Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Hierarchical $CoS_x/Ni(OH)_2$ heterostructure as bifunctional electrocatalyst for urea-assisted energy-efficient hydrogen production

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Experimental

Chemicals and materials

$Co(NO_3)_2·6H_2O$, NH_4F, CH_3CSNH_2, $Ni(NO_3)_2·6H_2O$ and urea were provided from Sinopharm Chemical Reagent Co. Ltd. Nickel foam (NF) were provided from Taiyuan source of power company.

Sample synthesis

Preparation of CoS_x/NF

A piece of NF (3 × 2 cm) was treated in HCl aqueous solution followed by subsequent washing of water and ethanol. Firstly, 2 mmol $Co(NO_3)_2$, 10 mmol urea and 6 mmol NH_4F were added in water and pre-treated NF was added into above solution. Secondly, after heating at 120 ℃ for 6 h $Co(OH)_2$/NF was obtained. Thirdly, the $Co(OH)_2$/NF was added to CH_3CSNH_2 solution and maintained at 200 °C for 6 h to prepare CoS_x/NF.

Preparation of CoS_x/$Ni(OH)_2$/NF

The CoS_x/NF was immersed mixed solution contained 0.5 mmol $Ni(NO_3)_2$ and 2 mmol urea, which was heated for 6 h at 120 ℃. Thereafter, CoS_x/$Ni(OH)_2$/NF was obtained with chilling to room temperature.

Materials characterization

The phase and microstructures were studied by X-ray diffraction (XRD, Bruker D8 diffractometer), scanning electron microscopy (SEM, S-4800) and transmission electron microscopy (TEM, FEI Talos F200X). Chemical valence states were analyzed *via* X-ray photo-electron spectrometer (XPS, Thermo ESCALAB 250).

Electrochemical measurements

Electrochemical tests were performed on biologic VMP3 electrochemical workstation with obtained catalysts as working electrode. Polarization curves were carried out and corresponding potentials were rectified. Electrochemical impedance spectroscopy (EIS) was measured at a frequency range from 100 kHz to 0.1 Hz.

Figures

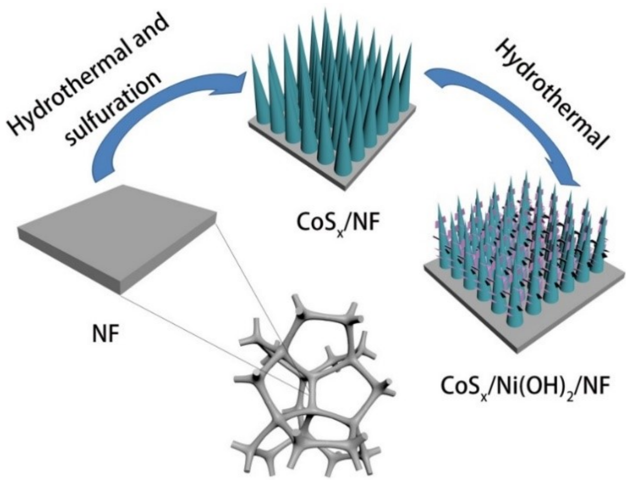

Fig. S1 Schematic illustration for preparing $CoS_x/Ni(OH)_2/NF$.

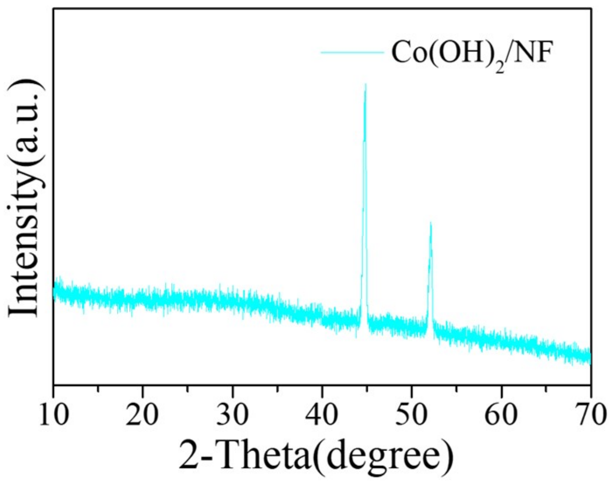

Fig. S2 XRD pattern of $Co(OH)_2/NF$.

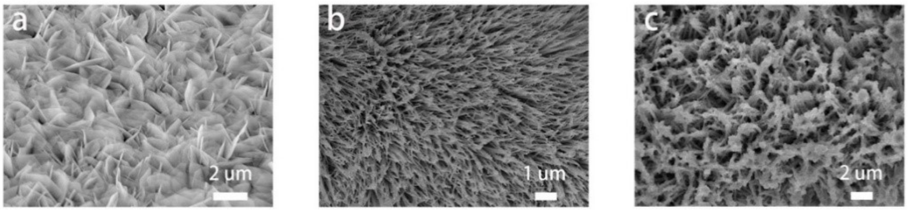

Fig. S3 SEM image of of $Ni(OH)_2$/NF (a), CoS_x/NF (b), CoS_x/$Ni(OH)_2$/NF (c).

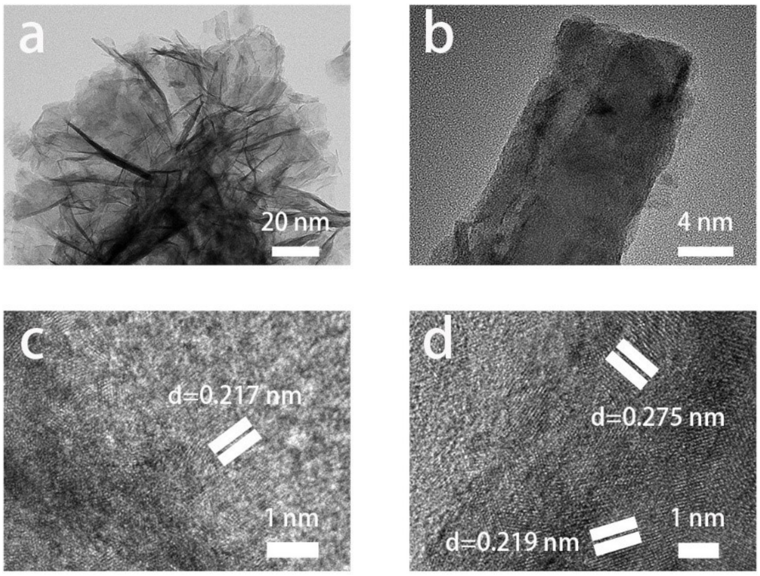

Fig. S4 Low and high-resolution TEM images of $Ni(OH)_2$/NF (a, c) and CoS_x/NF (b, d).

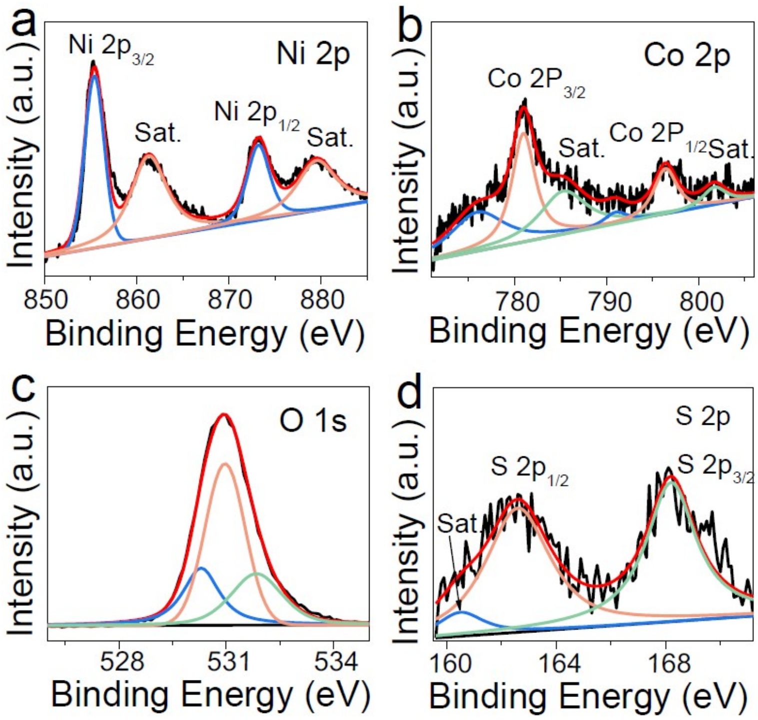

Fig. S5 XPS spectra of (a) Ni 2p, (b) Co 2p, (c) O 1s, and (d) S 2p for $CoS_x/Ni(OH)_2$.

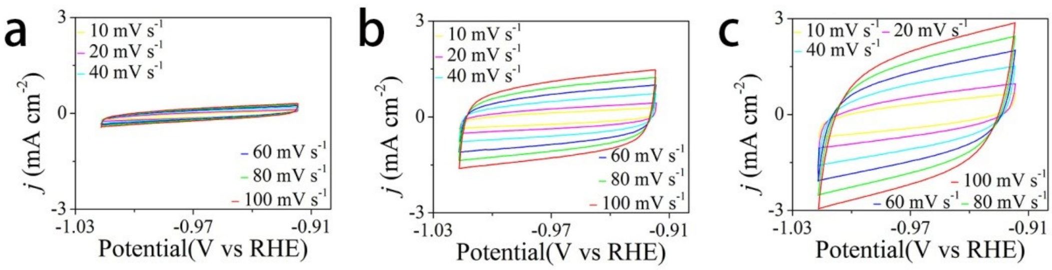

Fig. S6 CV curves of $Ni(OH)_2$/NF (a), CoS_x/NF (b), $CoS_x/Ni(OH)_2$/NF (c).

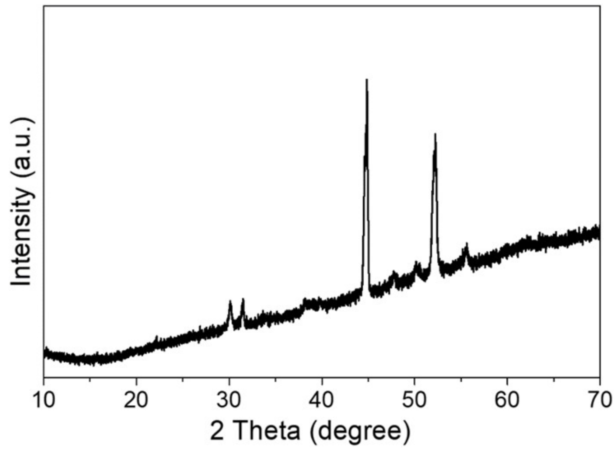

Fig. S7 XRD pattern of $CoS_x/Ni(OH)_2/NF$ after the HER stability.

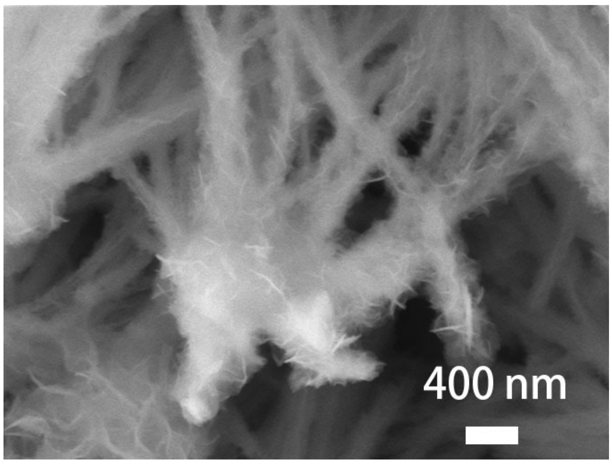

Fig. S8 SEM image of $CoS_x/Ni(OH)_2/NF$ after the HER stability.

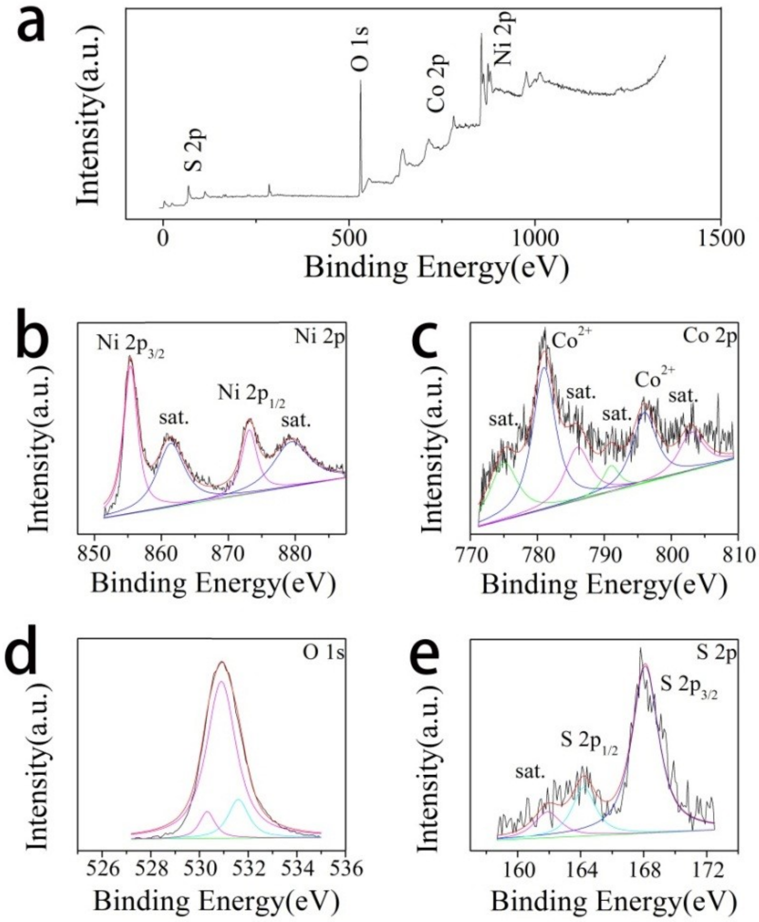

Fig. S9 XPS spectra of (a) wide scan spectrum, (b) Ni 2p, (c) Co 2p, (d) O 1s, and (e) S 2p for $CoS_x/Ni(OH)_2/NF$ after the HER stability.

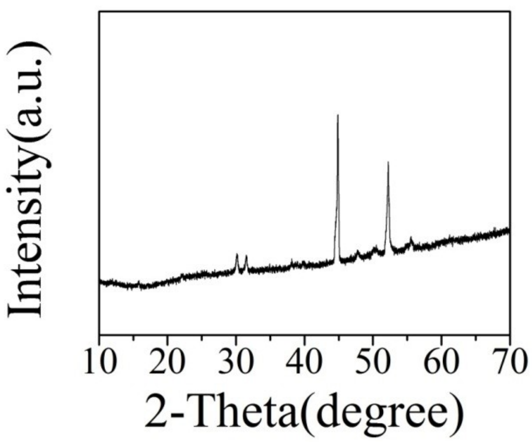

Fig. S10 XRD pattern of $CoS_x/Ni(OH)_2/NF$ after the UOR stability.

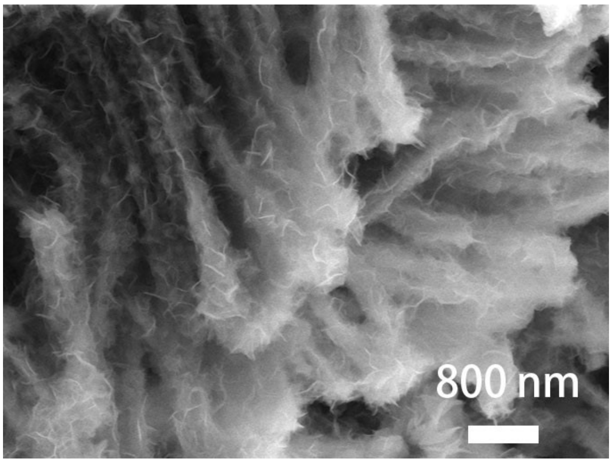

Fig. S11 SEM image of $CoS_x/Ni(OH)_2$/NF after the UOR stability.

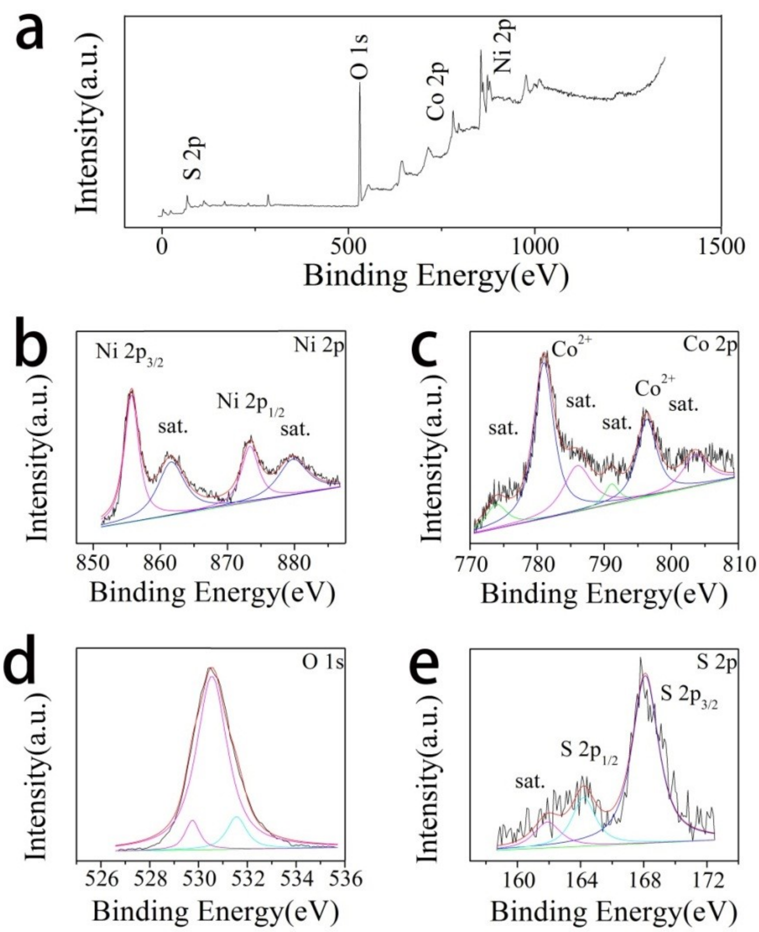

Fig. S12 XPS spectra of (a) wide scan spectrum, (b) Ni 2p, (c) Co 2p, (d) O 1s, and (e) S 2p for $CoS_x/Ni(OH)_2$/NF after the UOR stability.

Table S1. Comparison of HER performance of $CoS_x/Ni(OH)_2/NF$ with other reported catalysts.

Catalysts	Overpotential (mV) at 10 mA cm^{-2}	Tafel slope (mV dec^{-1})	References
$CoS_x/Ni(OH)_2/NF$	**148**	**99**	**This work**
CoP/rGO	150	38	S1
$Ni(OH)_2@Co_3O_4/NF$	159	114	S2
$Ni_2P@NF$	202	120	S2
Ni_3S_2 nanorod array foam	200	107	S3
Ni_3S_2 nanowires	199.2	106.1	S4
NCO NWs/NF	175	157.84	S5
NF-MoS_2/Ni_3S_2-thiourea	187	93.41	S6
NF-MoS_2/Ni_3S_2-L-cysteine	148	68.81	S6
Co-W/CeO_2	166	110	S7
Ni-S/CeO_2	170	118	S8
Ni_3FeN-NPs	158	42	S9

Table S2. Comparison of UOR performance of $CoS_x/Ni(OH)_2/NF$ in the 1.0 M KOH solution containing 0.5 M urea with other reported catalysts.

Catalysts	Voltage for urea electrolysis at *j* (V @ mA cm^{-2})	References
$CoS_x/Ni(OH)_2/NF$	**1.339@10** **1.409@100**	**This work**
Fe_2O_3/NF	1.41@10	[S10]
$Mo\text{-}Ni_2P$	1.41@10	[S11]
Ni_2P/CFC	1.42@10	[S12]
$P\text{-}CoS_2$	1.51@10	[S13]
$Ni_2P@Ni\text{-}MOF/NF$	1.41@100	[S14]
CoN NF/NF	1.41@100	[S15]
FQD/CoNi-LDH/NF	1.42@100	[S16]
$CoS_x/Co\text{-}MOF$	1.43@100	[S17]
$MS\text{-}Ni_2P/Ni_{0.96}S/NF$	1.441@100	[S18]
$CoMoO_4/Co_9S_8/NF$	1.50@100	[S19]

Table S3. Comparison of water electrolysis performances of $CoS_x/Ni(OH)_2/NF$ with recently reported catalysts.

Catalysts	Voltage (V) at 10 mA cm^{-2}	References
$CoS_x/Ni(OH)_2/NF$	**1.628**	**This work**
$NiFe/Co(PO_3)_2@NF$	1.63	[S20]
ZIF-67DC/NiMoCo/CNT	1.64	[S21]
Cu_8S_5/NSC	1.64	[S22]
CNO@NSG	1.67	[S23]
FeCoP/NF	1.67	[S24]
FeNiOH/NF	1.67	[S25]
$Mn\text{-}CoP/Co_2P$	1.67	[S26]
Co–Fe–B–P	1.68	[S27]
CoP/rGO	1.7	[S1]
Hollow CoP@NC	1.72	[S28]

Table S4. Comparison of urea electrolysis performances of Mn-Ni_2P/NiFe LDH with recently reported catalysts.

Catalysts	Voltage (V) at 10 mA cm^{-2}	References
CoS_x/$Ni(OH)_2$/NF	**1.485**	**This work**
CoMn/$CoMn_2O_4$	1.51	[S29]
$NiTe_2$/$Ni(OH)_2$	1.52	[S30]
Ni-MOF	1.52	[S31]
Fe_7Se_8@Fe_2O_3	1.55	[S32]
Bulk MnO_2	1.55	[S33]
Ni@NCNT-3	1.56	[S34]
MnO_2/$MnCo_2O_4$/Ni	1.58	[S35]
FQD/CoNi LDH/NF	1.59	[S16]
HC-NiMoS/Ti	1.59	[S36]
$Ni(OH)_2$NS@NW/NF	1.68	[S37]

References

1 L. Jiao, Y. X. Zhou, H. L. Jiang, *Chem. Sci.*, 2016, **7**, 1690.
2 F. H. Huang, J. Z. Wang, M. Wang, C. Zhang, Y. N. Xue, J. Liu, T. Xu, N. Cai, W. M. Chen, F. Q. Yu, *Colloid Surf. A-Physicochem. Eng. Asp.*, 2021, **623**, 126526.
3 Y. J. Qu, M. Y. Yang, J. W. Chai, Z. Tang, M. M. Shao, C. T. Kwok, M. Yang, Z. Y. Wang, D. Chua, S. J. Wang, Z. G. Lu, H. Pan, *ACS Appl. Mater. Interfaces.*, 2017, **9**, 5959.
4 J. Zhang, T. Wang, D. Pohl, B. Rellinghaus, R. H. Dong, S. H. Liu, X. D. Zhuang, X. L. Feng, *Angew. Chem. Int. Edit.*, 2016, **55**, 6702.
5 W. J. Chu, Z. J. Shi, Y. D. Hou, D. N. Ma, X. Bai, Y. F. Gao, N. J. Yang, *ACS Appl. Mater. Interfaces.*, 2020, **12**, 2763.
6 X. L. Liu, P. Wang, Q. Q. Zhang, B. B. Huang, Z. Y. Wang, Y. Y. Liu, Z. K. Zheng, Y. Dai, X. Y. Qin, X. Y. Zhang, *Appl. Surf. Sci.*, 2018, **459**, 422.
7 M. Q. Sheng, W. P. Weng, Y. Wang, Q. Wu, S. Y. Hou, *J. Alloy. Compd.*, 2018, **743**, 682.
8 M. Q. Zhao, H. F. Dong, Z. H. Chen, Z. P. Ma, L. X. Wang, G. L. Wang, W. Yang, G. J. Shao, *Int. J. Hydrog. Energy.*, 2016, **41**, 20485.
9 X. D. Jia, Y. F. Zhao, G. B. Chen, L. Shang, R. Shi, X. F. Kang, G. L. N. Waterhouse, L. Z. Wu, C. H. Tung, T. R. Zhang, *Adv. Energy Mater.*, 2016, **6**, 1502585.
10 H. A. Bandal, H. Kim, *J. Colloid Interf. Sci.*, 2022, **627**, 1030.
11 K. Zhang, G. Zhang, J. H. Qu, H. J. Liu, *J. Mater. Chem. A.*, 2018, **6**, 10297.
12 X. Zhang, Y. Y. Liu, Q. Z. Xiong, G. Q. Liu, C. J. Zhao, G. Z. Wang, Y. X. Zhang, H. M. Zhang, H. J. Zhao, *Electrochim. Acta.*, 2017, **254**, 44.
13 Y. Jiang, S. S. Gao, J. L. Liu, G. C. Xu, Q. Jia, F. S. Chen, X. M. Song, *Nanoscale.*, 2020, **12**, 11573.
14 H. T. Wang, H. Y. Zou, Y. Y. Liu, Z. L. Liu, W. S. Sun, K. A. Lin, T. L. Li, S. J. Luo, *Sci. Rep.*, 2021, **11**, 21414.
15 Y. M. Chen, P. J. Sun, W. W. Xing, *J. Chem. Sci.*, 2019, **131**, 101.
16 Y. Q. Feng, X. Wang, J. F. Huang, P. P. Dong, J. Ji, J. Li, L. Y. Cao, L. L. Feng, P. Jin, C. R. Wang, *Chem. Eng. J.*, 2020, **390**, 124525.
17 H. Z. Xu, K. Ye, K. Zhu, J. L. Yin, J. Yan, G. L. Wang, D. X. Cao, *Inorg. Chem. Front.*, 2020, **7**, 2602.
18 M. X. He, C. Q. Feng, T. Liao, S. N. Hu, H. M. Wu, Z. Q. Sun, *ACS Appl. Mater. Inter.*, 2020, **12**, 2225.
19 X. Q. Du, C. R. Huang, X. S. Zhang, *Int. J. Hydrog. Energy.*, 2019, **44**, 19595.
20 F. Gu, Q. Zhang, X. H. Chen, T. Li, H. C. Fu, H. Q. Luo, N. B. Li, *Int. J. Hydrog. Energy.*, 2022, **47**, 28475.
21 C. Zhang, Z. Xu, Y. C. Yu, A. C. Long, X. L. Ge, Y. K. Song, Y. R. An, Y. Y. Gu, *Electrochim. Acta.*, 2022, **424**, 140613.
22 Y. L. Zhang, L. Chen, B. Yan, F. P. Zhang, Y. L. Shi, X. H. Guo, *Chem. Eng. J.*, 2023, **45**, 138497.

23 H. Q. Li, H. H. Fu, J. Yu, L. P. Wang, Y. L. Shi, L. Chen, *J. Alloy. Compd.*, 2022, **922**, 166254.
24 L. H. Shen, S. H. Tang, L. M. Yu, Q. K. Huang, T. L. Zhou, S. Yang, H. L. Yu, H. X. Xiong, M. J. Xu, X. Zhong, L. Zhang, *J. Solid State Chem.*, 2022, **314**, 123434.
25 J. T. Ren, G. G. Yuan, C. C. Weng, L. Chen, Z. Y. Yuan, *Nanoscale.*, 2018, 10, 10620.
26 F. Tang, Y. W. Zhao, Y. Ge, Y. G. Sun, Y. Zhang, X. L. Yang, A. M. Cao, J. H. Qiu, X. J. Lin, *J. Colloid Interface Sci.*, 2022, **628**, 524.
27 Z. X. Wu, D. Z. Nie, M. Song, T. T. Jiao, G. T. Fu, X. E. Liu, *Nanoscale.*, 2019, **11**, 7506.
28 Y. Y. Xie, M. Q. Chen, M. K. Cai, J. Teng, H. F. Huang, Y. N. Fan, M. Barboiu, D. W. Wang, C. Y. Su, *Inorg. Chem.*, 2019, **58**, 14652.
29 C. Wang, H. L. Lu, Z. Y. Mao, C. L. Yan, G. Z. Shen, X. F. Wang, *Adv. Funct. Mater.*, 2020, **30**, 2000556.
30 B. Xu, X. D. Yang, X. P. Liu, W. X. Song, Y. Q. Sun, Q. S. Liu, H. X. Yang, C. C. Li, *J. Power Sources*, 2020, **449**, 227585.
31 S. S. Zheng, Y. Zheng, H. G. Xue, H. Pang, *Chem. Eng. J.*, 2020, **395**, 125166.
32 J. X. Li, X. Q. Du, X. S. Zhang, Z. P. Wang, *Int. J. Hydrog. Energy.*, 2022, **47**, 35203.
33 S. Chen, J. J. Duan, A. Vasileff, S. Z. Qiao, *Angew. Chem. Int. Edit.*, 2016, **55**, 3804.
34 Q. Zhang, F. M. D. Kazim, S. X. Ma, K. G. Qu, M. Li, Y. G. Wang, H. Hu, W. W. Cai, Z. H. Yang, *Appl. Catal. B-Environ.*, 2021, **280**, 119436.
35 C. L. Xiao, S. Li, X. Y. Zhang, D. R. MacFarlane, *J. Mater. Chem. A.*, 2017, **5**, 7825.
36 X. X. Wang, J. M. Wang, X. P. Sun, S. Wei, L. Cui, W. R. Yang, J. Q. Liu, *Nano Res.*, 2018, **11**, 988.
37 Z. H. Yue, S. Y. Yao, Y. Z. Li, W. X. Zhu, W. T. Zhang, R. Wang, J. Wang, L. J. Huang, D. Y. Zhao, J. L. Wang, *Electrochim. Acta.*, 2018, **268**, 211.