Electronic Supplementary Information

One-step hydrothermal synthesis of cobalt-vanadium based nanocomposites as bifunctional catalysts for overall water splitting

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Fig. S1. EDS patterns of $Co_{0.2}$ -VOOH, inset shows the corresponding element ratio.



Fig. S2. The morphology adjustment with the different content of cobalt doping. SEM images of (a) pure VOOH, (b) $Co_{0.1}$ -VOOH, (c) $Co_{0.2}$ -VOOH, and (d) $Co_{0.3}$ -VOOH.



Fig. S3. AFM image of $Co_{0.3}$ -VOOH and corresponding height profile.



Fig. S4. FT-IR spectra of VOOH and $Co_{0.2}$ -VOOH.



Fig. S5. (a) XRD pattern, (b) SEM image, (c) TEM image, (d) elemental maps of the $Co_{0,2}$ -VOOH electrocatalyst after long-time OER process.



Fig. S6. XPS spectrum of the $Co_{0,2}$ -VOOH electrocatalyst after long-time OER process.



Fig. S7. High-resolution XPS spectra of a) V 2p and b) Co 2p for $Co_{0,2}$ -VOOH after OER and HER process, respectively.



Fig. S8. Cyclic voltammograms of a) pure VOOH, b) $Co_{0.1}$ -VOOH, c) $Co_{0.2}$ -VOOH, and d) $Co_{0.3}$ -VOOH with various scan rates in 1.0 M KOH.



Fig. S9. Nyquist plots of various catalysts toward OER. Inset: relevant equivalent electric circuit.



Fig. S10. a) XRD pattern, b) SEM image, c) TEM image, d) elemental maps of the $Co_{0,2}$ -VOOH electrocatalyst after long-time HER process.



Fig. S11. XPS spectrum of the $Co_{0.2}$ -VOOH electrocatalyst after long-time HER process.



Fig. S12. Polarization curves of $Co_{0,2}$ -VOOH before and after the overall water splitting stability test.

Catalyst	V (wt%)	Co (wt%)	Molar radio
VOOH	34.72	-	-
Co _{0.1} -VOOH	33.96	3.69	1:0.09
Co _{0.2} -VOOH	33.91	8.15	1:0.21
Co _{0.3} -VOOH	33.29	11.63	1:0.30

Table S1. Mass ratios of V and Co of various catalysts obtained from ICP-OES.

Catalyst	Substrate	Catalyst loading (mg cm ⁻²)	Tafel Slope (mV dec ⁻¹)	Overpotential at 10 mA cm ⁻² (mV)	Ref.
Co _{0.2} -VOOH	Carbon cloth	0.5	30.8	210	This work
Mo-doped CoP	Carbon cloth	2.5	56	305	1
CoO/Co(OH) ₂	Carbon cloth	-	142	340	2
(Ni _{0.33} Co _{0.67})S ₂ NWs	Carbon cloth	-	78	334	3
CoNi/CoNiO2@NC	Carbon cloth	2	63	181	4
CoMnP	Glassy carbon	0.284	61	330	5
Ni _{0.75} V _{0.25} LDH	Glassy carbon	0.143	50	318	6
Ni ₂ P NPs	Glassy carbon	0.14	47	290	7
Co ₃ O ₄	Glassy carbon	0.35	62	408	8
Co(OH) ₂	Glassy carbon	0.35	58	360	9
NiPS ₃ @NiOOH	Glassy carbon	0.382	80	225*	10
MoO ₂	Ni foam	2.9	54	260	11
Fe _x N	Ni foam	4	44.5	238	12
NiSe	Ni foam	2.8	64	250	13
VOOH	Ni foam	0.8	68	270	14
CoFePO	Ni foam	2.187	51.7	274.5	15
NiFe-NS	Ni foam	0.07	40	302	16
$Fe(PO_3)_2$	Ni foam	8	51.9	177	17
Fe doped CoP	Ti foil	1.03	67	230	18
Co-P film	Cu foil	2.6	47	345	19

Table S2. Comparison of the OER performance for the $Co_{0,2}$ -VOOH catalyst in this work with reported non-noble OER electrocatalysts in 1.0 M alkaline medium.

* The value is estimated from the curves displayed in the references.

Catalyst	Substrate	Catalyst loading (mg cm ⁻²)	Tafel Slope (mV dec ⁻¹)	Overpotential at 10 mA cm ⁻² (mV)	Ref.
Co _{0.2} -VOOH	Carbon cloth	0.5	58.2	130	This work
V-doped WS ₂	Carbon cloth	-	85	134	20
Fe-doped CoP	Carbon cloth	-	69	98	21
Ni-Co-P	Carbon cloth	0.27	69	57	22
CNTs@CoS _x Se _{2(1-x)}	Carbon cloth	0.81	96	225	23
Fe-doped Co ₉ S ₈	Carbon cloth	95.3	83	95.3	24
c-CoSe ₂	Carbon cloth	-	85	190	25
CP/CTs/Co-S	Carbon paper	0.32	131	190	26
Co@NG	Carbon paper	1	112	220	27
NiCoP/rGO	Carbon fiber	0.15	124.1	209	28
Ni-Co-P	Glassy carbon	0.286	60	150	29
Ni@NC-800	Glassy carbon	0.8	160	205	30
MoC/Mo ₂ C	Glassy carbon	0.14	42	120	31
VOOH	Ni foam	0.8	104	164	14
Ni _{2.5} Co _{0.5} Fe	Ni foam	0.3	93	275	32
Janus Co/CoP	Ni foam	0.22	73.8	193	33
Ni ₃ FeN/rGO	Ni foam	0.5	90	94	34
CoO _x @CN	Ni foam	0.42	115	232	35
Co ₃ O ₄ microtube	Ni foam	-	98	190*	36
Ni _{0.9} Fe _{0.1} /NC	Ni foam	2	111	231	37
NiFe/NiCo ₂ O ₄	Ni foam	-	88	105	38
Cu@NiFe LDH	Cu foam	2.2	58.9	116	39

Table S3. Comparison of the HER performance for the $Co_{0,2}$ -VOOH catalyst in this work with reported non-noble HER electrocatalysts in 1.0 M alkaline medium.

* The value is estimated from the curves displayed in the references.

Table S4. Comparison of the bifunctional water splitting activity of the $Co_{0,2}$ -VOOH catalyst in this work with other reported bifunctional electrocatalysts in 1.0 M alkaline medium.

		Catalyst	Current	Voltage at the	
Catalyst	Substrate	loading	density	corresponding j	Ref.
		$(mg cm^{-2})$	$(j \text{ mA cm}^{-2})$	(V)	
Co _{0.2} -VOOH	Carbon cloth	0.5	10	1.57	This work
			100	1.74	
			200	1.80	
Mo-doped CoP	Carbon cloth	2.5	10	1.56	1
			100	1.6*	
CNTs@CoS _x Se _{2(1-x)}	Carbon cloth	0.81	10	1.74	23
Ni-NiFe ₂ O ₄	Carbon cloth	-	10	1.57	40
CP/CTs/Co-S	Carbon paper	0.32	10	1.743	26
VOOH	Ni foam	0.8	10	1.62	14
			100	1.82*	
NiCoP	Ni foam	1.6	10	1.58	41
			100	1.82	
			200	1.98	
Ni@NC-800	Ni foam	0.8	10	1.60	30
			20	1.64	
Ni ₃ Se ₂	Ni foam	8.87	10	1.612	42
Ni ₂ P NPs	Ni foam	0.14	10	1.63	7
$Cu@CoS_x$	Cu foam	3.9	10	1.5	43
			100	1.8*	
Ni-Mo alloy	Cu foil	4.2	10	1.59	44
			100	1.9*	
Fe doped CoP	Ti foil	1.03	10	1.6	18
			60	1.73*	
Ni ₅ P ₄	Ni foil	0.35	10	1.7*	45

*The value is estimated from the curves displayed in the references.

References

- C. Guan, W. Xiao, H. Wu, X. Liu, W. Zang, H. Zhang, J. Ding, Y. P. Feng, S. J. Pennycook, J. Wang, *Nano Energy*. 2018, 48, 73.
- [2] K. Kordek, H. Yin, P. Rutkowski, H. Zhao, *Inter. J. Hydro. Energy.* 2019, 44, 23.
- [3] Q. Zhang, C. Ye, X. L. Li, Y. H. Deng, B. X. Tao, W. Xiao, L. J. Li, N. B. Li,
 H. Q. Luo, ACS Appl. Mater. Interfaces. 2018, 10, 27723.
- [4] Q. Zhang, X. L. Li, B. X. Tao, X. H. Wang, Y. H. Deng, X. Y. Gu, L. J. Li,
 W. Xiao, N. B. Li, H. Q. Luo, *Appl. Catal.*, *B: Environ.* 2019, 254, 634.
- [5] D Li, H. Baydoun, C. N. Verani, S. L. Brock, J. Am. Chem. Soc. 2016, 138, 4006.
- [6] K. Fan, H. Chen, Y. Ji, H. Huang, P. M. Claesson, Q. Daniel, B. Philippe, H. Rensmo, F. Li, Y. Luo, *Nat. Commun.* 2016, 7, 11981.
- [7] L. A. Stern, L. Feng, F. Song, X. Hu, *Energy Environ. Sci.* 2015, *8*, 2347.
- [8] J. Jiang, L. Huang, X. Liu, L. Ai, ACS Appl. Mater. Interfaces 2017, 9, 7193.
- [9] L. Huang, J. Jiang, L. Ai, ACS Appl. Mater. Interfaces 2017, 9, 7059.
- B. Konkena, J. Masa, A. J. R. Botz, I. Sinev, W. Xia, J. Koßmann, R. Drautz,
 M. Muhler, W. Schuhmann, ACS Catal. 2017, 7, 229.
- [11] Y. Jin, H. Wang, J. Li, X. Yue, Y. Han, P. K. Shen, Y. Cui, Adv. Mater. 2016, 28, 3785.
- [12] F. Yu, H. Zhou, Z. Zhu, J. Sun, R. He, J. Bao, S. Chen, Z. Ren, ACS Catal.
 2017, 7, 2052.
- [13] C. Tang, N. Cheng, Z. Pu, W. Xing, X. Sun, Angew. Chem. Int. Ed. 2015, 54, 9351.
- [14] H. Shi, H. Liang, F. Ming, Z. Wang, Angew. Chem. Int. Ed. 2017, 56, 573.
- [15] J. Duan, S. Chen, A. Vasileff, S. Z. Qiao, ACS Nano 2016, 10, 8738.
- [16] F. Song, X. Hu, Nat. Commun. 2014, 5, 4477.
- [17] H, Zhou, F. Yu, J. Sun, R. He, S. Chen, C. W. Chu, Z. Ren, *PNAS* 2017, *114*, 5607.

- [18] C. Tang, Ro. Zhang, W. Lu, L. He, X. Jiang, A. M. Asiri, X. Sun, *Adv. Mater*.
 2017, 29, 1602441.
- [19] N. Jiang, B. You, M. Sheng, Y. Sun, Angew. Chem. Int. Ed. 2015, 54, 6251.
- [20] A. Jiang, B. Zhang, Z. Li, G. Jin, J. Hao, *Chem. Asian J.* 2018, **13**, 1438.
- [21] E. Hu, J. Ning, D. Zhao, C. Xu, Y. Lin, Y. Zhong, Z. Zhang, Y. Wang, Y. Hu, Small. 2018, 14, 1704233.
- [22] Y. Tian, J. Yu, H. Zhang, C. Wang, M. Zhang, Z. Lin, J. Wang, *Electrochimica Acta*. 2019, 300, 217.
- [23] Y. Zhang, Y. Qiu, X. Ji, T. Ma, Z. Ma, P. A. Hu, *ChenSusChem*, 2019, DOI: 10.1002/cssc.201901628
- [24] K. Ao, D. Li, Y. Yao, P. Lv, Y. Cai, Q. Wei, *Electrochimica Acta*. 2018, 264, 157.
- [25] P. Chen, K. Xu, S. Tao, T. Zhou, Y. Tong, H. Ding, L. Zhang, W. Chu, C. Wu, Y. Xie, *Adv. Mater.* 2016, 28, 7527.
- [26] J. Wang, H. X. Zhong, Z. L. Wang, F. L. Meng, X. B. Zhang, ACS Nano 2016, 10, 2342.
- [27] M. Zeng, Y. Liu, F. Zhao, K. Nie, N. Han, X. Wang, W. Huang, X. Song, J. Zhong, Y. Li, *Adv. Funct. Mater.* 2016, *26*, 4397.
- [28] J. Li, M. Yan, X. Zhou, Z. Q. Huang, Z. Xia, C. R. Chang, Y. Ma, Y. Qu, Adv. Funct. Mater. 2016, 26, 6785.
- [29] Y. Feng, X. Y. Yu, U. Paik, Chem. Commun. 2016, 52, 1633.
- [30] Y. Xu, W. Tu, B. Zhang, S. Yin, Y. Huang, M. Kraft, R. Xu, *Adv. Mater*.
 2017, 29, 1605957.
- [31] H. Lin, Z. Shi, S. He, X. Yu, S. Wang, Qi. Gao, Y. Tang, Chem. Sci. 2016, 7, 3399.
- [32] X. Zhu, C. Tang, H. F Wang, B. Q. Li, Q. Zhang, C. Li, C. Yang, F. Wei, J. Mater. Chem. A 2016, 4, 7245.
- [33] Z. H. Xue, H. Su, Q. Y. Yu, B. Zhang, H. H. Wang, X. H. Li, J. S. Chen, Adv. Energy Mater. 2017, 7, 1602355.

- [34] Y. Gu, S. Chen, J. Ren, Y. A. Jia, C. Chen, S. Komarneni, D. Yang, X. Yao, ACS Nano 2018, 12, 245.
- [35] H. Jin, J. Wang, D. Su, Z. Wei, Z. Pang, Y. Wang, J. Am. Chem. Soc. 2015, 137, 2688.
- [36] Y. P. Zhu, T. Y. Ma, M. Jaroniec, S. Z. Qiao, Angew. Chem. Int. Ed. 2017, 56, 1324.
- [37] X. Zhang, H. Xu, X. Li, Y. Li, T. Yang, Y. Liang, ACS Catal. 2016, 6, 580.
- [38] C. Xiao, Y. Li, X. Lu, C. Zhao, Adv. Funct. Mater. 2016, 26, 3515.
- [39] L. Yu, H. Zhou, J. Sun, F. Qin, F. Yu, J. Bao, Y. Yu, S. Chen, Z. Ren, *Energy Environ. Sci.* 2017, 10, 1820.
- [40] J. Zhang, Y. Jiang, Y. Wang, C. Yu, J. Cui, J. Wu, X. Shu, Y. Qin, J. Sun, J. Yan. H. Zheng, Y. Zhang, Y. Wu, *Electrochimica Acta*. 2019, **321**, 134652.
- [41] H. Liang, A. N. Gandi, D. H. Anjum, X. Wang, U. Schwingenschlögl, H. N. Alshareef, *Nano Lett* 2016, *16*, 7718.
- [42] R. Xu, R. Wu, Y. Shi, J. Zhang, B. Zhang, Nano Energy 2016, 24, 103.
- [43] Y. Liu, Q. Li, R. Si, G. D. Li, W. Li, D. P. Liu, D. Wang, L. Sun, Y. Zhang,
 X. Zou, *Adv. Mater.* 2017, 29, 1606200.
- [44] L. L. Feng, G. Yu, Y. Wu, G. D. Li, H. Li, Y. Sun, T. Asefa, W. Chen, X. Zou, J. Am. Chem. Soc. 2015, 137, 14023.
- [45] M. Ledendecker, S. K. Calderýn, C. Papp, H. P. Steinrîck, M. Antonietti, M. Shalom, Angew. Chem. Int. Ed. 2015, 54, 12361.