

Supporting materials

Hierarchical $\text{FeCo}_2\text{S}_4@\text{CoFe}$ layered double hydroxide on Ni foam as bifunctional electrocatalyst for overall water splitting

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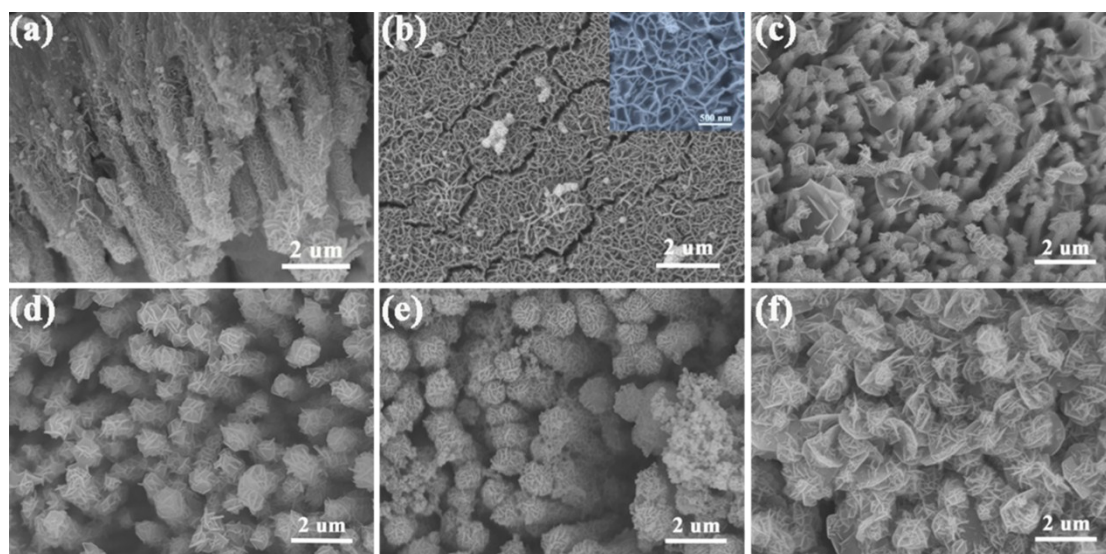


Figure S1. The cross-section SEM image of $\text{FeCo}_2\text{S}_4@\text{CoFe}$ LDH. (b) SEM image of CoFe LDH at the electrodeposition time of 60 s. SEM image of $\text{FeCo}_2\text{S}_4@\text{CoFe}$ LDH at different electrodeposition time: (c) 30 s, (d) 60 s, (e) 90 s, (f) 200 s.

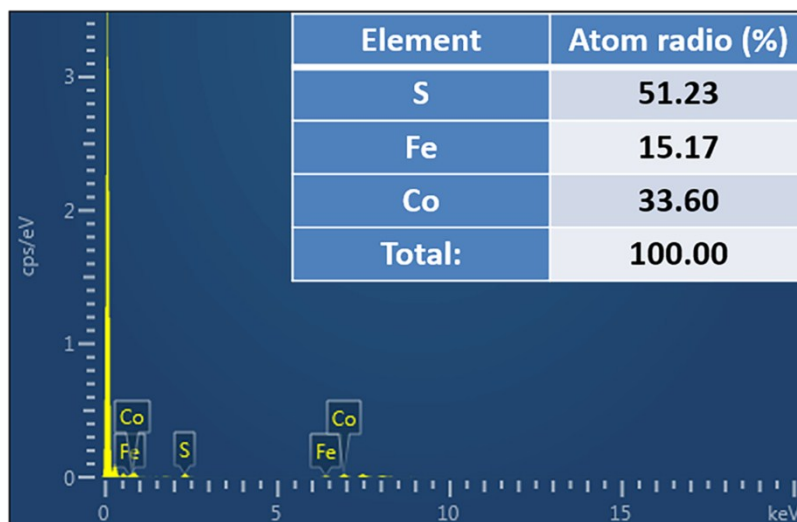


Figure S2. EDX spectra of FeCo₂S₄@CoFe LDH.

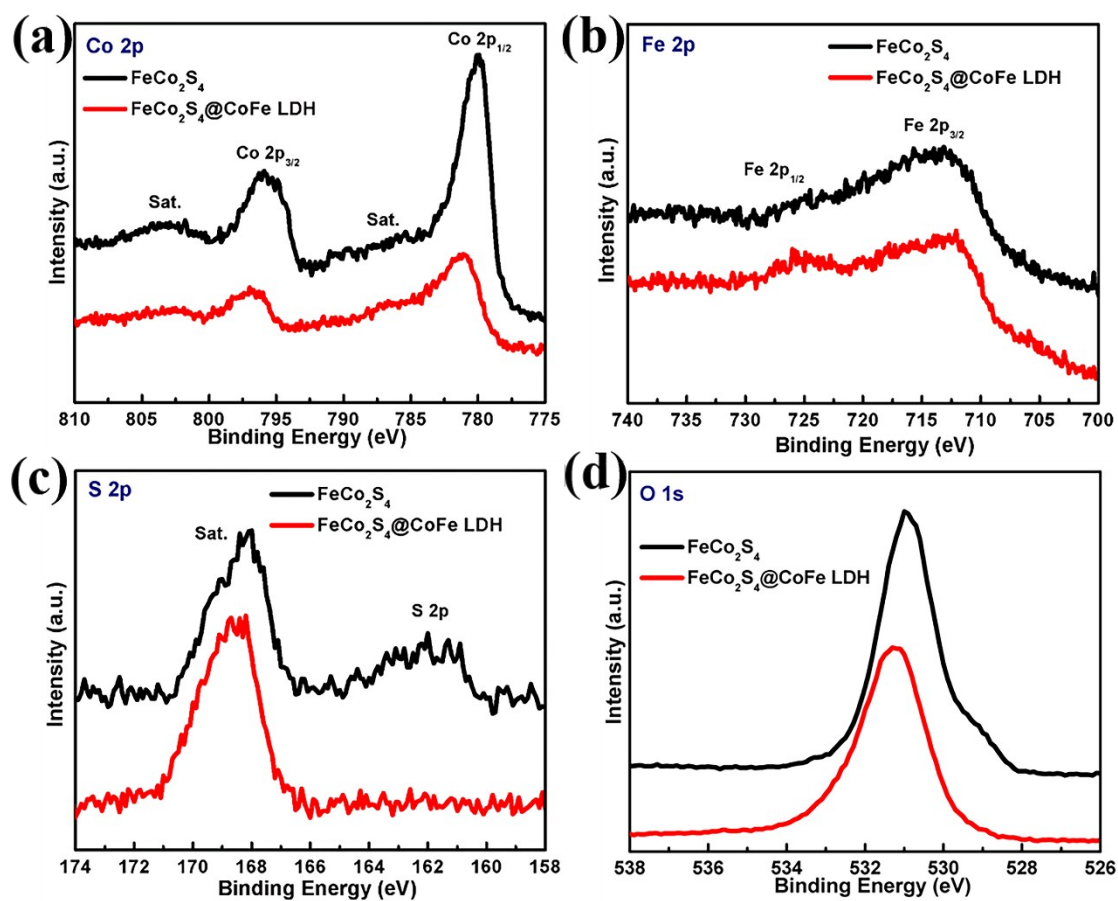


Figure S3. XPS spectra of (a) Co 2p, (b) Fe 2p, (c) S 2p and (d) O 1s from the FeCo₂S₄ and FeCo₂S₄@CoFe LDH, respectively.

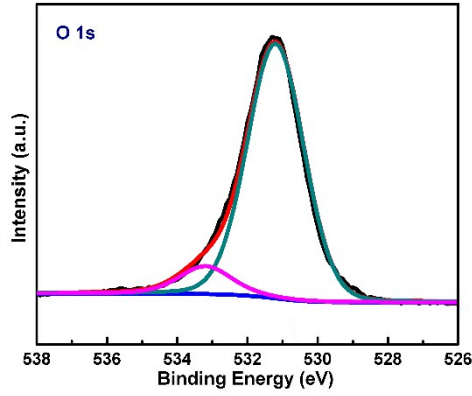


Figure S4. XPS spectra of O 1s from FeCo₂S₄@CoFe LDH.

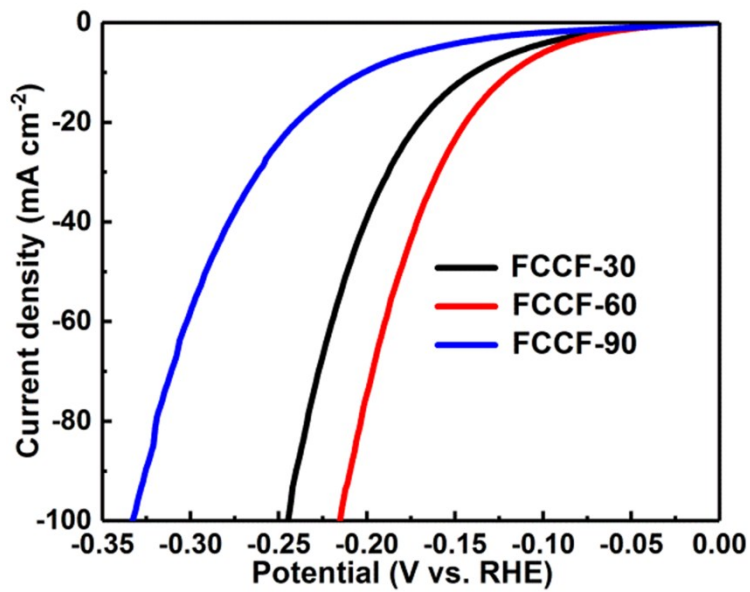


Figure S5. HER polarization curves of FCCF-30, FCCF-60 and FCCF-90.

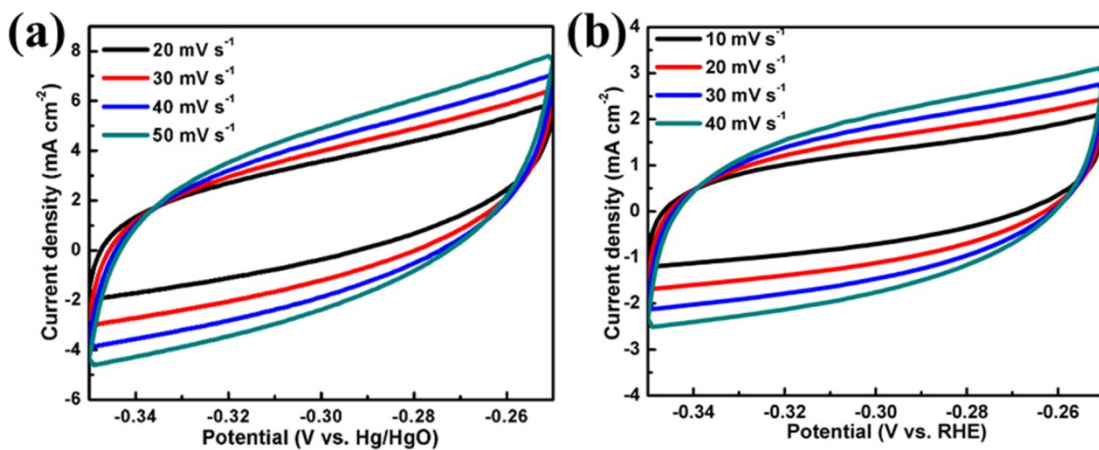


Figure S6. CV curves of (a) FeCo₂S₄@CoFe LDH, and (b) FeCo₂S₄ at different scan rates, respectively.

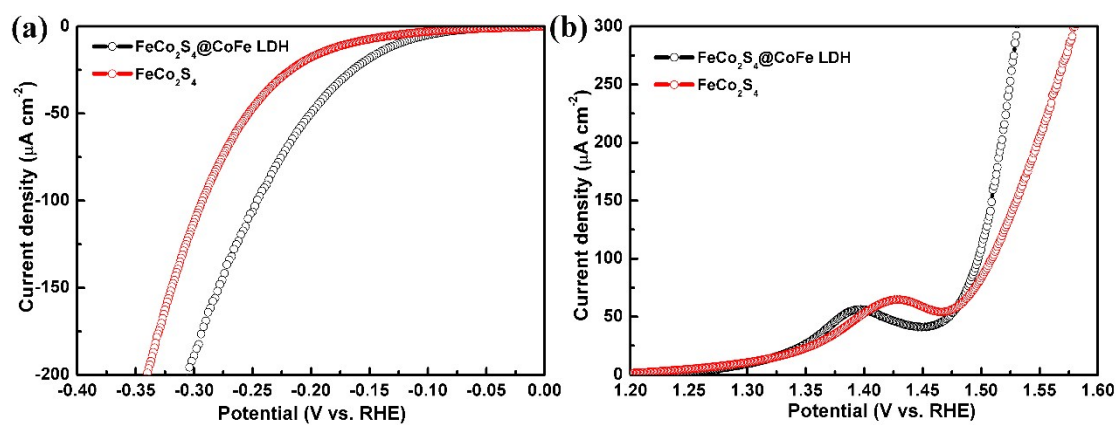


Figure S7. ECSA-normalized polarization curves of $\text{FeCo}_2\text{S}_4@\text{CoFe LDH}$ and FeCo_2S_4 for (a) HER and (b) OER.

The ECSA of the catalyst can be calculated according to the equation: $\text{ECAS} = C_{dl}/C_s$, where the specific capacitance C_s is usually between 20~60 $\mu\text{F cm}^{-2}$. Here we assume it as 40 $\mu\text{F cm}^{-2}$ in the following calculations of ECSA.¹

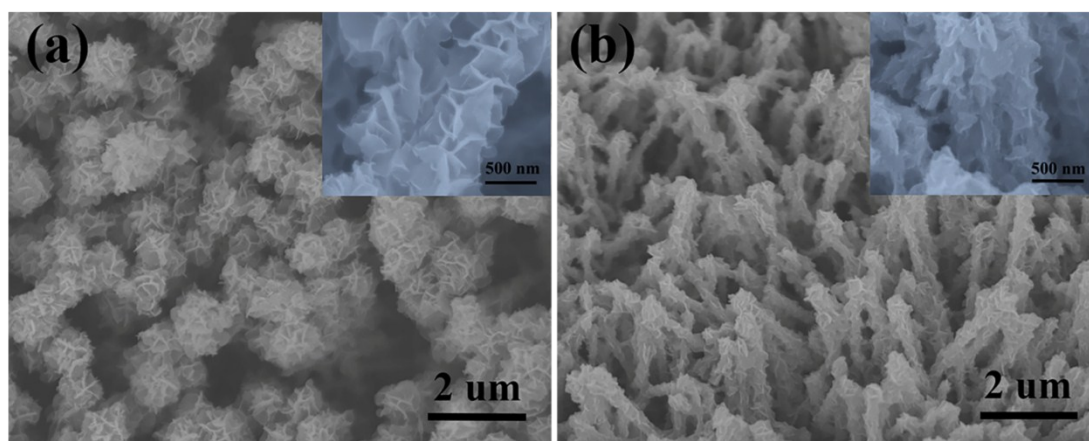


Figure S8. SEM images of $\text{FeCo}_2\text{S}_4@\text{CoFe LDH}$ after (a) HER and (b) OER stability test, the inset images are the corresponding SEM images at high resolution.

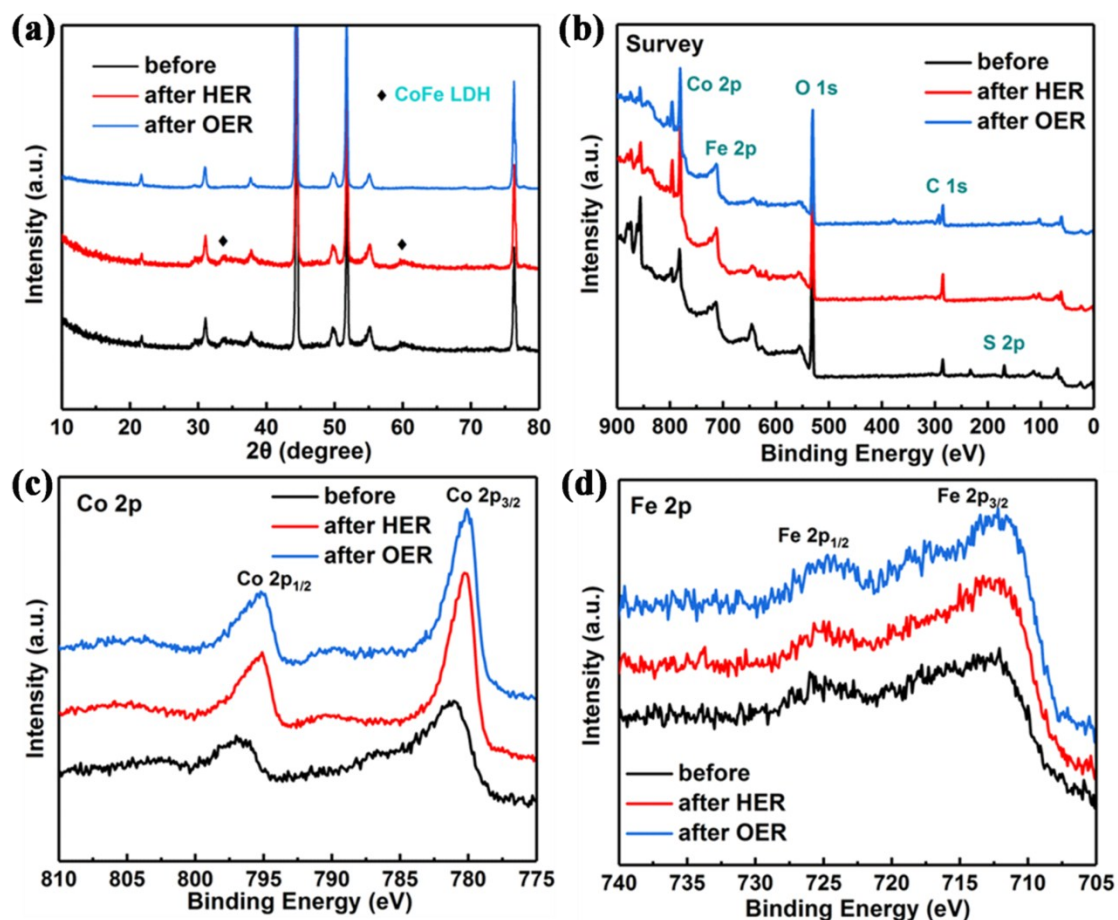


Figure S9. (a) XRD patterns and (b) XPS surveys of $\text{FeCo}_2\text{S}_4@\text{CoFe}$ LDH before test, after HER and OER stability test. XPS spectra of (c) Co 2p and (d) Fe 2p characteristic peaks from $\text{FeCo}_2\text{S}_4@\text{CoFe}$ LDH before test, after HER and OER stability test.

Table S1. Comparison of HER activity data with other reported non-noble catalysts.

Catalyst	Electrolyte	$\eta(\text{mV})@j(\text{mA cm}^{-2})$	Tafel slope (mV dec^{-1})	Time
$\text{FeCo}_2\text{S}_4@\text{CoFe}$ LDH/NF	1 M KOH	115@10	72.8	24 h (this work)
CoP/CC ²	1 M KOH	209@10	129	*
$\text{Ni}_9\text{S}_8/\text{NF}^3$	1 M KOH	230@10	123.3	24 h
$\text{NiCo}_2\text{O}_4@\text{NiFe}$ LDH/NF ⁴	1 M KOH	192@10	59	10 h
$\text{FeNiP}_x/\text{NF}^5$	1 M KOH	153@10	80	90 h
$\text{NiFe}_2\text{O}_4/\text{NiFe}$ LDH/NF ⁶	1 M KOH	101@10	67.1	
NiFeS^7	1 M KOH	180@10	53	200 h
NiCo_2S_4 NA/CC ⁸	1 M KOH	228@20	141	12 h

Table S2. Comparison of OER activity with other reported non-noble catalysts.

Catalyst	Electrolyte	$\eta(\text{mV})@j(\text{mA cm}^{-2})$	Tafel slope (mV dec^{-1})	Time
FeCo₂S₄@CoFe LDH/NF	1 M KOH	259@100	68.9	24 h (this work)
CoFe⁹	1 M KOH	286@10	48	5 h
CoFe-LDH/TEG¹⁰	1 M KOH	301@10	52	5 h
Co_{0.75}Ni_{0.25}Se/NF¹¹	1 M KOH	269@50	74	40 h
FeOOH/NiFe LDH	1 M KOH	208@10	42.5	5 h
CoFe-LDH NS¹²	1 M KOH	280@10	33.4	8 h
CoFe₂O₄/CFP¹³	1 M KOH	378@10	73	40 h
Cu(OH)₂@CoNiCH NTs/CF¹⁴	1 M KOH	288@30	74	12 h

Table S3. Comparison of the electrocatalytic performance for FeCo₂S₄@CoFe LDH catalyst with other reported catalysts in 1 M KOH electrolyte.

Catalyst	HER		OER		Cell voltage@10 mA cm ⁻²
	$\eta(\text{mV})@j(\text{mA cm}^{-2})$	Tafel slope (mV dec^{-1})	$\eta(\text{mV})@j(\text{mA cm}^{-2})$	Tafel slope (mV dec^{-1})	
FeCo ₂ S ₄ @CoFe LDH/NF	118@10	81.5	259@100	68.9	1.6 (this work)
CoFe@NiFe-200/NF¹⁵	240	84.69	190@10	45.71	1.59
NiFe LDH-NiSe/NF¹⁶	276@10	70	240@100	65.6	1.53
	0				
Cu@CoFe LDH/CF¹⁷	171@10	36.4	240@10	44.4	1.68
NiCo₂S₄ NW /NF¹⁸	210@10	58.9	260@10	40.1	1.63
EG/Co_{0.85}Se/NiFe-LDH¹⁹	260@10	160	270@150	57	1.67
NiFe-NCs/CFP²⁰	197@10	130	271@10	48	1.67
NiFe₂O₄/NiFe LDH/NF⁶	101@10	67.1	213@100	28.2	1.535
NiFe/NiCo₂O₄/NF²¹	105@10	88	240@10	38.8	1.67
NiCo₂O₄@Ni_{0.796}Co LDH/NF²²	115@10	56.42	193@10	37.59	1.6
NiCoFe LTHs/CFC²³	200@10	70	239@10	32	1.55
NiCo₂S₄@NiFe LDH/NF²⁴	200@10	46.3	201@60	101.1	1.6
NiCo₂O₄@NiO@Ni/NF²⁵	124@10	58	240@10	43	1.6
Co₃S₄@MoS₂²⁶	136@10	74	280@10	43	1.58
NiS/NF²⁷	158@20	83	335@50	89	1.64

References

1. R. Xiang, Y. J. Duan, L. S. Peng, Y. Wang, C. Tong, L. Zhang and Z. D. Wei, *Applied Catalysis B-Environmental*, 2019, **246**, 41-49.
2. J. Q. Tian, Q. Liu, A. M. Asiri and X. P. Sun, *Journal of the American Chemical Society*, 2014, **136**, 7587-7590.

3. G. F. Chen, T. Y. Ma, Z. Q. Liu, N. Li, Y. Z. Su, K. Davey and S. Z. Qiao, *Advanced Functional Materials*, 2016, **26**, 3314-3323.
4. Z. Q. Wang, S. Zeng, W. H. Liu, X. W. Wang, Q. W. Li, Z. G. Zhao and F. X. Geng, *Acs Applied Materials & Interfaces*, 2017, **9**, 1488-1495.
5. C. H. Xiao, B. Zhang and D. Li, *Electrochim. Acta*, 2017, **242**, 260-267.
6. Z. C. Wu, Z. X. Zou, J. S. Huang and F. Gao, *Acs Applied Materials & Interfaces*, 2018, **10**, 26283-26292.
7. P. Ganesan, A. Sivanantham and S. Shanmugam, *Journal of Materials Chemistry A*, 2016, **4**, 16394-16402.
8. D. N. Liu, Q. Lu, Y. L. Luo, X. P. Sun and A. M. Asiri, *Nanoscale*, 2015, **7**, 15122-15126.
9. A. M. P. Sakita, R. Della Noce, E. Valles and A. V. Benedetti, *Applied Surface Science*, 2018, **434**, 1153-1160.
10. C. Yu, X. T. Han, Z. B. Liu, C. T. Zhao, H. W. Huang, J. Yang, Y. Y. Niu and J. S. Qiu, *Carbon*, 2018, **126**, 437-442.
11. S. Liu, Y. M. Jiang, M. Yang, M. J. Zhang, Q. F. Guo, W. Shen, R. X. He and M. Li, *Nanoscale*, 2019, **11**, 7959-7966.
12. R. Gao and D. P. Yan, *Nano Research*, 2018, **11**, 1883-1894.
13. A. Kargar, S. Yavuz, T. K. Kim, C. H. Liu, C. Kuru, C. S. Rustomji, S. Jin and P. R. Bandaru, *Acs Applied Materials & Interfaces*, 2015, **7**, 17851-17856.
14. J. H. Kang, J. L. Sheng, J. Q. Xie, H. Q. Ye, J. H. Chen, X. Z. Fu, G. P. Du, R. Sun and C. P. Wong, *Journal of Materials Chemistry A*, 2018, **6**, 10064-10073.
15. R. Yang, Y. M. Zhou, Y. Y. Xing, D. Li, D. L. Jiang, M. Chen, W. D. Shi and S. Q. Yuan, *Applied Catalysis B-Environmental*, 2019, **253**, 131-139.
16. S. Dutta, A. Indra, Y. Feng, T. Song and U. Paik, *Acs Applied Materials & Interfaces*, 2017, **9**, 33766-33774.
17. L. Yu, H. Q. Zhou, J. Y. Sun, F. Qin, D. Luo, L. X. Xie, F. Yu, J. M. Bao, Y. Li, Y. Yu, S. Chen and Z. F. Ren, *Nano Energy*, 2017, **41**, 327-336.
18. A. Sivanantham, P. Ganesan and S. Shanmugam, *Advanced Functional Materials*, 2016, **26**, 4661-4672.
19. Y. Hou, M. R. Lohe, J. Zhang, S. H. Liu, X. D. Zhuang and X. L. Feng, *Energy & Environmental Science*, 2016, **9**, 478-483.
20. A. Kumar and S. Bhattacharyya, *Acs Applied Materials & Interfaces*, 2017, **9**, 41906-41915.
21. C. L. Xiao, Y. B. Li, X. Y. Lu and C. Zhao, *Advanced Functional Materials*, 2016, **26**, 3515-3523.
22. W. F. Wei, X. W. Cui, W. X. Chen and D. G. Ivey, *Chemical Society Reviews*, 2011, **40**, 1697-1721.
23. A. L. Wang, H. Xu and G. R. Li, *Acs Energy Letters*, 2016, **1**, 445-453.
24. J. Liu, J. S. Wang, B. Zhang, Y. J. Ruan, L. Lv, X. Ji, K. Xu, L. Miao and J. J. Jiang, *Acs Applied Materials & Interfaces*, 2017, **9**, 15364-15372.
25. L. Y. Wang, C. D. Gu, X. Ge, J. L. Zhang, H. Y. Zhu and J. P. Tu, *Particle & Particle Systems Characterization*, 2017, **34**, 1700228.
26. Y. N. Guo, J. Tang, Z. L. Wang, Y. M. Kang, Y. Bando and Y. Yamauchi, *Nano Energy*, 2018, **47**, 494-502.
27. W. X. Zhu, X. Y. Yue, W. T. Zhang, S. X. Yu, Y. H. Zhang, J. Wang and J. L. Wang, *Chemical Communications*, 2016, **52**, 1486-1489.