

**Heterostructured ZnCo<sub>2</sub>O<sub>4</sub>-CoOOH nanosheets on Ni foam  
for a high performance bifunctional alkaline  
water splitting catalyst**

Congli Wang,<sup>a</sup> Hongfang Jiu,<sup>\*a</sup> Lixin Zhang,<sup>\*b,c</sup> Wei Song,<sup>c</sup> Yufang Zhang,<sup>a</sup> Hao  
Wei,<sup>a</sup> Qianwen Xu,<sup>a</sup> Yaqi Qin,<sup>a</sup> Sicong Che,<sup>a</sup> and Zhixin Guo,<sup>c</sup>

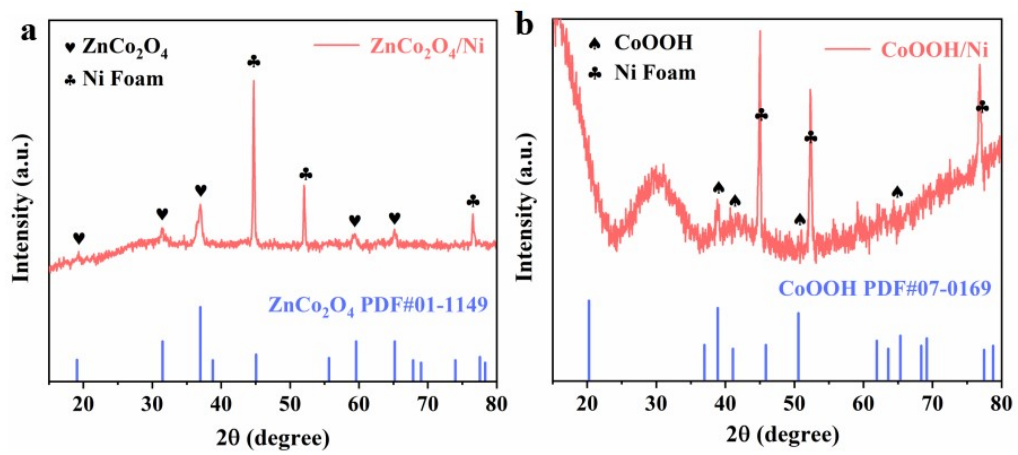
<sup>a</sup> School of Science, North University of China, Taiyuan, 030051, People's Republic  
of China

<sup>b</sup> Shanxi Key Laboratory of High Performance Battery Materials and Devices, North  
University of China, Taiyuan, 030051, People's Republic of China

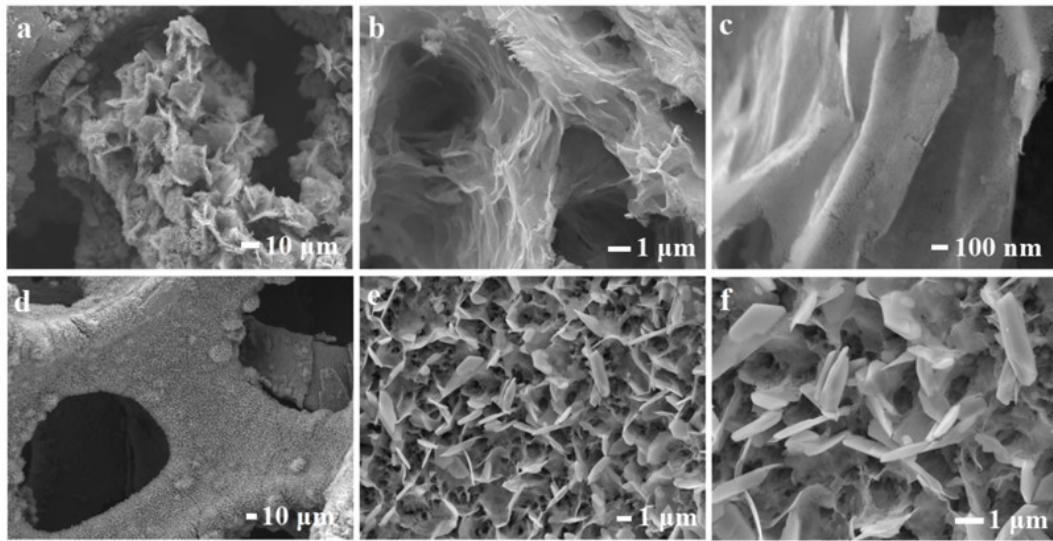
<sup>c</sup> School of Chemical Engineering and Technology, North University of China,  
Taiyuan, 030051, People's Republic of China

\* Corresponding author.

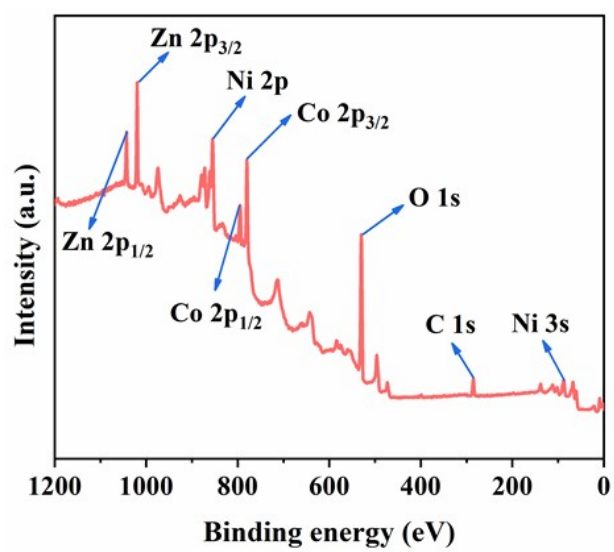
E-mail address: hongfangjiu@163.com (H. F. Jiu), edwardzlx@163.com (L. X.  
Zhang).



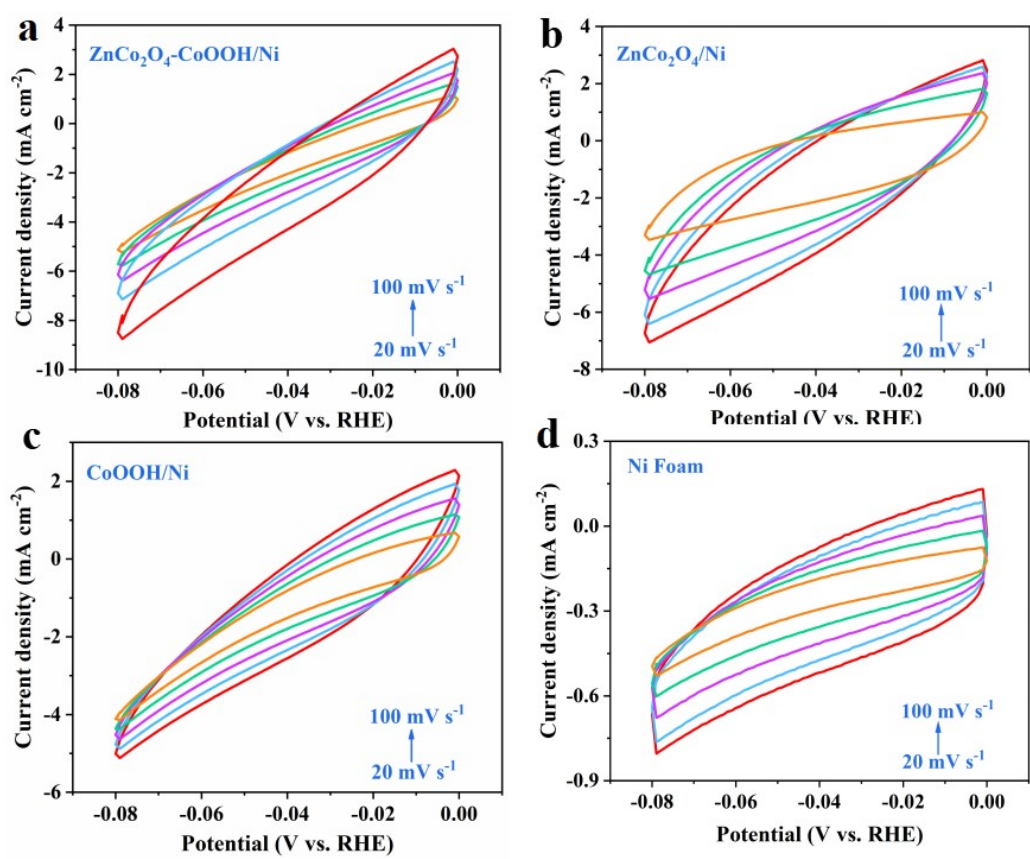
**Fig. S1.** XRD modes of (a) ZnCo<sub>2</sub>O<sub>4</sub>/Ni, (b) CoOOH/Ni.



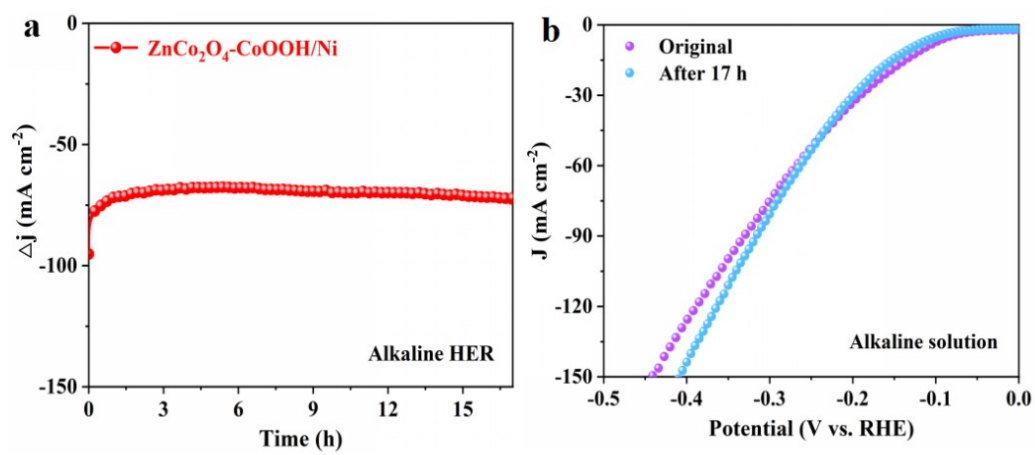
**Fig. S2.** SEM images of (a-c) ZnCo<sub>2</sub>O<sub>4</sub>/Ni, (d-f) CoOOH/Ni.



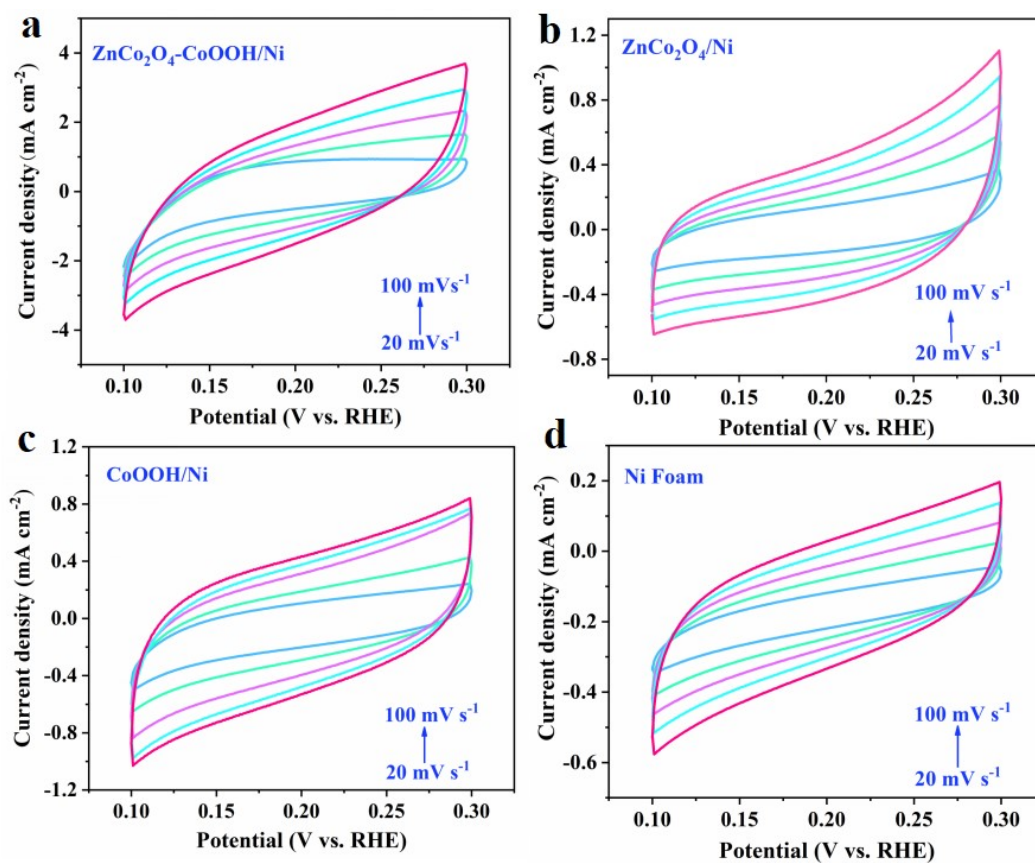
**Fig. S3.** XPS survey.



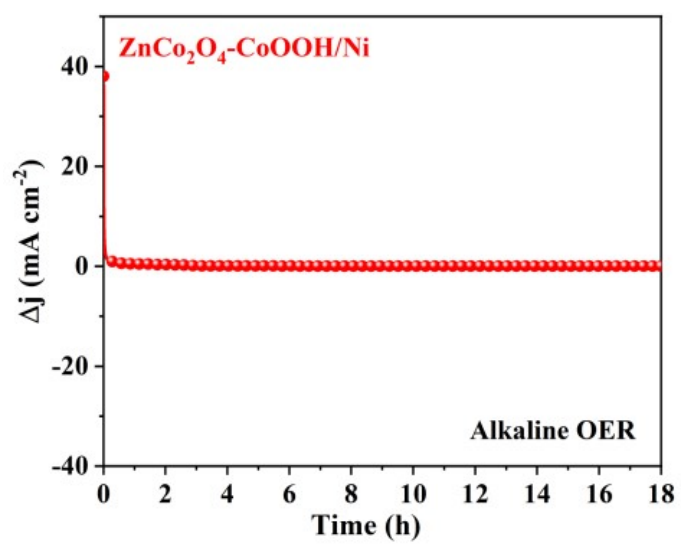
**Fig. S4.** CV curves of (a) ZnCo<sub>2</sub>O<sub>4</sub>-CoOOH/Ni, (b) ZnCo<sub>2</sub>O<sub>4</sub>/Ni, (c) CoOOH/Ni, (d) Ni Foam for HER.



**Fig. S5.** (a)  $I$ - $t$ , (b) LSV curves of the original and after 17 h.

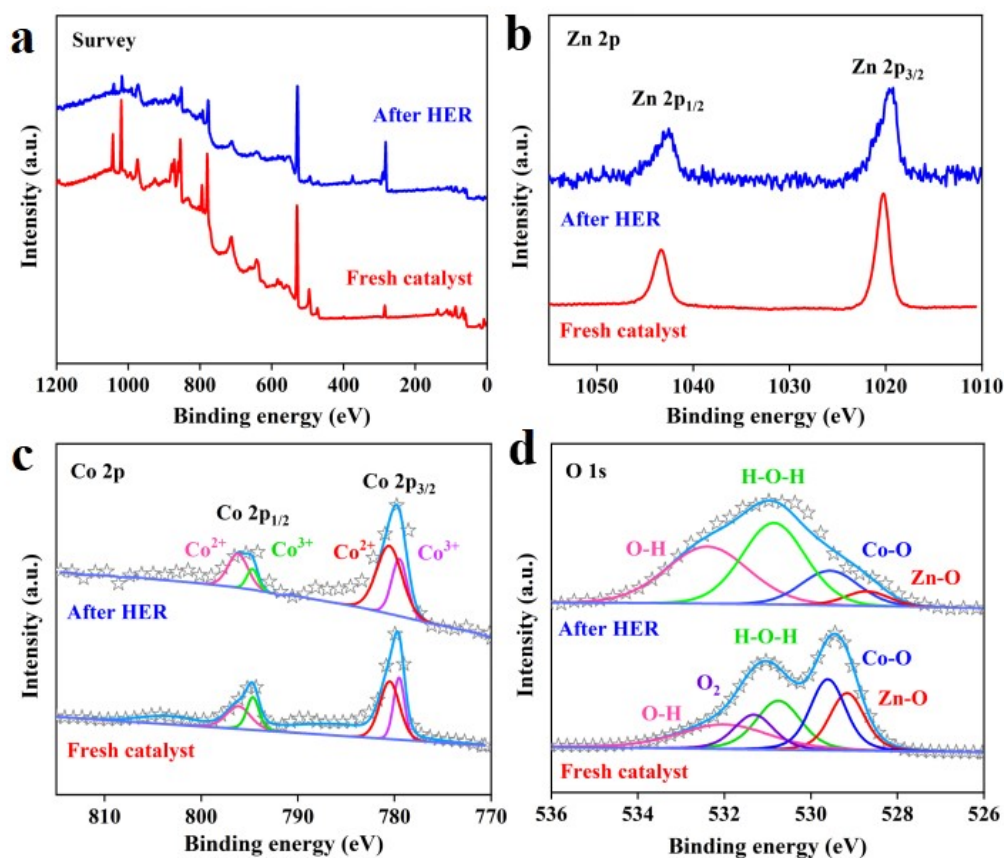


**Fig. S6.** CV curves of (a) ZnCo<sub>2</sub>O<sub>4</sub>-CoOOH/Ni, (b) ZnCo<sub>2</sub>O<sub>4</sub>/Ni, (c) CoOOH/Ni, (d) Ni Foam for OER.



**Fig. S7.** *I*-*t* test for OER.

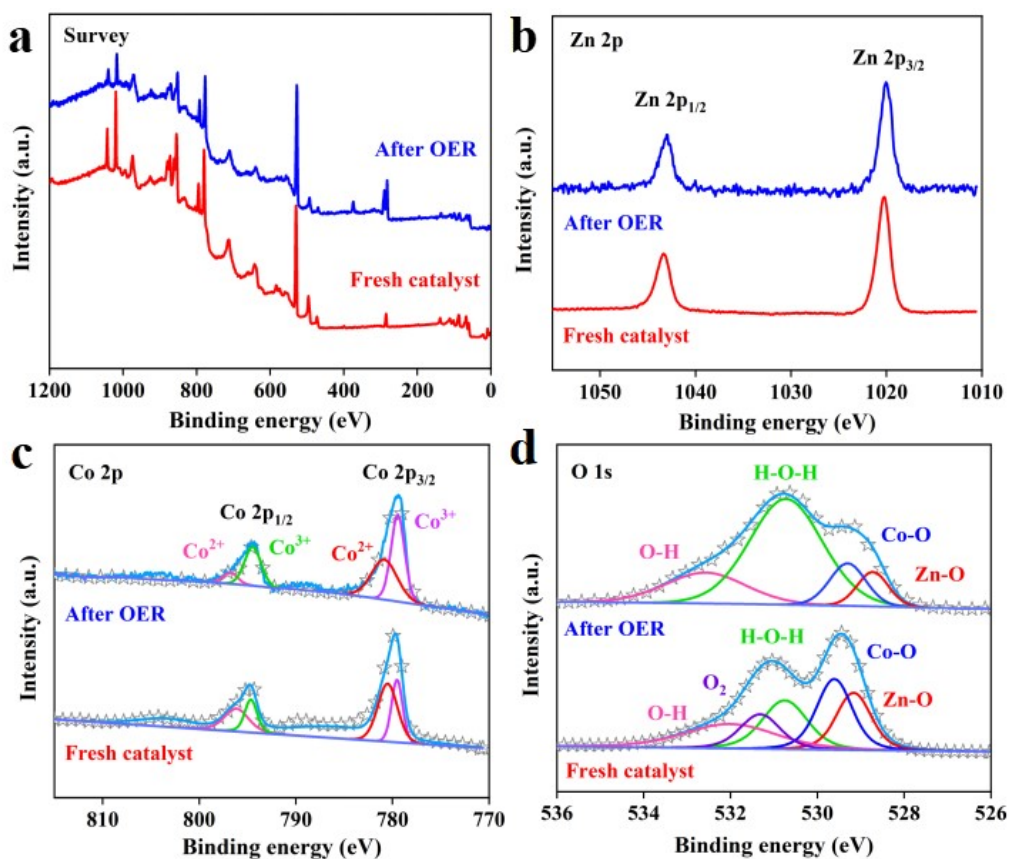




**Fig. S8.** XPS of ZnCo<sub>2</sub>O<sub>4</sub>-CoOOH/Ni fresh and recovered for HER reaction.

Meanwhile, XPS data are subsequently employed to further study the changes in the value states of ZnCo<sub>2</sub>O<sub>4</sub>-CoOOH/Ni after HER process. Importantly, the full XPS spectrum of ZnCo<sub>2</sub>O<sub>4</sub>-CoOOH/Ni has no obvious change before and after HER reactions (Fig. S8a). After HER measurement, the peak of Zn 2p presents a slight negative shift compared to the fresh catalyst (0.5 eV) (Fig. S8b). The negative shift shows the enhanced electron occupation, which can give rise to the improvement of the electron-donating ability of the catalyst.<sup>1</sup> This may be because its special ZnCo<sub>2</sub>O<sub>4</sub>-CoOOH heterostructure can optimize the electronic structure. The synergistic effect between ZnCo<sub>2</sub>O<sub>4</sub> and CoOOH can realize the optimization of the electronic structure of the catalyst surface, which in turn optimizes the adsorption ability to intermediate during HER process and further enhances the catalytic activity.<sup>2</sup> The surface of the catalyst is dominated by Co<sup>2+</sup> after HER.<sup>3</sup> After HER test,

the O 1s peak can be only deconvoluted into four components: Zn-O, Co-O, H<sub>2</sub>O, OH<sup>-</sup> (Fig. S8d). Compared to the fresh ZnCo<sub>2</sub>O<sub>4</sub>-CoOOH/Ni, all M-O (M=metal) species in the product express negative shift after HER. And the electronic structure of active sites could be greatly optimized and the catalytic performance of catalyst may be improved due to the presence of heterointerface.<sup>4</sup> The enhancement of the activities may arise from massive active sites, the accelerated charge transfer and optimal adsorption ability of intermediates originating from the synergistic effect of heterostructure, all of which result in better reaction kinetics and thus improving the catalytic activities.<sup>5</sup> Thus, the hydroxides offer active sites for water dissociation and the generated H\* intermediates are then adsorbed on the nearby catalyst, which are favoring the formation of H\* (H<sup>+</sup> + e<sup>-</sup>=H\*), and subsequent combination (H\* + H\* =H<sub>2</sub>), resulting in an improved catalytic activity.<sup>6</sup>



**Fig. S9.** XPS of ZnCo<sub>2</sub>O<sub>4</sub>-CoOOH/Ni fresh and recovered for OER reaction.

The surface chemistry of the post-OER material is also studied by XPS. It can be seen the presence of respective elements (Fig. S9a). As shown in Fig. S9b, the position of the Zn 2p XPS peak shows no clear difference after OER reaction. As shown in Fig. S9c, the surface of the catalyst is dominated by Co<sup>3+</sup> after OER.<sup>7</sup> The Co<sup>3+</sup> specie plays a vital role in the improvement of surface electrochemical activities, which is helpful for reducing the energy barrier in the formation of -OH\* and -OOH\* intermediates during OER process and boosting catalytic activity.<sup>8</sup> After OER test, the O 1s peak is consistent with HER. The M-O (M=metal) species express negative migration, which is consistent with the negative shift of HER. However, a more serious shift degree happened on the OER progress. This can be attributed to the formation of the heterostructure and it can greatly optimize the electronic structure to enhance OER catalytic performance. In addition, the optimization of electronic

structure is also ascribed to the synergistic effect between  $\text{ZnCo}_2\text{O}_4$  and  $\text{CoOOH}$ .<sup>9</sup> Therefore, it can be inferred that the formed M-OH/OOH on the surface of  $\text{ZnCo}_2\text{O}_4$ - $\text{CoOOH}/\text{Ni}$  heterostructure worked as the real active sites during the water splitting reaction.<sup>10</sup>

**Table. S1.** Comparison of HER performance with reported electrocatalysts in alkaline media.

Catalyst	J (mA cm <sup>-2</sup> )	$\eta$ (mV)	Tafel slope (mV dec <sup>-1</sup> )	Stability test	Ref.
ZnCo <sub>2</sub> O <sub>4</sub> -CoOOH/Ni	10	115	75.1	17 h	This work
Pt/C	10	29	66	1000 CV cycles	11
Co <sub>0.75</sub> Mo <sub>0.25</sub> Sx	10	130	87	10 h	12
ZnCo <sub>2</sub> O <sub>4</sub> @PPy-50	10	133	62.4	10 h	13
Ni/Co <sub>3</sub> O <sub>4</sub>	10	145	83	12 h	14
Co <sub>1</sub> Fe <sub>1</sub> Mo <sub>1.8</sub> O NMs@NF	10	157	112	24 h	15
CuCo <sub>2</sub> S <sub>4</sub>	10	167	139	-	16
Co <sub>2</sub> P/NPSC-800	10	173	106.52	35 h	17
NiCo <sub>2</sub> Se <sub>4</sub> /NiCoS <sub>4</sub>	10	180	156.1	12 h	18
CoNiMn/NC	10	191	64.38	14 h	19
NiCoV-LTH/NF	10	213	142	20 h	20

**Table. S2.** Comparison of OER performance with reported electrocatalysts in alkaline media.

Catalyst	J (mA cm <sup>-2</sup> )	$\eta$ (mV)	Tafel slope (mV dec <sup>-1</sup> )	Stability test	Ref.
ZnCo <sub>2</sub> O <sub>4</sub> -CoOOH/Ni	20	238	62.53	18 h	This work
Co <sub>3</sub> O <sub>4</sub> -CoOOH/CP	10	245	68.8	20 h	21
FeCoOOH	10	252	61.8	40 h	22
NiCo-LDH/ZnCo <sub>2</sub> O <sub>4</sub>	10	260	105.2	25000 s	23
IrO <sub>2</sub>	10	272	59	45 h	24
RuO <sub>2</sub>	10	287	86.8	30 h	25
Co/PANI HNSs	10	291	54	20 h	26
ZnCo <sub>2</sub> O <sub>4</sub> @FeOOH	10	299	69	15 h	27
B-CoOOH	10	330	75.4	10 h	28
Co <sub>2</sub> P NP	10	364	52	20 h	29
ZnCo <sub>2</sub> O <sub>4</sub> @ZnCo-LDH-1000	10	365	73	2000 CV circulations	30
ZnCo <sub>2</sub> O <sub>4</sub>	10	389	61.84	7200 s	31

**Table. S3.** Comparison of Overall water performance with reported electrocatalysts in alkaline media.

Catalyst	Scan rate (mV s <sup>-1</sup> )	J (mA cm <sup>-2</sup> )	Potential (V)	Stability test	Ref.
ZnCo <sub>2</sub> O <sub>4</sub> -CoOOH/Ni	5	10	1.494	22 h	This work
A-CoMoO <sub>4</sub>	1	10	1.51	25 h	32
NiMo/NiCo <sub>2</sub> O <sub>4</sub>	1	10	1.54	50 h	33
Co <sub>3</sub> O <sub>4</sub> @Ni <sub>2</sub> P	5	10	1.563	177 h 2 h per cycle	34
Mn <sub>3</sub> O <sub>4</sub> /CoP PNRs	5	10	1.599	20 h	35
NiCoP-0.01 M Fe	2	10	1.60	12 h	36
Pt/C    RuO <sub>2</sub>	5	10	1.61	-	37
Pt/C & NF    IrO <sub>2</sub> & NF	5	10	1.614	-	38
CoFe <sub>2</sub> O <sub>4</sub> /CoO	5	10	1.614	200000 sec	39
Co <sub>3</sub> S <sub>4</sub> /CeO <sub>2</sub> -CF	5	10	1.64	80 h	40
CoNi <sub>2</sub> S <sub>4</sub> /Ni <sub>3</sub> S <sub>2</sub>	5	10	1.65	10 h	41
CoMo@NC-800	5	10	1.67	Over 8 h	42

## References

- [1] W. Zhang, N. Han, J. Luo, X. Han, S. Feng, W. Guo, S. Xie, Z. Zhou, P. Subramanian, K. Wan, J. Arbiol, C. Zhang, S. Liu, M. Xu, X. Zhang and J. Fransaer, *Small*, 2022, **18**, 2103561.
- [2] H. Zhang, A. W. Maijenburg, X. Li, S. L. Schweizer and R. B. Wehrspohn, *Adv. Funct. Mater.*, 2020, **30**, 2003261.
- [3] D. Xu, J. Yao, X. Ma, Y. Xiao, C. Zhang, W. Lin and H. Gao, *J. Colloid Interface Sci.*, 2022, **619**, 298-306.
- [4] C.-F. Li, L.-J. Xie, J.-W. Zhao, L.-F. Gu, J.-Q. Wu and G.-R. Li, *Appl. Catal. B*, 2022, **306**, 121097.
- [5] T. Wu, E. Song, S. Zhang, M. Luo, C. Zhao, W. Zhao, J. Liu and F. Huang, *Adv. Mater.*, 2022, **34**, 2108505.
- [6] X. Yu, J. Zhao and M. Johnsson, *Adv. Funct. Mater.*, 2021, **31**, 2101578.
- [7] L. C. Seitz, D. Nordlund, A. Gallo and T. F. Jaramillo, *Electrochim. Acta*, 2016, **193**, 240-245.
- [8] W. Hu, Q. Liu, T. Lv, F. Zhou and Y. Zhong, *Electrochim. Acta*, 2021, **381**, 138276.
- [9] J. Yao, D. Xu, X. Ma, J. Xiao, M. Zhang and H. Gao, *J. Power Sources*, 2022, **524**, 231068.
- [10] H. Su, S. Song, S. Li, Y. Gao, L. Ge, W. Song, T. Ma and J. Liu, *Appl. Catal. B*, 2021, **293**, 120225.
- [11] G. Zhou, G. Liu, X. Liu, Q. Yu, H. Mao, Z. Xiao and L. Wang, *Adv. Funct. Mater.*, 2022, **32**, 2107608.
- [12] A. Mukherji, R. Bal and R. Srivastava, *ChemElectroChem*, 2020, **7**, 2740-2751.
- [13] X. Liu, Q. Li, Y. Qin and Y. Jiang, *RSC Adv.*, 2020, **10**, 28324-28331.
- [14] M. S. Riaz, S. Zhao, C. Dong, M. J. Iqbal, Y. Zhao and F. Huang, *Energy Technol.*, 2020, **8**, 1901310.
- [15] L. Pei, Y. Song, M. Song, P. Liu, H. Wei, B. Xu, J. Guo and J. Liang,



- Electrochim. Acta*, 2021, **368**, 137651.
- [16] X. Xu, Z. Huang, C. Zhao, X. Ding, X. Liu, D. Wang, Z. Hui, R. Jia and Y. Liu, *Ceram. Int.*, 2020, **46**, 13125-13132.
- [17] Y. Li, M. Cui, T. Li, Y. Shen, Z. Si and H.-g. Wang, *Int. J. Hydrogen Energy*, 2020, **45**, 16540-16549.
- [18] K. Wang, Z. Lin, Y. Tang, Z. Tang, C.-L. Tao, D.-D. Qin and Y. Tian, *Electrochim. Acta*, 2021, **368**, 137584.
- [19] B. Jiang and Z. Li, *J. Solid State Chem.*, 2021, **295**, 121912.
- [20] Q. Liu, J. Huang, D. Yang, Y. Feng, G. Li, X. Zhang, Y. Zhang, G. Xu and L. Feng, *Dalton Trans.*, 2021, **50**, 72-75.
- [21] L. Yan and B. Zhang, *Int. J. Hydrogen Energy*, 2021, **46**, 34287-34297.
- [22] J. Lv, X. Guan, Y. Huang, L. Cai, M. Yu, X. Li, Y. Yu and D. Chen, *Nanoscale*, 2021, **13**, 15755-15762.
- [23] M. Shamloofard, S. Shahrokhian and M. K. Amini, *J. Colloid Interface Sci.*, 2021, **604**, 832-843.
- [24] L. Li, H. Sun, Z. Hu, J. Zhou, Y.-C. Huang, H. Huang, S. Song, C.-W. Pao, Y.-C. Chang, A. C. Komarek, H.-J. Lin, C.-T. Chen, C.-L. Dong, J.-Q. Wang and L. Zhang, *Adv. Funct. Mater.*, 2021, **31**, 2104746.
- [25] B. Wang, Y. Ye, L. Xu, Y. Quan, W. Wei, W. Zhu, H. Li and J. Xia, *Adv. Funct. Mater.*, 2020, **30**, 2005834.
- [26] X. Chen, Y. Chen, Z. Shen, C. Song, P. Ji, N. Wang, D. Su, Y. Wang, G. Wang and L. Cui, *Appl. Surf. Sci.*, 2020, **529**, 147173.
- [27] Z. Yu, Y. Bai, N. Zhang, W. Yang, J. Ma, Z. Wang, W. Sun, J. Qiao and K. Sun, *J. Alloys Compd.*, 2020, **832**, 155067.
- [28] C. Meng, M. Lin, X. Sun, X. Chen, X. Chen, X. Du and Y. Zhou, *Chem. Commun.*, 2019, **55**, 2904-2907.
- [29] B. T. Jebaslinhepzybai, T. Partheeban, D. S. Gavali, R. Thapa and M. Sasidharan, *Int. J. Hydrogen Energy*, 2021, **46**, 21924-21938.

- [30] J. Pan, F. Wang, L. Zhang, S. Song and H. Zhang, *Inorg. Chem. Front.*, 2019, **6**, 220-225.
- [31] D. Zhang, Z. Wang, J. Li, C. Hu, X. Zhang, B. Jiang, Z. Cao, J. Zhang and R. Zhang, *RSC Adv.*, 2020, **10**, 9063-9069.
- [32] L. Ge, W. Lai, Y. Deng, J. Bao, B. Ouyang and H. Li, *Inorg. Chem.*, 2022, **61**, 2619-2627.
- [33] H. Chen, S. Qiao, J. Yang and X. Du, *Mol. Catal.*, 2022, **518**, 112086.
- [34] X. Hu, T. Yang, Z. Yang, Z. Li, R. Wang, M. Li, G. Huang, B. Jiang, C. Xu and F. Pan, *J Mater Sci Technol*, 2022, **115**, 19-28.
- [35] R. Dong, A. Zhu, W. Zeng, L. Qiao, L. Lu, Y. Liu, P. Tan and J. Pan, *Appl. Surf. Sci.*, 2021, **544**, 148860.
- [36] S. Kan, M. Xu, W. Feng, Y. Wu, C. Du, X. Gao, Y. A. Wu and H. Liu, *ChemElectroChem*, 2021, **8**, 539-546.
- [37] G. Wang, G. Zhang, X. Ke, X. Chen, X. Chen, Y. Wang, G. Huang, J. Dong, S. Chu and M. Sui, *Small*, 2022, **18**, 2107238.
- [38] K. Wang, H. Du, S. He, L. Liu, K. Yang, J. Sun, Y. Liu, Z. Du, L. Xie, W. Ai and W. Huang, *Adv. Mater.*, 2021, **33**, 2005587.
- [39] K. Srinivas, Y. Chen, Z. Su, B. Yu, M. Karpuraranjith, F. Ma, X. Wang, W. Zhang and D. Yang, *Electrochim. Acta*, 2022, **404**, 139745.
- [40] Z. Feng, J. Pu, M. Liu, W. Zhang, X. Zhang, L. Cui and J. Liu, *J. Colloid Interface Sci.*, 2022, **613**, 806-813.
- [41] W. Dai, K. Ren, Y.-a. Zhu, Y. Pan, J. Yu and T. Lu, *J. Alloys Compd.*, 2020, **844**, 156252.
- [42] R. Ge, J. Huo, Y. Li, T. Liao, J. Zhang, M. Zhu, T. Ahamad, S. Li, H. Liu, L. Feng and W. Li, *J. Alloys Compd.*, 2022, **904**, 164084.