## Molybdenum-doped $Co_3S_4$ nanoarrys as outstanding catalyst for overall water splitting



Fig. S1 The photograph of bare NF, Co-MOF/NF, Co<sub>3</sub>S<sub>4</sub>/NF, and Mo-Co<sub>3</sub>S<sub>4</sub>-0.1/NF.



Fig. S2 XRD pattern of Co-MOF.



**Fig. S3** SEM image of (a, b) bare NF.



Fig. S4 High resolution of XPS spectra of Mo-Co $_3S_4$ -X/NF: (a)Co2p, (b)Co2p $_{3/2}$ , (c)S2p.



Fig. S5 SEM image of (a,c) Mo-Co<sub>3</sub>S<sub>4</sub>-0.05/NF and (b,d) Mo-Co<sub>3</sub>S<sub>4</sub>-0.15/NF.



Fig. S6 LSV of the Mo-Co<sub>3</sub>S<sub>4</sub>-0.1/NF before and after 1000 CV cycles (a) HER and (b) OER.



Fig. S7 The LSV curves of HER performance for the Mo-Co<sub>3</sub>S<sub>4</sub>-0.05/NF, Mo-Co<sub>3</sub>S<sub>4</sub>-0.10/NF and Mo-Co<sub>3</sub>S<sub>4</sub>-0.15/NF. (b)The Nyquist plots of the Mo-Co<sub>3</sub>S<sub>4</sub>-0.05/NF, Mo-Co<sub>3</sub>S<sub>4</sub>-0.10/NF and Mo-Co<sub>3</sub>S<sub>4</sub>-0.15/NF.



Fig. S8 The LSV curves of OER performance for the Mo-Co<sub>3</sub>S<sub>4</sub>-0.05/NF, Mo-Co<sub>3</sub>S<sub>4</sub>-0.10/NF and Mo-Co<sub>3</sub>S<sub>4</sub>-0.15/NF. (b)The Nyquist plots of the Mo-Co<sub>3</sub>S<sub>4</sub>-0.05/NF, Mo-Co<sub>3</sub>S<sub>4</sub>-0.10/NF and Mo-Co<sub>3</sub>S<sub>4</sub>-0.15/NF measured in 1.0 M KOH.



Fig. S9 Cyclic voltammetry curves at different scan rates under for (a) Mo-Co<sub>3</sub>S<sub>4</sub>-0.05/NF, (b) Mo-Co<sub>3</sub>S<sub>4</sub>-0.15/NF and (c) Mo-Co<sub>3</sub>S<sub>4</sub>-0.10/NF under overpotential from 0 to 0.1 V vs. RHE. (d) the C<sub>dl</sub> values calculated from current densities vs scan rates.

<b>Table S1.</b> ICP-OES data of Mo-Co <sub>3</sub> S <sub>4</sub> - 0.1/NF.Samples	Sample element content (wt %)		
	Со	Mo	S
Mo-Co <sub>3</sub> S <sub>4</sub> -0.1/NF	29.34	3.75	32.47
	29.39	3.73	32.60

Samples	Sample element content (wt %)		
	Со	Мо	S
Mo-Co <sub>3</sub> S <sub>4</sub> -0.1/NF	29.06	3.15	30.49
	29.08	3.13	30.57

## Table S2. ICP-OES data of Mo-Co $_3S_4$ -0.1/NF after HER test.

## Table S3. ICP-OES data of Mo-Co $_3S_4$ -0.1/NF after OER test.

Samples	Sample element content (wt %)		
	Со	Мо	S
Mo-Co <sub>3</sub> S <sub>4</sub> -0.1/NF	29.15	2.53	14.15
	29.17	2.49	14.33



Figure.S10 SEM image of Mo-Co $_3S_4$ -0.1/NF after long-time test for HER.



**Figure.S11** SEM image of Mo-Co<sub>3</sub>S<sub>4</sub>-0.1/NF after long-time test for OER.



**Figure.S12** The high-resolution XPS spectra of (a) Co 2p, (b) S 2p, and (c) Mo 3d of the Mo-Co<sub>3</sub>S<sub>4</sub>-0.1/NF before and after HER test.



**Figure.S13** The high-resolution XPS spectra of (a) Co 2p, (b) S 2p, and (c) Mo 3d of the Mo-Co<sub>3</sub>S<sub>4</sub>-0.1/NF before and after OER test.

Samples	HER	ref
	Overpotential/Current	
	density (mV/mA cm <sup>-</sup>	
	2)	
Mo-Co <sub>3</sub> S <sub>4</sub> -0.1/NF	154/10	This work
Ni <sub>3</sub> S <sub>2</sub> /Co <sub>3</sub> S <sub>4</sub> /FeOOH@NF	158/10	1
CoMoP/Co <sub>3</sub> O <sub>4-x</sub> @NF	174/10	2
Co@Co-P@NPCNTs	160/10	3
$Co_9S_8@Co_9S_8@MoS_{2-x}$	173/10	4
Co-Ni <sub>3</sub> N	194/10	5
CoNiMo/NPC	182/10	6
Ce-doped	188/10	7
CoMoP/MoP@C		

**Table S4.** Comparison of the HER activity over  $Mo-Co_3S_4-0.1/NF$  with several Co-based electrocatalysts in alkaline media.

## **References:**

1. Chen Fan, Xiaoping Shen, Jia Cheng, Leiming Lang, Guangxiang Liu, Zhenyuan Ji and Guoxing Zhu, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2021, **631**, 127689.

2. Yawen Hao, Gaohui Du, Yi Fan, Lina Jia, Di Han, Wenqi Zhao, Qingmei Su, Shukai Ding and Bingshe Xu, *ACS APPL MATER INTER*, 2021, **13**, 55263-55271.

3. Jiqing Jiao, Wenjuan Yang, Yuan Pan, Chao Zhang, Shoujie Liu, Chen Chen and Dingsheng Wang, *SMALL*, 2020, **16**, 2002124.

4. Jing Li, Guangshe Li, Jianghao Wang, Chenglin Xue, Xiangshuai Li, Shuo Wang, Bingqi Han, Min Yang and Liping Li, *INORG CHEM FRONT*, 2020, **7**, 191-197.

 Changrong Zhu, An-Liang Wang, Wen Xiao, Dongliang Chao, Xiao Zhang, Nguyen Huy Tiep, Shi Chen, Jiani Kang, Xin Wang, Jun Ding, John Wang, Hua Zhang and Hong Jin Fan, *ADV MATER*, 2018, 30, 1705516.

6. Xiaobing Yang, Weisen Yang, Xingping Fu, Jiapeng Hu and Juan Chen, *INT J HYDROGEN ENERG*, 2021, **46**, 18318-18325.

7. Tianyun Chen, Yingyan Fu, Wenhao Liao, Yaqi Zhang, Min Qian, Haojiang Dai, Xianfeng Tong and Qinghua Yang, *ENERG FUEL*, 2021, **35**, 14169-14176.