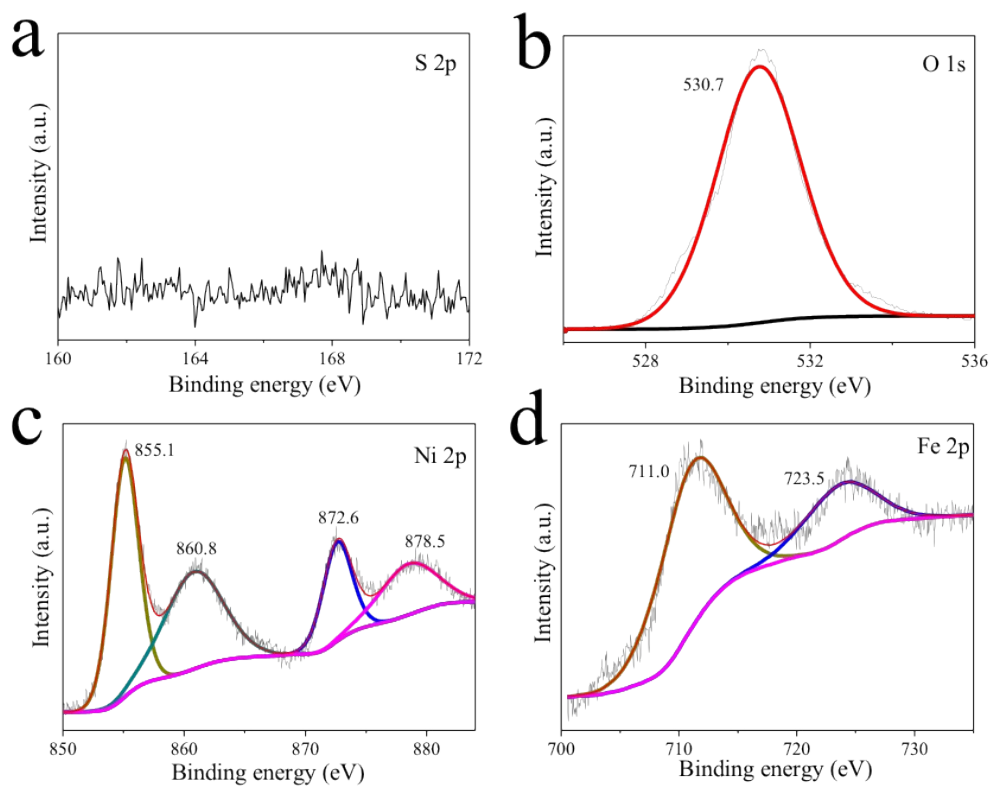


Figure S6. XPS spectra (a) in the S (2p) region, (b) in the O (1s) region, (c) in the Ni (2p) region and (d) in the Fe (2p) region of $\text{Ni}_{0.7}\text{Fe}_{0.3}\text{S}_2$ after OER test.

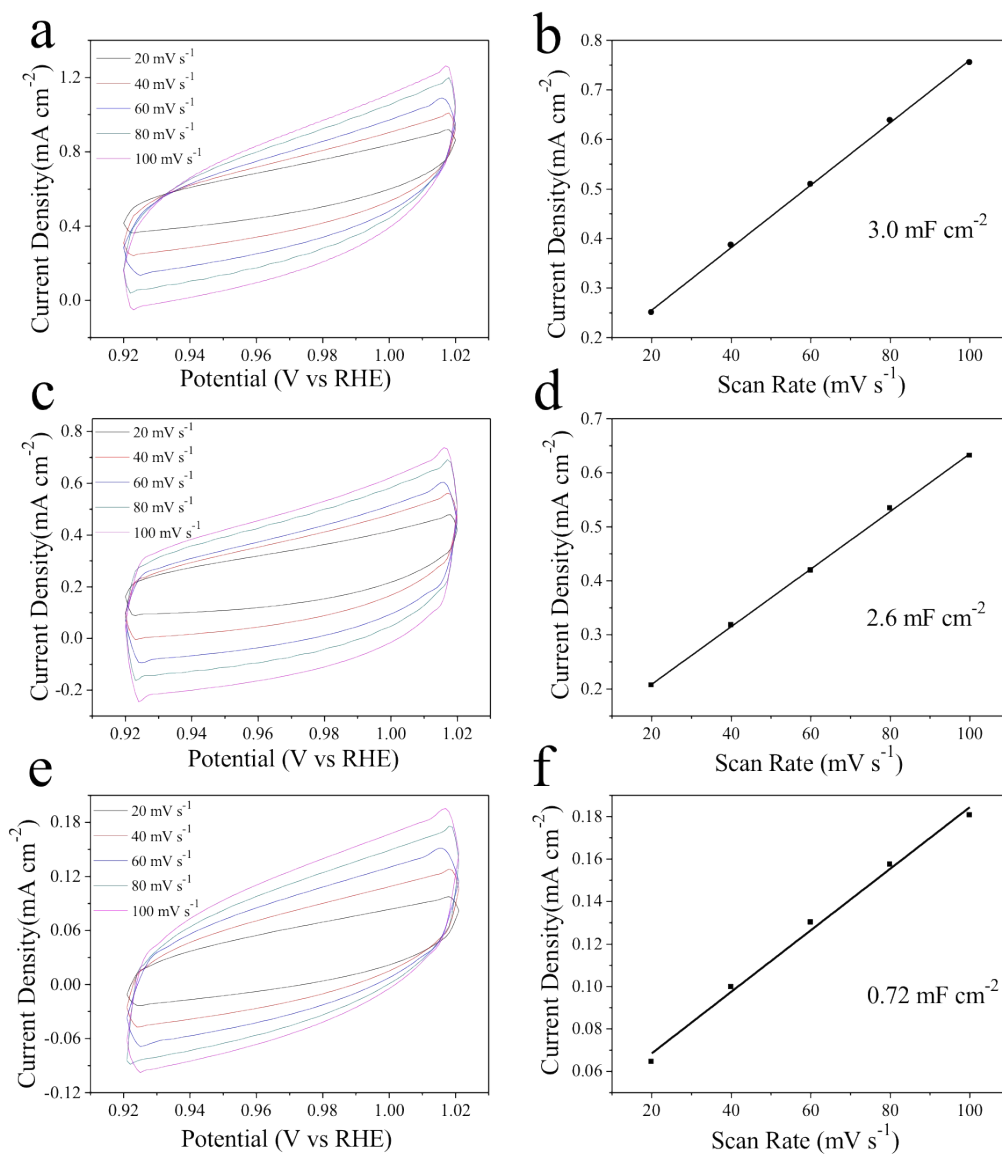


Figure S7. Cyclic voltammetry (CV) curves of (a) $\text{Ni}_{0.7}\text{Fe}_{0.3}\text{S}_2$, (c) NiS_2 and (e) NiFe LDH tested at various scan rates from 20 to 100 mV s^{-1} . Scan rate dependence of the current densities of (b) $\text{Ni}_{0.7}\text{Fe}_{0.3}\text{S}_2$, (d) NiS_2 and (f) NiFe LDH at 0.97 V vs RHE.

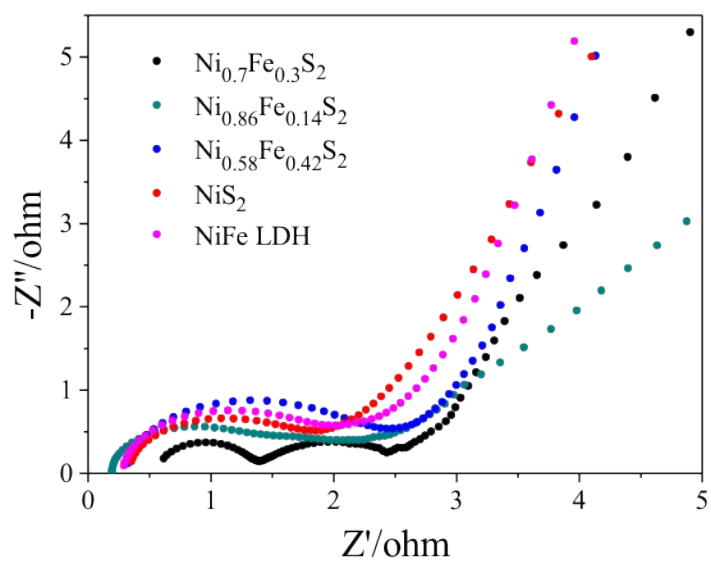


Figure S8. EIS spectra of $\text{Ni}_x\text{Fe}_{1-x}\text{S}_2$, NiS_2 and NiFe LDH .

Table S1 The actual Ni/Fe atomic ratios of different added

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}/\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ratios determined by ICP-AES.

Feed ratios	Ni (Atomic%)	Fe (Atomic%)
x=0.25	27.9	27.2
x=0.5	38.9	22.2
x=0.75	54.7	11.6

Table S2 Comparison of OER catalytic performance with other sulfides and non-noble metal based catalysts.

Materials	Current Density (mA cm ⁻²)	Overpotential (mV)	Reference
Ni _{0.7} Fe _{0.3} S ₂	10	198	This work
	20	212	
	50	245	
	100	287	
	200	360	
Ni _{2.3} %-CoS ₂ /CC	100	370	[1]
Co _{0.5} Fe _{0.5} S@N-MC	10	410	[2]
NiS/Ni foam	50	335	[3]
Ni-Fe disulfide@oxyhydroxide	10	230	[4]
Fe-Ni ₃ S ₂ /FeNi	10	282	[5]
NiCo ₂ S ₄ NA/CC	100	340	[6]
Ni-Co-S/CF	100	363	[7]
MoO _x /Ni ₃ S ₂ composite	200	373	[8]
CoNi-P-NS /NF	10	209	[9]
(Ni, Co) _{0.85} Se@NiCo-LDH	10	216	[10]
Co _{0.13} Ni _{0.87} Se ₂ /Ti	100	320	[11]
NiCoP	50	308	[12]
Sandwiched NiFe/C arrays	20	220	[13]
NiFe/RGO	10	245	[14]
FeNi-O	10	213	[15]
NiFe LDH	10	240	[16]

Table S3 Comparison of HER catalytic performance with other sulfides and non-noble metal based catalysts.

Materials	Current Density (mA cm⁻²)	Overpotential (mV)	Reference
Ni _{0.7} Fe _{0.3} S ₂	10	155	This work
NiCo ₂ S ₄ NA/CC	10	~190	[6]
Fe _{0.1} -NiS ₂ NA/Ti	10	~250	[17]
Ni ₂ P/NiO _x	10	220	[18]
EG/Co _{0.85} Se/NiFe-LDH	10	260	[19]
Co ₉ S ₈ -Ni _x S _y /Ni foam	10	163	[20]
Ni ₃ S ₂ /AT-Ni	10	200	[21]
CoP	10	209	[22]
NiFe LDH/NF	10	210	[16]
NiCoP/rGO	10	209	[23]
Co _{0.5} Fe _{0.5} S@N-MC	10	410	[2]

Table S4 Comparison of catalytic performance for water splitting with other sulfides and non-noble metal based catalysts.

Materials	Current Density (mA cm⁻²)	Cell voltage (V)	Reference
Ni _{0.7} Fe _{0.3} S ₂	10	1.625	This work
	50	1.751	
Ni-Co-S/CF	10	1.67	[7]
NiS/Ni foam	10	1.64	[3]
NiSe/Ni foam	10	1.63	[24]
Co-P/Cu foil	10	1.65	[25]
NiCo ₂ S ₄ NA/CC	10	1.68	[6]
NiCoP	50	1.77	[12]
Ni ₂ P/NiO _x	10	1.63	[18]
NiCoP	10	1.64	[26]
EG/Co _{0.85} Se/NiFe-LDH	10	1.67	[19]
NiCo ₂ O ₄	10	1.65	[27]

References

- 1 W. Fang, D. Liu, Q. Lu, X. Sun, A. M. Asiri, *Electrochem. Commun.*, 2016, **63**, 60.
- 2 M. Shen, C. Ruan, Y. Chen, C. Jiang, K. Ai, L. Lu, *Appl. Mater. Interfaces*, 2015, **7**, 1207.
- 3 W. Zhu, X. Yue, W. Zhang, S. Yu, Y. Zhang, J. Wang, J. Wang, *Chem. Commun.*, 2016, **52**, 1486.
- 4 M. Zhou, Q. Weng, X. Zhang, X. Wang, Y. Xue, X. Zeng, Y. Bando, D. Golberg, *J. Mater. Chem. A*, 2017, **5**, 4335.
- 5 C.-Z. Yuan, Z.-T. Sun, Y.-F. Jiang, Z.-K. Yang, N. Jiang, Z.-W. Zhao, U. Y. Qazi, W.-H. Zhang, A.-W. Xu, *Small*, 2017, 1604161.
- 6 D. Liu, Q. Lu, Y. Luo, X. Sun, A. M. Asiri, *Nanoscale*, 2015, **7**, 15122.
- 7 T. Liu, X. Sun, A. M. Asiri, Y. He, *Int. J. Hydrogen Energy*, 2016, **41**, 7264.
- 8 Y. Wu, G.-D. Li, Y. Liu, L. Yang, X. Lian, T. Asefa, X. Zou, *Adv. Funct. Mater.*, 2016, **26**, 4839.
- 9 X. Xiao, C.-T. He, S. Zhao, J. Li, W. Lin, Z. Yuan, Q. Zhang, S. Wang, L. Dai, D. Yu, *Energy Environ. Sci.*, 2017, **10**, 893.
- 10 C. Xia, Q. Jiang, C. Zhao, M. N. Hedhili, H. N. Alshareef, *Adv. Mater.* **2016**, **28**, 77.
- 11 T. Liu, A. M. Asiri, X. Sun, *Nanoscale*, 2016, **8**, 3911.

- 12 Y. Li, H. Zhang, M. Jiang, Y. Kuang, X. Sun, X. Duan, *Nano Res.*, 2016, **9**, 2251.
- 13 Y. Feng, H. Zhang, L. Fang, Y. Mu, Y. Wang, *ACS Catal.*, 2016, **6**, 4477.
- 14 D. H. Youn, Y. B. Park, J. Y. Kim, G. Magesh, Y. J. Jang, J. S. Lee, *Journal of Power Sources*, 2015, **294**, 437.
- 15 X. Long, Z. Ma, H. Yu, X. Gao, X. Chen, S. Yang, Z. Yi, *J. Mater. Chem. A*, 2016, **4**, 14939.
- 16 J. Luo, J.-H. Im, M. T. Mayer, M. Schreier, M. K. Nazzeeruddin, N.-G. Park, S. D. Tilley, H. J. Fan, M. Grätzel, *Science*, 2014, **345**, 1593.
- 17 N. Yang, C. Tang, K. Wang, G. Du, A. M. Asiri, X. Sun, *Nano Res.*, 2016, **9**, 3346.
- 18 L.-A. Stern, L. Feng, F. Song, X. Hu, *Energy Environ. Sci.*, 2015, **8**, 2347.
- 19 Y. Hou, M. R. Lohe, J. Zhang, S. Liu, X. Zhuang, X. Feng, *Energy Environ. Sci.*, 2016, **9**, 478.
- 20 D. Ansovini, C. J. J. Lee, C. S. Chua, L. T. Ong, H. R. Tan, W. R. Webb, R. Raja, Y.-F. Lim, *J. Mater. Chem. A*, 2016, **4**, 9744.
- 21 C. Ouyang, X. Wang, C. Wang, X. Zhang, J. Wu, Z. Ma, S. Dou, S. Wang, *Acta Electron.*, 2015, **174**, 297.
- 22 J. Tian, Q. Liu, A. M. Asiri, X. Sun, *J. Am. Chem. Soc.*, 2014, **136**, 7587.

- 23 J. Li, M. Yan, X. Zhou, Z.-Q. Huang, Z. Xia, C.-R. Chang, Y. Ma, Y. Qu, *Adv. Funct. Mater.*, 2016, **26**, 6785.
- 24 C. Tang, N. Cheng, Z. Pu, W. Xing, X. Sun, *Angew. Chem. Int. Ed.*, 2015, **54**, 9351.
- 25 N. Jiang, B. You, M. Sheng, Y. Sun, *Angew. Chem. Int. Ed.*, 2015, **54**, 6251.
- 26 C. Wang, J. Jiang, T. Ding, G. Chen, W. Xu, Q. Yang, *Adv. Mater. Interfaces*, 2016, **3**, 1500454.
- 27 X. Gao, H. Zhang, Q. Li, X. Yu, Z. Hong, X. Zhang, C. Liang, Z. Lin, *Angew. Chem. Int. Ed.*, 2016, **55**, 6290.