Electronic Supplementary Material (ESI) for RSC Advances.

MoS_2/Ni_3S_2 Nanorod Arrays Well-aligned on Ni Foam: A 3D Hierarchical Efficient Bifunctional Catalytic Electrode for Overall Water Splitting

Nan Zhang[a], Junyu Lei[b], Jianpeng Xie[a], Haiyan Huang[a], Ying Yu[a]**

[a] State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing, Beijing, P. R. China, 102249, TEL：+86-010-89739132

[b] Petrochemical Research Institute, PetroChina, Beijing, P. R. China, 100195

Corresponding authors: E-Mail: zhangnan@cup.edu.cn; yybjpudhx@foxmail.com

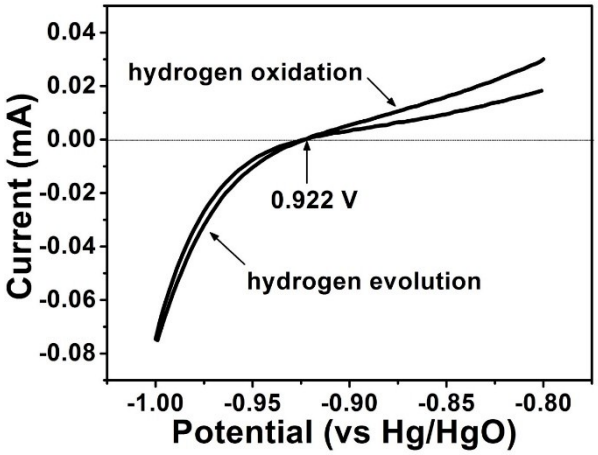

Figure S1. Cyclic voltammogram for the potential calibration procedure of the reference electrode -- Hg/HgO in 1.0 M KOH solution.

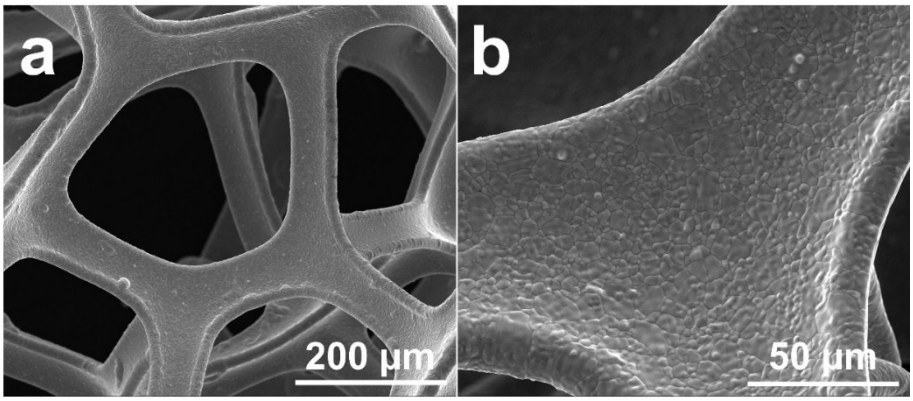

Figure S2. The SEM images of bare Ni foam (NF) at different magnifications.

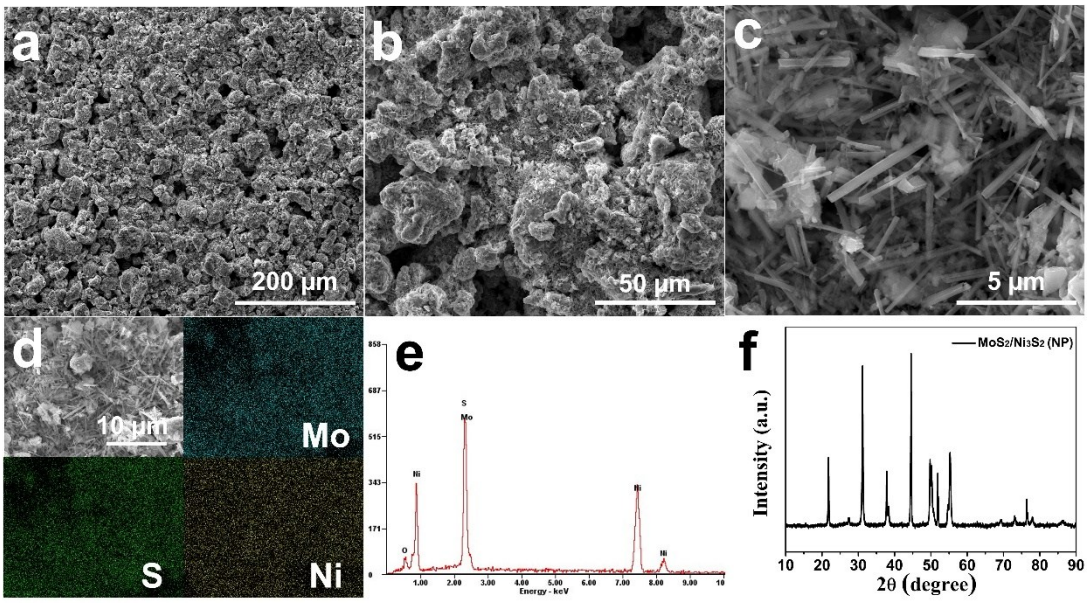

Figure S3. (a, b, c) The SEM images, (d) SEM and the corresponding elemental mapping images, (e) the EDX spectrum, and (f) the XRD pattern of MoS_2/Ni_3S_2 (NP).

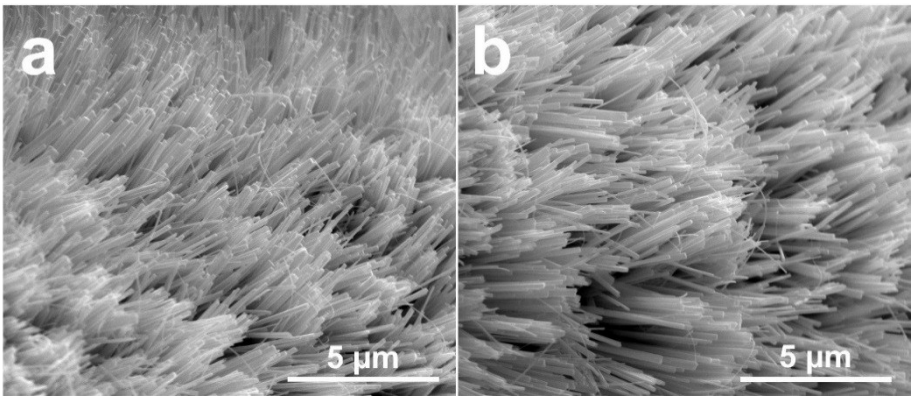

Figure S4. The SEM images of MoS_2/Ni_3S_2/NF (a) before and (b) after the ultrasonication treatment for 30 min.

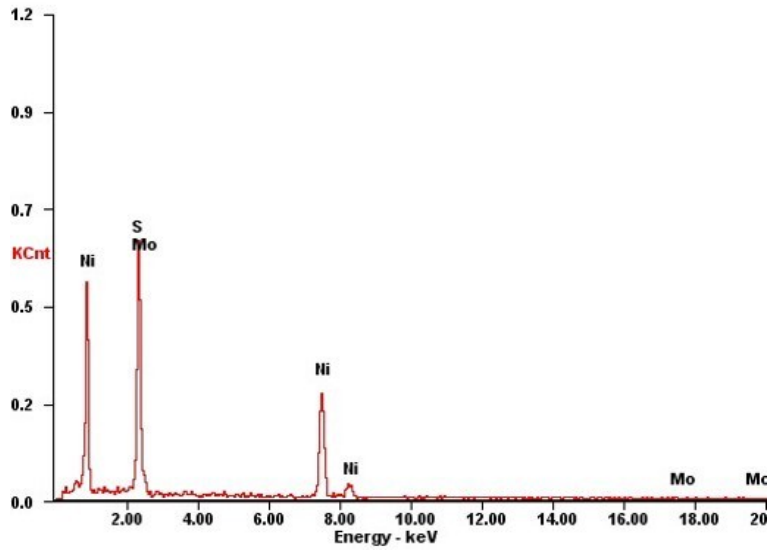

Figure S5. The EDX spectrum of MoS_2/Ni_3S_2 nanorods.

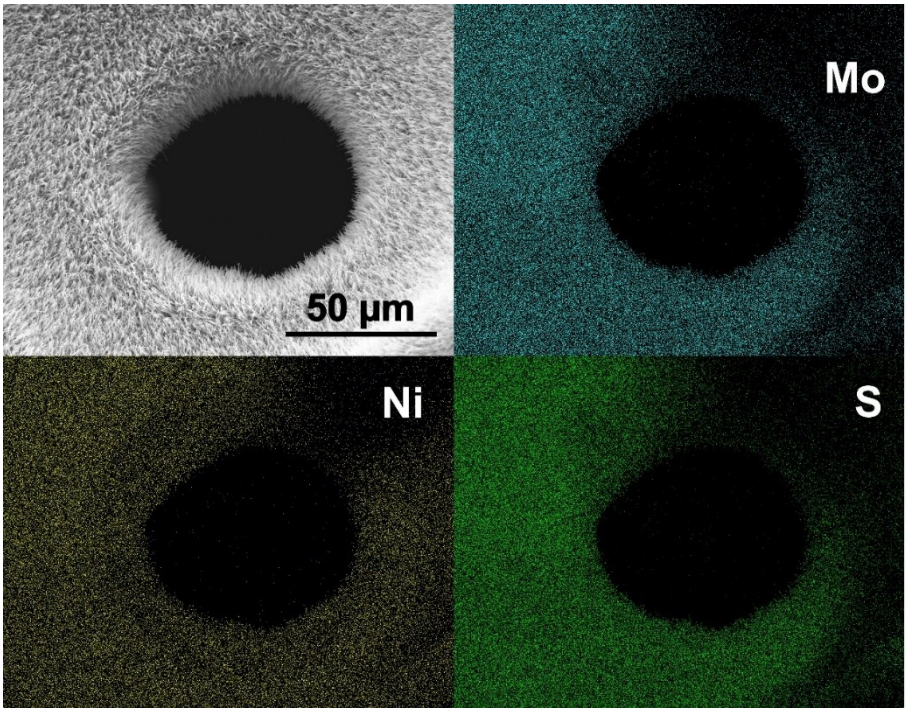

Figure S6. The SEM and the corresponding elemental mapping images of MoS_2/Ni_3S_2/NF 3D electrode.

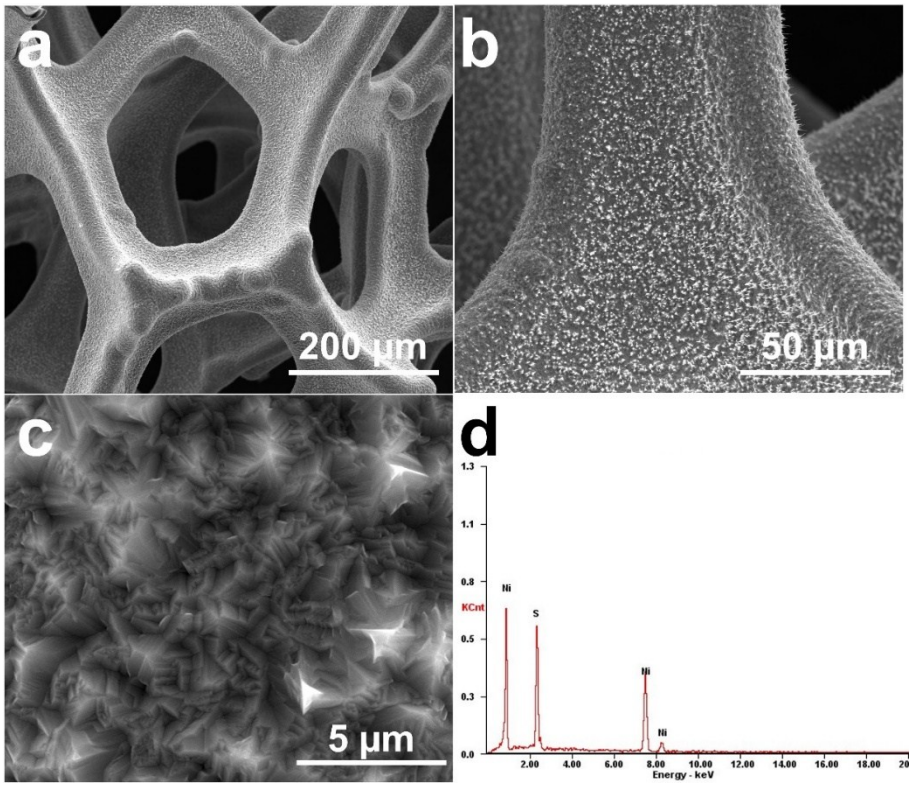

Figure S7. (a, b, c) The SEM images of Ni_3S_2/NF, (d) the EDX spectrum of Ni_3S_2/NF.

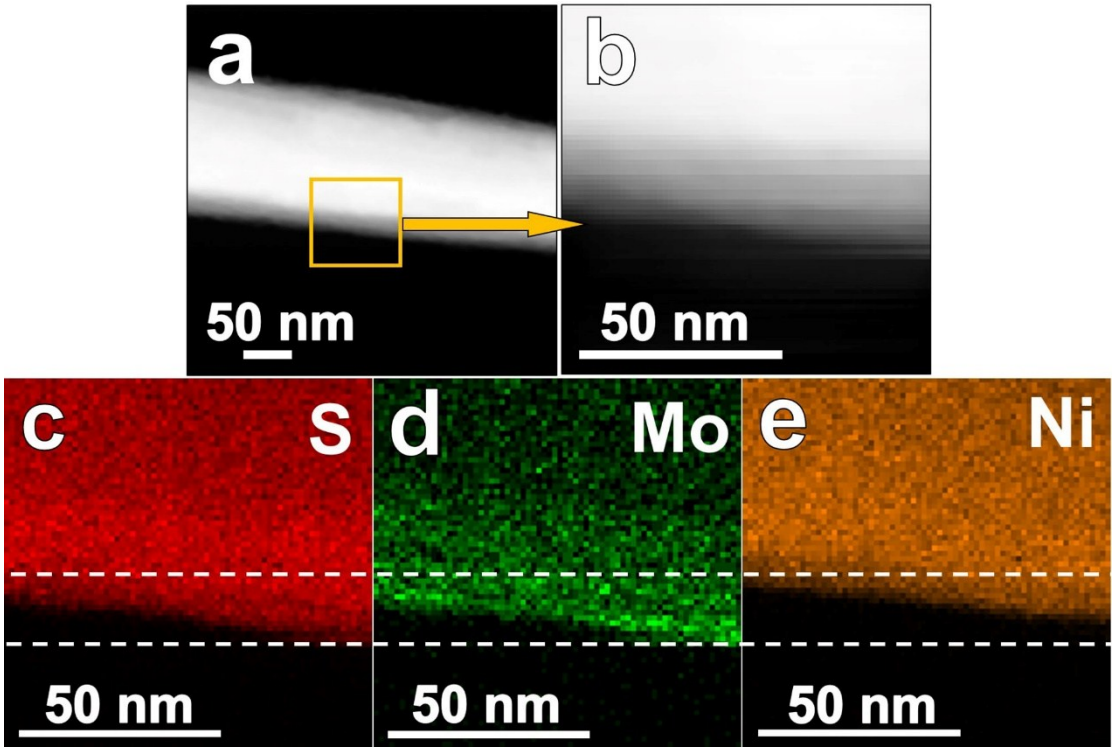

Figure S8. The elemental mapping images of the edge of a MoS_2/Ni_3S_2 nanorod.

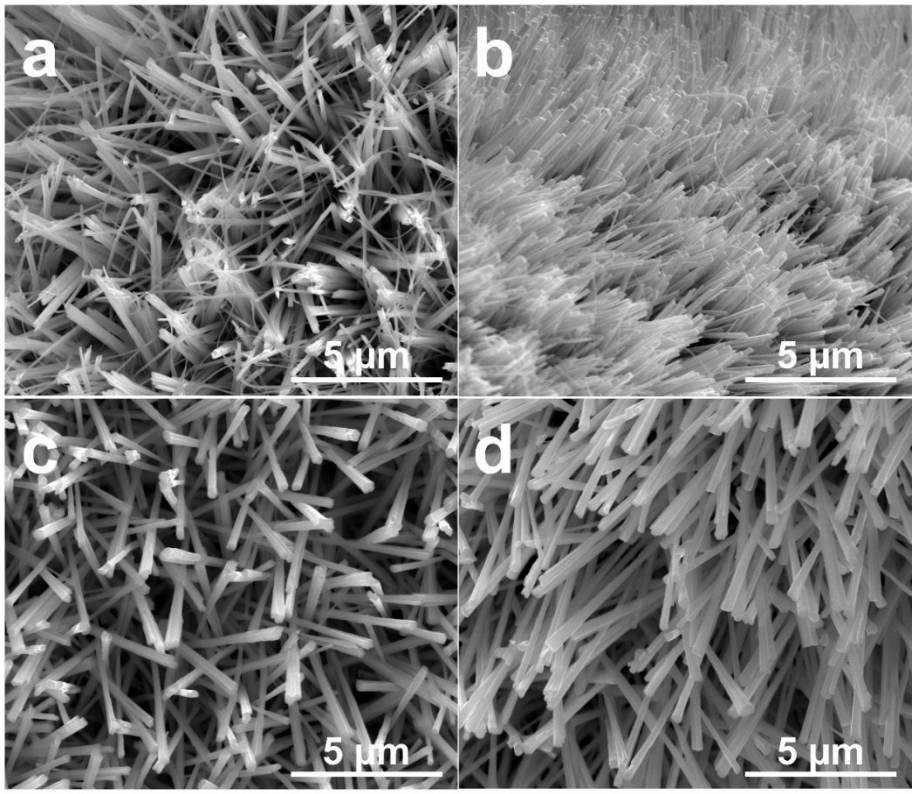

Figure S9. SEM images of (a) MoS_2/Ni_3S_2/NF (Mo:S=0.5:10), (b) MoS_2/ Ni_3S_2/NF (Mo:S=1:10), (c) MoS_2/Ni_3S_2/NF (Mo:S=2:10) and (d) MoS_2/ Ni_3S_2/NF (Mo:S=3:10).

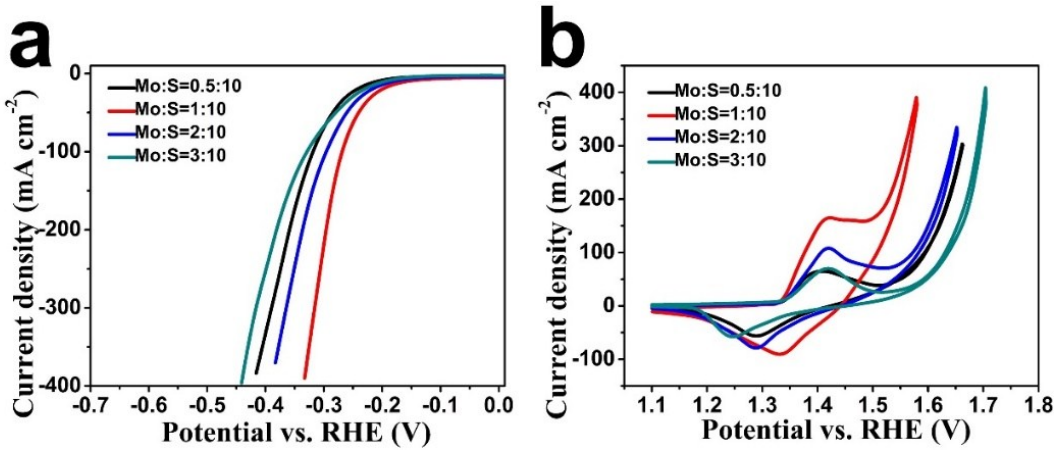

Figure S10. (a) HER and (b) OER polarization curves of MoS_2/Ni_3S_2/NF (Mo:S=0.5:10), MoS_2/Ni_3S_2/NF (Mo:S=1:10), MoS_2/Ni_3S_2/NF (Mo:S=2:10) and MoS_2/Ni_3S_2/NF (Mo:S=3:10).

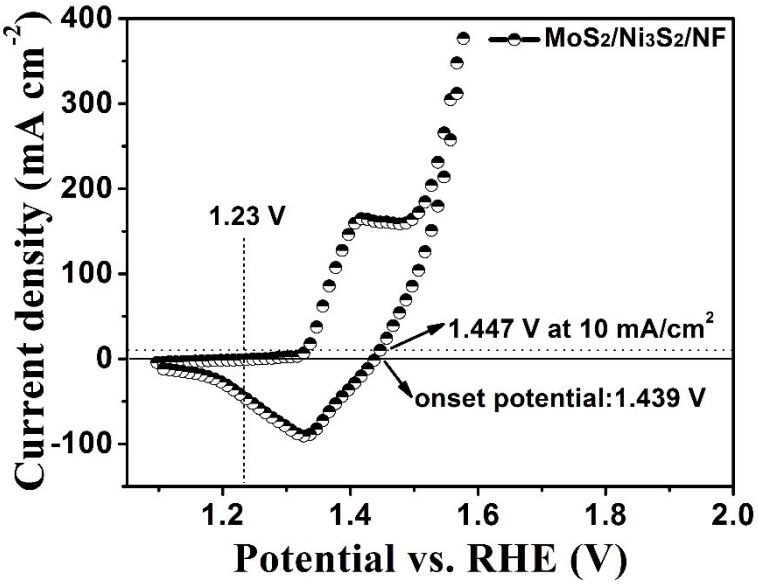

Figure S11. The cyclic voltammogram of the MoS_2/Ni_3S_2/NF which consists of a forward scan and a backward scan. While due to the strong oxidative peak in forward scan, it is difficult to confirm the applied potential when the corresponding current density is below 165 mA/cm^2. Therefore, the backward scan was employed to assess the OER activities of the applied electrocatalysts. The onset potential lies at the zero current point when oxygen generation occurred. Overpotential is defined relatively to the thermodynamic potential for OER reaction of 1.23 V versus reversible hydrogen electrode (RHE). As a consequence, MoS_2/Ni_3S_2/NF's onset potential is approximately 1.439 V, and its onset overpotential is approximately 209 mV.

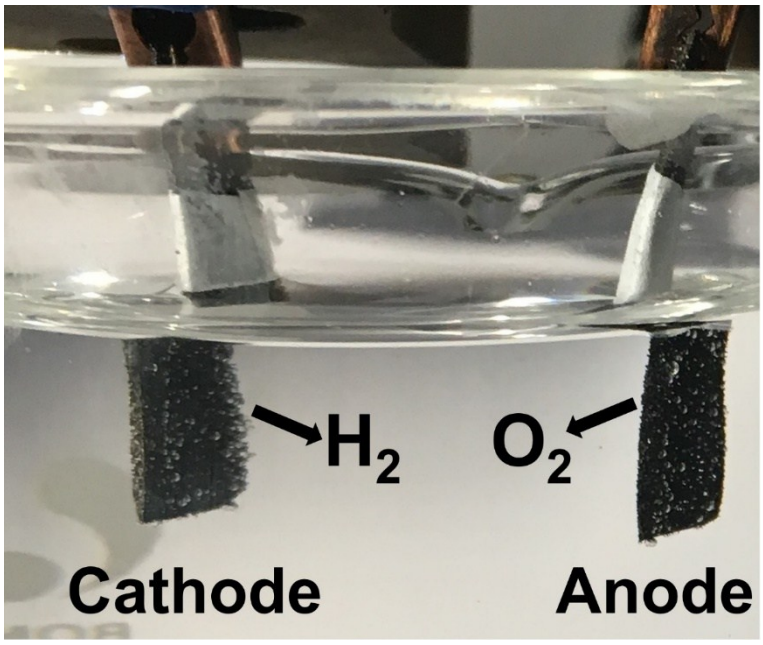

Figure S12. A presentative photograph of the system depicting H_2 (left) and O_2 (right) generation during overall water electrolysis.

Table S1. The composition of MoS_2/Ni_3S_2 nanorods measured through EDX.

Element	Wt%	At%
Mo	8.05	4.05
S	29.86	44.93
Ni	62.09	51.02

Table S2. Comparison of HER, OER and overall water splitting performance of the recently reported non-noble-based bifunctional electrocatalysts.

Catalyst	Electrolyte	Scan rate (mV/s)	HER		OER		Full water splitting	Ref.
			Overpotential@onset, 10 mA cm^{-2}, (mV)	Tafel slope (mV dec^{-1})	Overpotential@onset, 10 mA cm-2, (mV)	Tafel slope (mV dec^{-1})	Potential@ 10 mA cm^{-2} , (V)	
NiMo-alloy	1M KOH	2	60, 92	76	300, 310	47	1.64	[1]
$Ni_{0.9}Fe_{0.1}$/NC	1M KOH	10	-, 219	111	-, 330	45	1.58	[2]
CoOx/CN	1M KOH	5	85, 232	115	-, 260	-	1.55@20 mA cm^{-2}	[3]
Co_3O_4@NCNTs/CP	0.1M KOH	2	260, 380	120	330, 470	-	-	[4]
Co3O4/CF	1M KOH	5	50, -	116	290, -	101	1.91	[5]
$NiCo_2O_4$	1M NaOH	3	50, 110	49.7	230, 290	53	1.65	[6]
Ni_2P/NiO_x	1M KOH	5	-, 220	-	-, 290	47	1.63	[7]
MoO_2	1M KOH	-	-, 27	41	200, 260	54	1.53	[8]
$NiFeO_x$	1M KOH	5	40, 88	-	200, 230	31.5	1.51	[9]
NiFe LDH/NF	1M NaOH	1	-, 210	-	-, 240	-	1.7	[10]
Co-P/Cu	1M KOH	2	50, 94	42	300, 345	47	1.74@100 mA cm^{-2}	[11]
CoP-MNA/NF	1M KOH	2	0, 54	51	270, 290	-	1.62	[12]
Ni2P/Ni/NF	1M KOH	2	40, 98	72	190, 200	-	1.49	[13]
CoP/CNTs	0.1M NaOH	5	220, -	56	290, 330	50	-	[14]
Ni5P4/NF	0.5M H_2SO_4	10	-, 140	40	250, -	-	1.70	[15]
CoP/rGO	0.5M H_2SO_4	5	13, 105	50	-, 340	66	1.70	[16]
NiCoP NPs	1M KOH	5	42, 97	50	-, 310	52	1.64	[17]
CoP	1M KOH	2	-, 154	51	270, 354	52	2.0@165 mA cm^{-2}	[18]
Co-N_x	0.1M KOH	0.5	-, 220	81	-, 270@5 mA cm^{-2}	83.3	-	[19]
TiN@Ni3N NW	1M KOH	5	15, 21	42.1	290, 350	93.7	1.64	[20]
$NiSe_2$/Ti	1M KOH	5	20, 96	82	270, 300@20 mA cm^{-2}	82	1.66	[21]
$Co_{0.13}Ni_{0.87}Se_2$/Ti	1M KOH	5	-, 64	63	-, 350@100 mA cm^{-2}	94	1.62	[22]
Co_9S_8@MoS_2/CNFs	0.5M H_2SO_4	2	64, 190	110	350, 430 (test in 1M KOH)	61	-	[23]
Ni_2S_3/NF	1M KOH	50	-, 223	-	-,260	-	1.76@13 mA cm^{-2}	[24]
Ni-Co-S NS/CF	1M KOH	5	-, 140	96	-, 363@100 mA cm^{-2}	109	1.67	[25]
$Zn_{0.76}Co_{0.24}S/CoS_2$	1M KOH	5	170, 238@20 mA cm^{-2}	164	316, 330@20 mA cm^{-2}	79	1.66	[26]
Ni2.3%-CoS2/CC	1M KOH	2	136, 231@100 mA cm^{-2}	106	300, 510@100 mA cm^{-2}	119	1.66	[27]
NiS/NF	1M KOH	5	-, 158@20 mA cm^{-2}	83	320, 340@50 mA cm^{-2}	89	1.64	[28]
$NiCo_2S_4$ NW/NF	1M KOH	10	-, 210	58.9	-, 260	40	1.63	[29]
20 nm BSCF-NF	0.1M KOH	5	-, -	-	-, 500	73	1.62 (Pt-NF as cathode in 1M KOH)	[30]
$SrNb_{0.1}Co_{0.7}Fe_{0.2}O_{3-\delta}$ perovskite nanorods	0.1M KOH 1M KOH	5	150, 262 232	134 103	290, 389 370	61 48	1.68	[31]
MoS_2/Ni_2S_3/NF	1M KOH	5	50, 187	90	209, 217	38	1.47	This work

	274@100 mA cm^{-2},	275@100 mA cm^{-2},	1.59@100 mA cm^{-2}
	300@200 mA cm^{-2},	313@200 mA cm^{-2},	1.64@200 mA cm^{-2}
	320@300 mA cm^{-2}	335@300 mA cm^{-2}	1.66@300 mA cm^{-2}

REFERENCES

1. J. Tian, N. Cheng, Q. Liu, X. Sun, Y. He and A. M. Asiri, *J. Mater. Chem. A*, 2015, **3**, 20056-20059.
2. X. Zhang, H. Xu, X. Li, Y. Li, T. Yang and Y. Liang, *Acs Catal.*, 2016, **6**, 580-588.
3. H. Jin, J. Wang, D. Su, Z. Wei, Z. Pang and Y. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 2688-2694.
4. T. Sharifi, E. Gracia-Espino, X. Jia, R. Sandstrom and T. Wagberg, *Acs Appl. Mater. Inter.*, 2015, **7**, 28148-28155.
5. S. Du, Z. Ren, J. Zhang, J. Wu, W. Xi, J. Zhu and H. Fu, *Chem. Commun.*, 2015, **51**, 8066-8069.
6. X. Gao, H. Zhang, Q. Li, X. Yu, Z. Hong, X. Zhang, C. Liang and Z. Lin, *Angew. Chem. Int. Ed.*, 2016, **55**, 6290-6294.
7. L.-A. Stern, L. Feng, F. Song and X. Hu, *Energy Environ. Sci.*, 2015, **8**, 2347-2351.
8. Y. Jin, H. Wang, J. Li, X. Yue, Y. Han, P. K. Shen and Y. Cui, *Adv. Mater.*, 2016, **28**, 3785-3790.
9. H. Wang, H.-W. Lee, Y. Deng, Z. Lu, P.-C. Hsu, Y. Liu, D. Lin and Y. Cui, *Nature Communications*, 2015, **6**.
10. J. Luo, J.-H. Im, M. T. Mayer, M. Schreier, M. K. Nazeeruddin, N.-G. Park, S. D. Tilley, H. J. Fan and M. Graetzel, *Science*, 2014, **345**, 1593-1596.
11. N. Jiang, B. You, M. Sheng and Y. Sun, *Angew. Chem. Int. Ed.*, 2015, **54**, 6251-6254.
12. Y.-P. Zhu, Y.-P. Liu, T.-Z. Ren and Z.-Y. Yuan, *Adv. Funct. Mater.*, 2015, **25**, 7337-7347.
13. B. You, N. Jiang, M. Sheng, M. W. Bhushan and Y. Sun, *Acs Catal.*, 2016, **6**, 714-721.
14. C.-C. Hou, S. Cao, W.-F. Fu and Y. Chen, *Acs Applied Materials & Interfaces*, 2015, **7**, 28412-28419.
15. M. Ledendecker, S. K. Calderon, C. Papp, H.-P. Steinrueck, M. Antonietti and M.

Shalom, *Angew. Chem. Int. Ed.*, 2015, **54**, 12361-12365.

16. L. Jiao, Y.-X. Zhou and H.-L. Jiang, *Chemical Science*, 2016, **7**, 1690-1695.
17. C. Wang, J. Jiang, T. Ding, G. Chen, W. Xu and Q. Yang, *Advanced Materials Interfaces*, 2016, **3**.
18. B. You, N. Jiang, M. Sheng, S. Gul, J. Yano and Y. Sun, *Chem. Mater.*, 2015, **27**, 7636-7642.
19. B. Bayatsarmadi, Y. Zheng, Y. Tang, M. Jaroniec and S.-Z. Qiao, *Small*, 2016, **12**, 3703-3711.
20. Q. Zhang, Y. Wang, Y. Wang, A. M. Al-Enizi, A. A. Elzatahry and G. Zheng, *J. Mater. Chem. A*, 2016, **4**, 5713-5718.
21. Z. Pu, Y. Luo, A. M. Asiri and X. Sun, *Acs Appl. Mater. Inter.*, 2016, **8**, 4718-4723.
22. T. Liu, A. M. Asiri and X. Sun, *Nanoscale*, 2016, **8**, 3911-3915.
23. H. Zhu, J. Zhang, R. Yanzhang, M. Du, Q. Wang, G. Gao, J. Wu, G. Wu, M. Zhang, B. Liu, J. Yao and X. Zhang, *Adv. Mater.*, 2015, **27**, 4752-4759.
24. L.-L. Feng, G. Yu, Y. Wu, G.-D. Li, H. Li, Y. Sun, T. Asefa, W. Chen and X. Zou, *J. Am. Chem. Soc.*, 2015, **137**, 14023-14026.
25. T. Liu, X. Sun, A. M. Asiri and Y. He, *Int. J. Hydrogen Energy*, 2016, **41**, 7264-7269.
26. Y. Liang, Q. Liu, Y. Luo, X. Sun, Y. He and A. M. Asiri, *Electrochim. Acta*, 2016, **190**, 360-364.
27. W. Fang, D. Liu, Q. Lu, X. Sun and A. M. Asiri, *Electrochem. Commun.*, 2016, **63**, 60-64.
28. W. Zhu, X. Yue, W. Zhang, S. Yu, Y. Zhang, J. Wang and J. Wang, *Chemical Communications*, 2016, **52**, 1486-1489.
29. A. Sivanantham, P. Ganesan and S. Shanmugam, *Adv. Funct. Mater.*, 2016, **26**, 4661-4672.
30. G. Chen, W. Zhou, D. Guan, J. Sunarso, Y. Zhu, X. Hu, W. Zhang and Z. Shao, *Sci. Adv.*, 2017, **3**, e1603206.
31. Y. Zhu, W. Zhou, Y. Zhong, Y. Bu, X. Chen, Q. Zhong, M. Liu and Z. Shao, *Adv.*

Energy Mater., 2017, **7**, 1602122.