

## Supplementary Materials

# **Engineering hierarchical manganese molybdenum sulfide nanosheets integrated cathode for high-energy density hybrid supercapacitors**

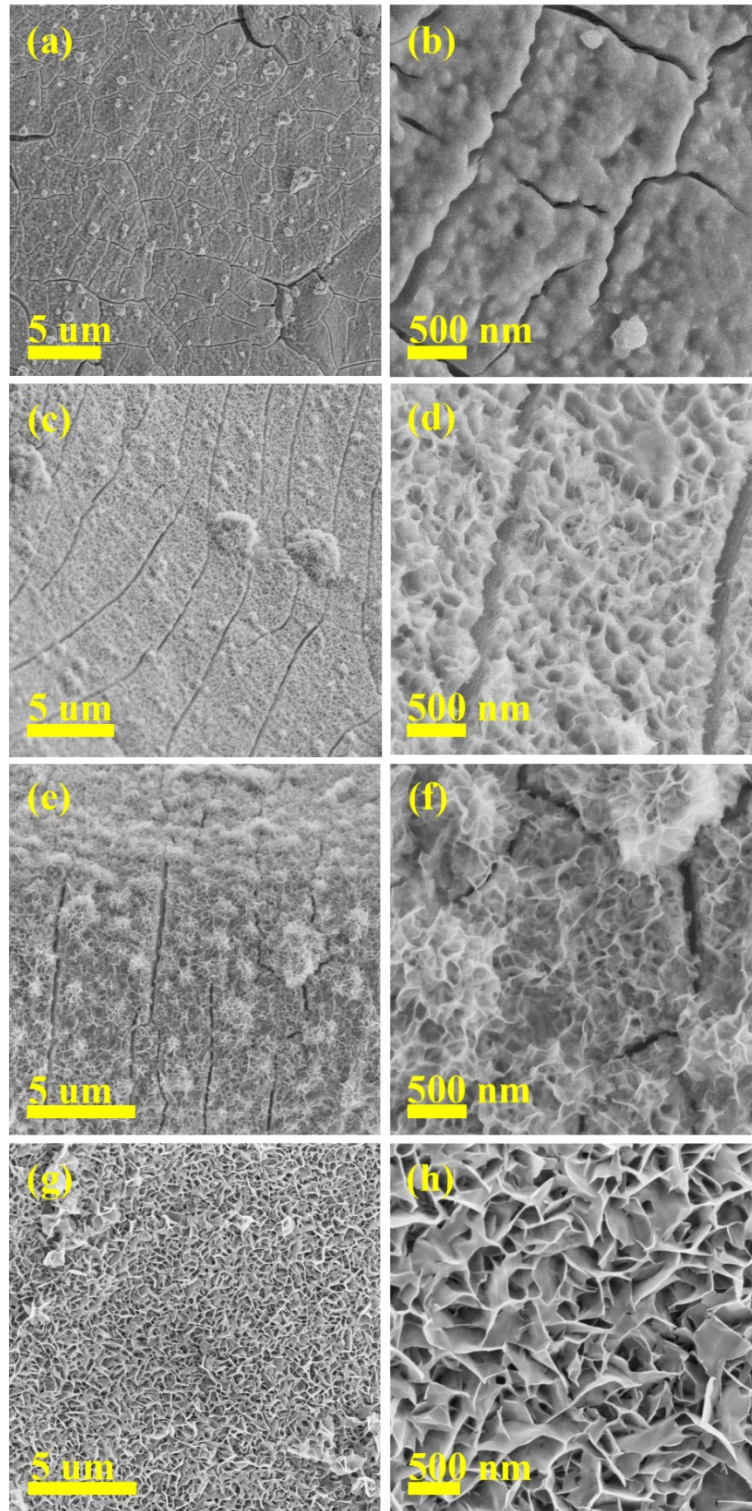
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**Fig.S1.** Low- and high-magnification SEM images for  $\text{MnMoO}_4 \cdot \text{H}_2\text{O}$  NSs by performing the hydrothermal reactions for 2-8h; (a) and (b) for  $\text{MnMoO}_4 \cdot \text{H}_2\text{O}$  NSs-2; (c) and (d) for  $\text{MnMoO}_4 \cdot \text{H}_2\text{O}$  NSs-4; (e) and (f) for  $\text{MnMoO}_4 \cdot \text{H}_2\text{O}$  NSs-6; (g) and (h) for  $\text{MnMoO}_4 \cdot \text{H}_2\text{O}$  NSs-8.

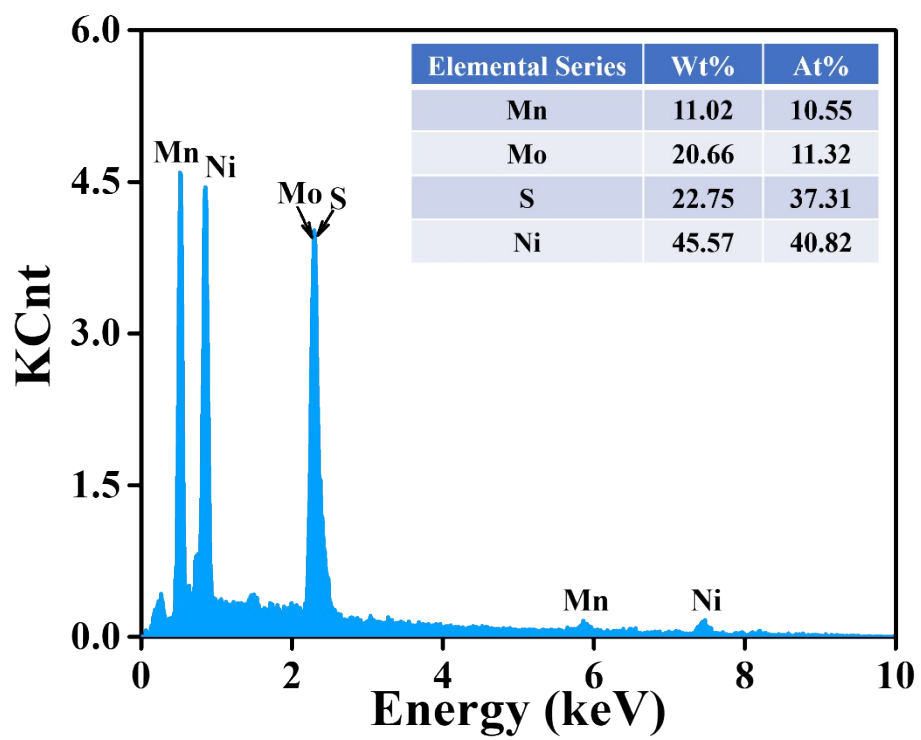


Fig.S2. EDAX spectrum for Mn-Mo-S NSs.

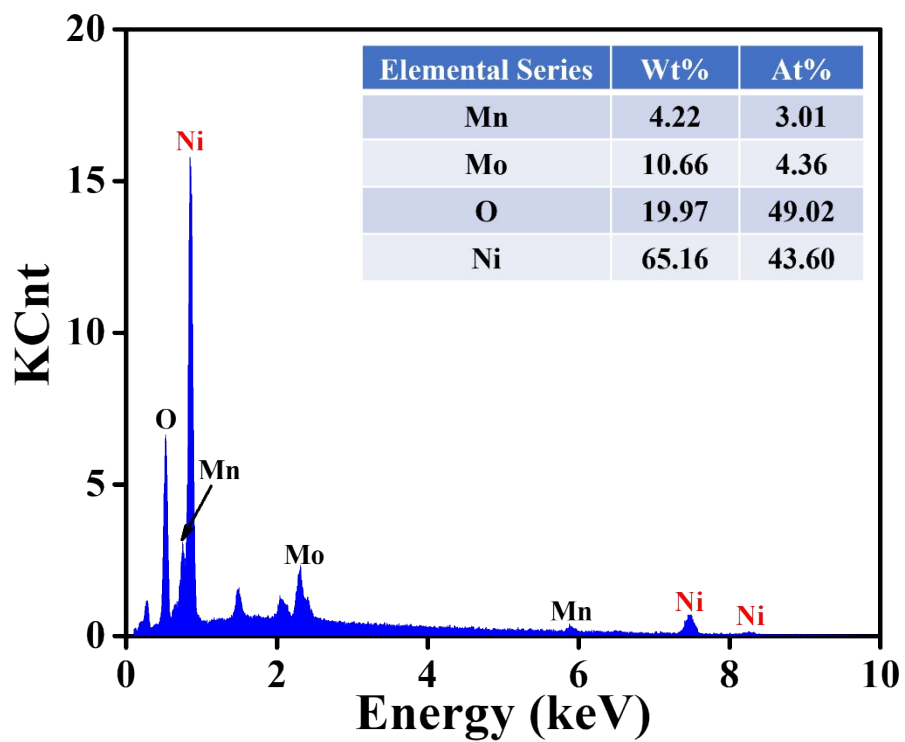
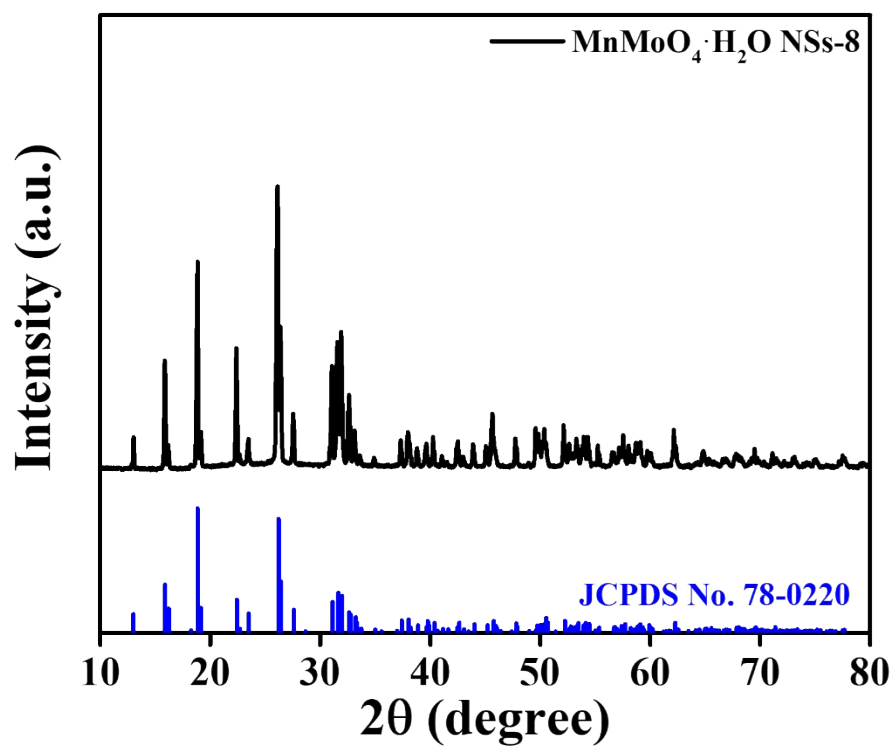
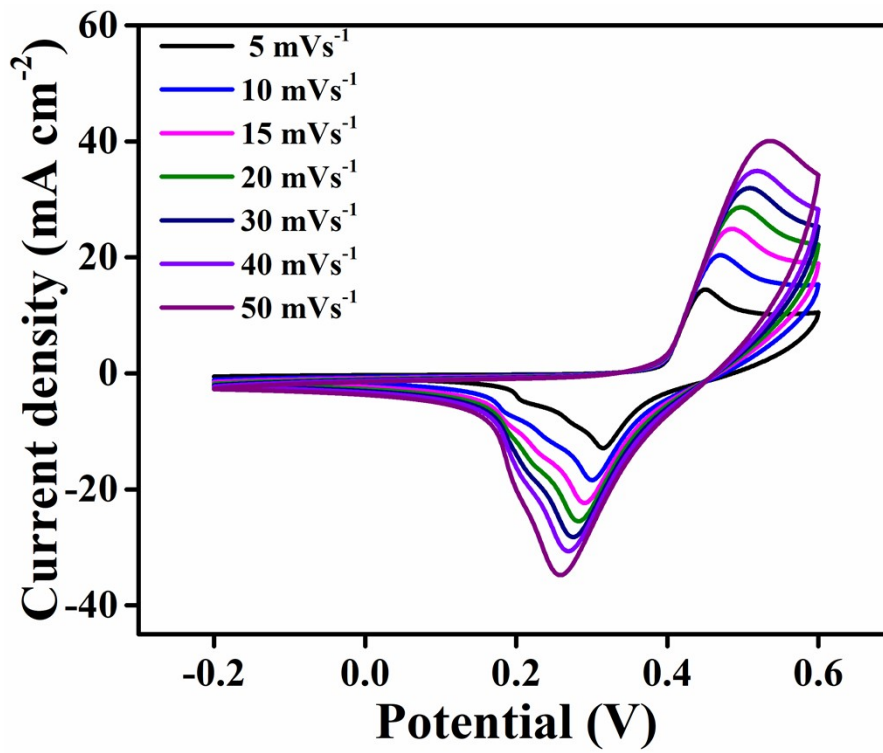


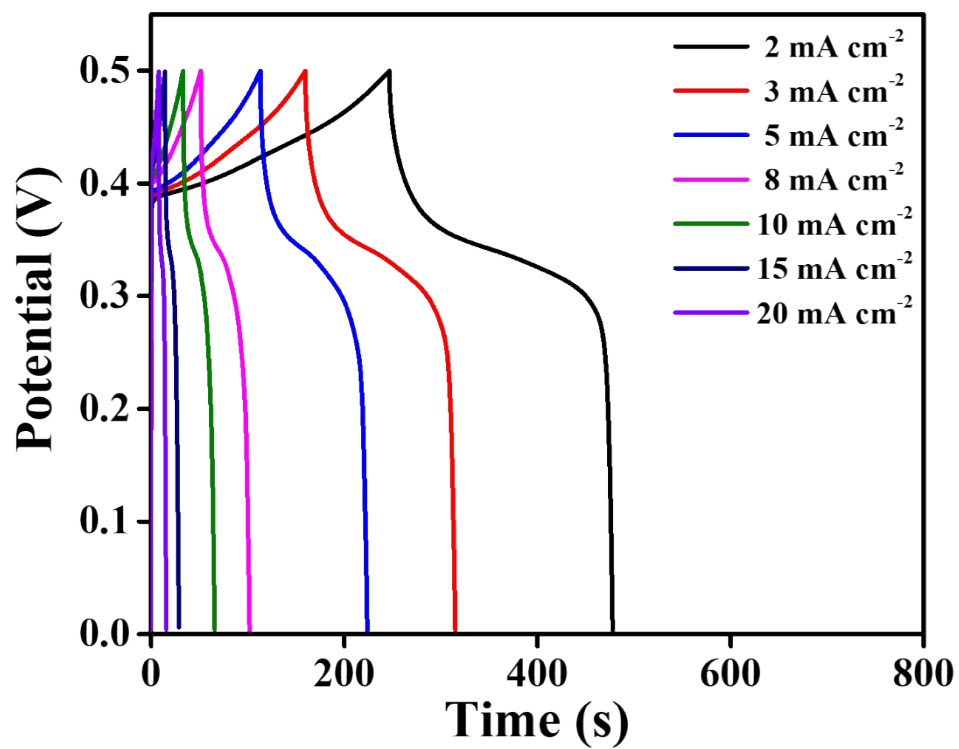
Fig.S3. EDAX spectrum for MnMoO<sub>4</sub>·H<sub>2</sub>O NSs-8.



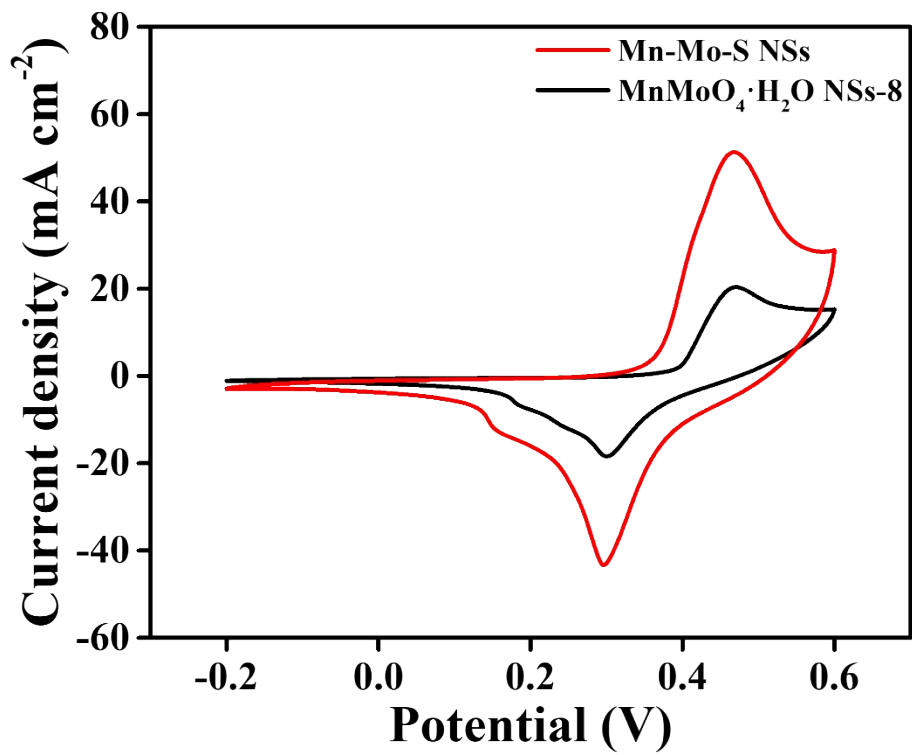
**Fig.S4.** XRD pattern for MnMoO<sub>4</sub>·H<sub>2</sub>O NSs-8.



**Fig.S5.** CV curves for MnMoO<sub>4</sub>·H<sub>2</sub>O NSs-8.

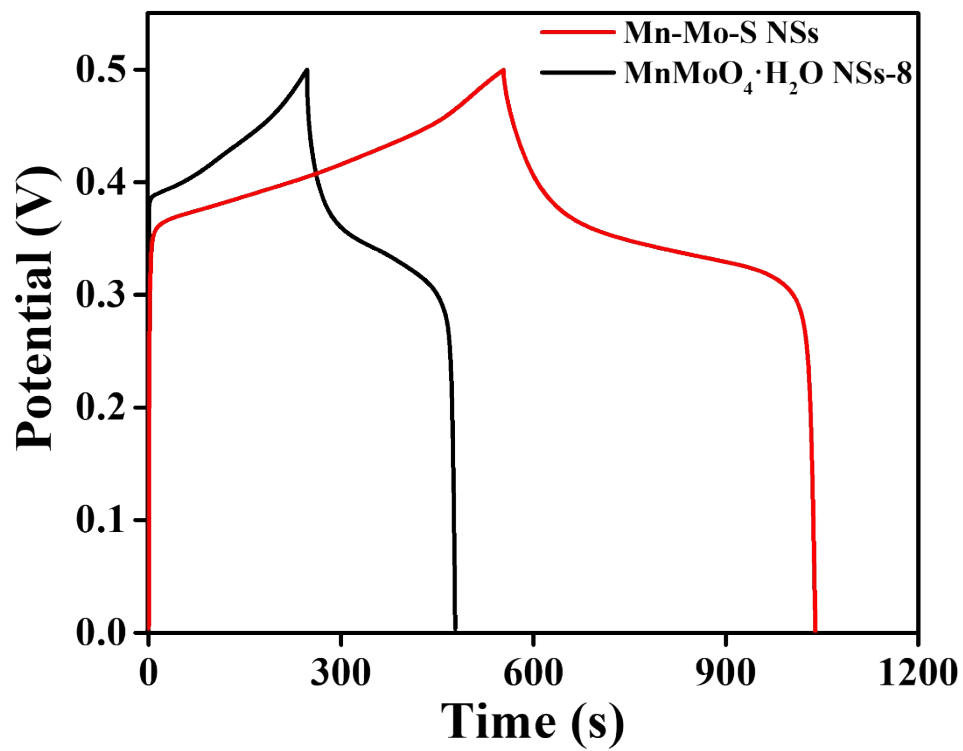


**Fig.S6.** GCD curves for MnMoO<sub>4</sub>·H<sub>2</sub>O NSs-8.



**Fig.S7.** CV curves comparison of Mn-Mo-S NSs and MnMoO<sub>4</sub>·H<sub>2</sub>O NSs-8 at 10 mV s<sup>-1</sup>.





**Fig.S8.** GCD curves comparison of Mn-Mo-S NSs and MnMoO<sub>4</sub>·H<sub>2</sub>O NSs-8 at 2 mA cm<sup>-2</sup>.

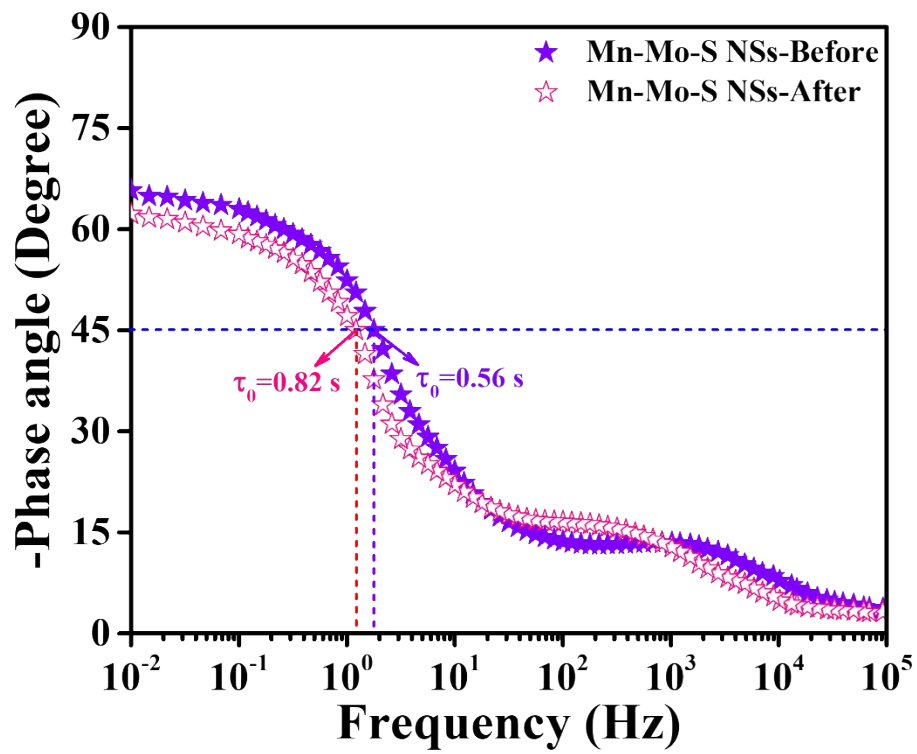
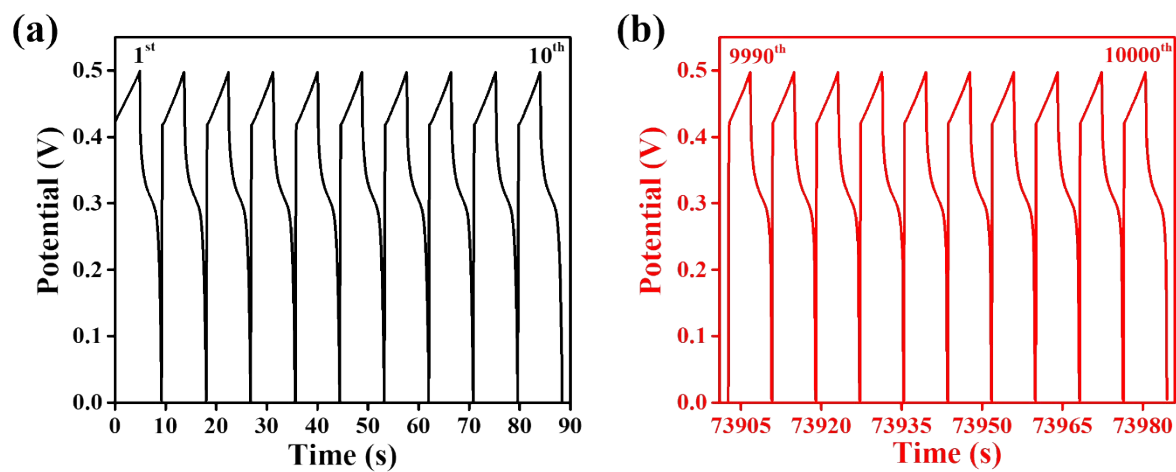
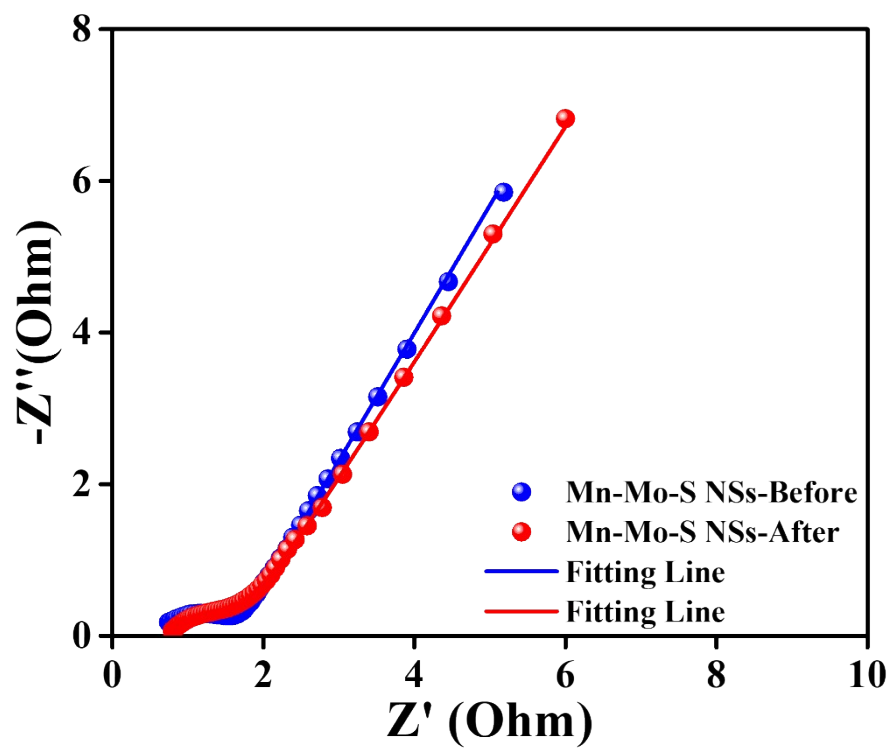


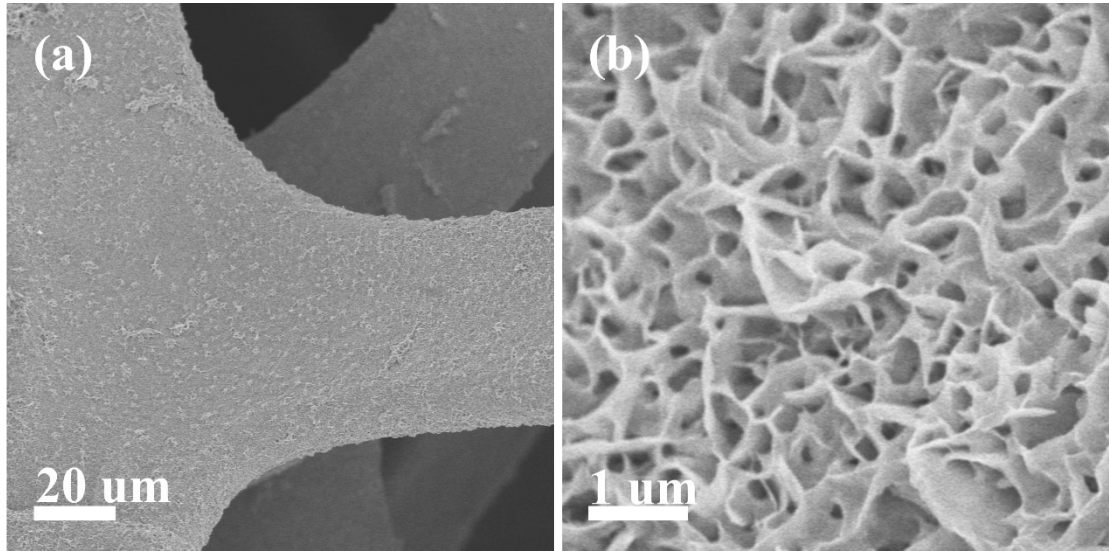
Fig.S9. Bode phase angle plots of Mn-Mo-S NSs-Before and Mn-Mo-S NSs-After.



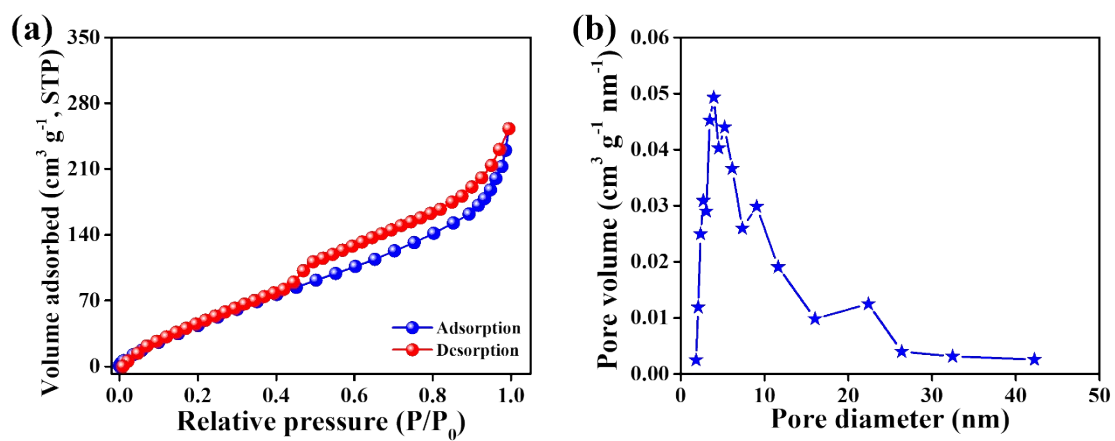
**Fig.S10.** The initial and final 10 GCD cycles for Mn-Mo-S NSs integrated cathode in the cyclic stability test at  $50 \text{ mA cm}^{-2}$  for 10000 GCD cycles.



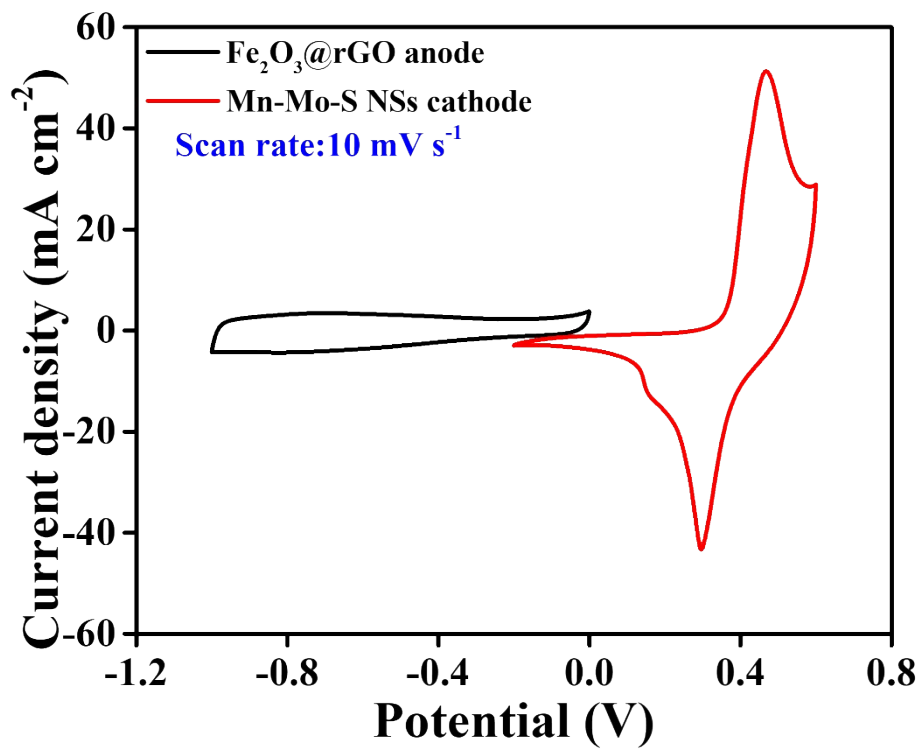
**Fig.S11.** EIS spectra comparison of Mn-Mo-S NSs-Before and Mn-Mo-S NSs-After.



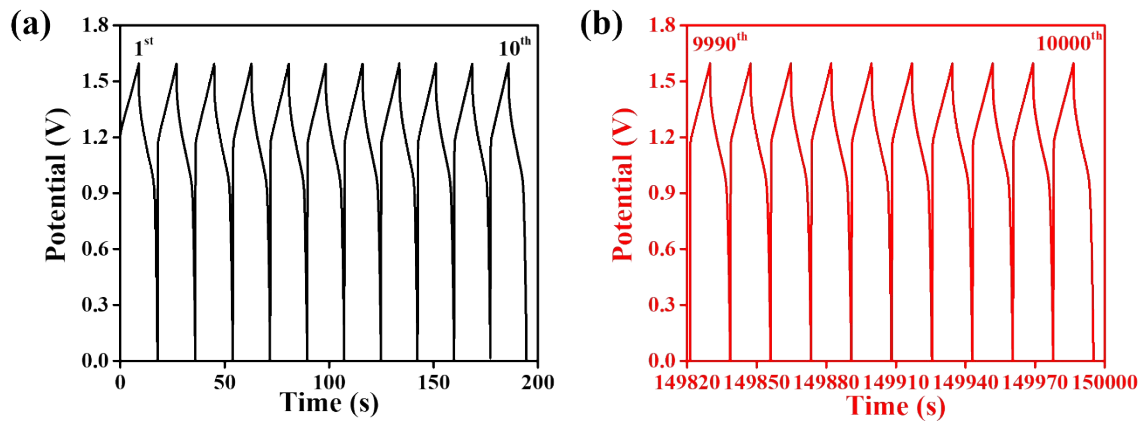
**Fig.S12.** SEM images for Mn-Mo-S NSs-After.



**Fig.S13.** (a)  $N_2$  adsorption-desorption isotherm and (b) pore size distribution for Mn-Mo-S NSs-After.



**Fig.S14.** CV curves of Mn-Mo-S NSs cathode and Fe<sub>2</sub>O<sub>3</sub>@rGO anode at 10 mV s<sup>-1</sup>.



**Fig.S15.** The initial and final 10 GCD cycles for Mn-Mo-S NSs//Fe<sub>2</sub>O<sub>3</sub>@rGO HSC in the cyclic stability test at 50 mA cm<sup>-2</sup> for 10000 GCD cycles.



**Table S1.** The elemental composition of Mn-Mo-S NSs integrated cathode before and after cycling tests confirmed by the ICP-OES measurements.

<b>Electrode materials</b>	<b>Mn (at.%)</b>	<b>Mo (at.%)</b>	<b>S (at.%)</b>	<b>O (at.%)</b>
Mn-Mo-S NSs-Before	12.21	36.72	48.73	2.34
Mn-Mo-S NSs-After	12.13	36.67	47.33	3.87

**Table S2.** The corresponding electrochemical performance for  $\text{MnMoO}_4 \cdot \text{H}_2\text{O}$  NS-8 and Mn-Mo-S NSs integrated cathode obtained from the CV data in Fig.S5 and Fig.4a.

Electrode materials	Scan rate ( $\text{mVs}^{-1}$ )	Anodic peak position (V)	Anodic peak current (A)	Cathodic peak position (V)	Cathodic peak current (A)	CV integrated area
$\text{MnMoO}_4 \cdot \text{H}_2\text{O}$ NS-8	5	0.449	0.0289	0.315	-0.0258	0.0097
	10	0.471	0.0408	0.301	-0.0368	0.0151
	15	0.484	0.0498	0.291	-0.0447	0.0186
	20	0.497	0.0573	0.282	-0.0511	0.0215
	30	0.509	0.0639	0.275	-0.0565	0.0260
	40	0.518	0.0698	0.269	-0.0613	0.0297
	50	0.536	0.0801	0.259	-0.0696	0.0329
Mn-Mo-S NSs	5	0.446	0.0342	0.309	-0.0291	0.0105
	10	0.467	0.0513	0.298	-0.0432	0.0173
	15	0.485	0.0639	0.288	-0.0532	0.0225
	20	0.499	0.0745	0.281	-0.0614	0.0291
	30	0.52	0.0918	0.268	-0.0745	0.0348
	40	0.536	0.1063	0.258	-0.0854	0.0412
	50	0.555	0.1192	0.248	-0.0947	0.0466

**Table S3.** The corresponding electrochemical performance for MnMoO<sub>4</sub>·H<sub>2</sub>O NSs-8 and Mn-Mo-S NSs integrated cathode obtained from the GCD data in Fig.S6 and Fig.4b.

Electrode materials	Current density (mA cm <sup>-2</sup> )	Charge time (s)	Discharge time (s)	Charge capacity (mAh cm <sup>-2</sup> /mAh g <sup>-1</sup> )	Discharge capacity (mAh cm <sup>-2</sup> /mAh g <sup>-1</sup> )	Rate capability
MnMoO <sub>4</sub> ·H <sub>2</sub> O NSs-8	2	232.4	231.2	0.14/264.2	0.139/262.3	53.2%
	3	162.6	159.8	0.129/243.4	0.128/241.5	
	5	118.7	113.2	0.115/217	0.114/215.1	
	8	52.1	51.2	0.107/201.9	0.106/200	
	10	34.6	33.3	0.103/194.4	0.102/192.5	
	15	15.7	14.5	0.087/166.1	0.086/164.2	
	20	9.2	8	0.075/141.5	0.074/139.6	
Mn-Mo-S NSs	2	556.8	553.4	0.375/394.7	0.373/392.6	60.6%
	3	319.7	317.4	0.345/363.2	0.344/362.1	
	5	166.4	165	0.29/305.3	0.289/304.2	
	8	89.1	87.5	0.258/271.6	0.257/270.5	
	10	64.2	63.5	0.243/255.8	0.242/254.7	
	15	36.3	35	0.236/248.5	0.235/247.4	
	20	23.4	22.5	0.227/239	0.226/237.9	

**Table S4.** EIS spectra fitting results for MnMoO<sub>4</sub>·H<sub>2</sub>O NSs-8, Mn-Mo-S NSs integrated cathode before and after cycling stability measurements.

<b>Electrode materials</b>	<b>R<sub>s</sub> (Ω)</b>	<b>CPE<sub>1</sub>-T (mF)</b>	<b>R<sub>ct</sub> (Ω)</b>	<b>Z<sub>w</sub>-R (Ω)</b>	<b>Z<sub>w</sub>-T (Ω)</b>	<b>CPE<sub>2</sub>-T (mF)</b>
MnMoO <sub>4</sub> ·H <sub>2</sub> O NSs-8	1.138	0.0053	1.635	6.265	11.62	0.355
Mn-Mo-S NSs-Before	0.763	0.0649	0.838	0.305	2.73	1.598
Mn-Mo-S NSs-After	0.791	0.0376	1.086	0.772	8.66	1.339

**Table S5.** Electrochemical properties comparison of Mn-Mo-S NSs with recently reported TMSs-type electrode materials in literatures.

Electrode materials	Areal capacitance/ capacity (F cm <sup>-2</sup> /mAh cm <sup>-2</sup> )	Specific capacitance/ capacity (F g <sup>-1</sup> /mAh g <sup>-1</sup> )	Current load (A g <sup>-1</sup> /mA cm <sup>-2</sup> )	Electrolyte	Stability (Cycles)	Ref.
MnMoS <sub>4</sub> @CNF	-	1727.9 F g <sup>-1</sup>	1 A g <sup>-1</sup>	3M KOH	84% 6000	1
FeCo <sub>2</sub> S <sub>4</sub> @Ni@Gr	-	390 mAh g <sup>-1</sup>	1 A g <sup>-1</sup>	3M KOH	58.1% 10000	2
NiCo <sub>2</sub> S <sub>4</sub> /rGO	-	1072 F g <sup>-1</sup>	1 A g <sup>-1</sup>	6M KOH	-	3
NiCoS@PPy	-	2316.6 F g <sup>-1</sup>	1 A g <sup>-1</sup>	2M KOH	-	4
rGO/PANI@NiMoS <sub>4</sub>	-	194 mAh g <sup>-1</sup>	0.75 A g <sup>-1</sup>	1M KOH	-	5
NiCo <sub>2</sub> S <sub>4</sub> @HCs	-	3178.2 F g <sup>-1</sup>	1 A g <sup>-1</sup>	2M KOH	95.9% 5000	6
ZnCo <sub>2</sub> S <sub>4</sub> @ppy	-	1486 F g <sup>-1</sup>	1 A g <sup>-1</sup>	3M KOH	72.9% 5000	7
MnCo <sub>2</sub> S <sub>4</sub>	-	129.7 mAh g <sup>-1</sup>	1 A g <sup>-1</sup>	3M KOH	87.81% 4000	8
Ravine-like MnCo <sub>2</sub> S <sub>4</sub> nanosheets	-	231 mAh g <sup>-1</sup>	1 A g <sup>-1</sup>	3M KOH	94% 5000	9
NiMn-S	-	2510.15 F g <sup>-1</sup>	1 A g <sup>-1</sup>	6M KOH	84.5% 5000	10
CoNi <sub>2</sub> S <sub>4</sub> /CNFs	-	1870 mAh g <sup>-1</sup>	4 A g <sup>-1</sup>	6M KOH	85.1% 5000	11
ZnGa <sub>2</sub> S <sub>4</sub> hollow spheres	-	358.4 mAh g <sup>-1</sup>	2 A g <sup>-1</sup>	6M KOH	98.4% 5000	12
Mn-Mo-S NSs	0.373 mAh cm <sup>-2</sup>	392.6 mAh g <sup>-1</sup>	2 mA cm <sup>-2</sup>	2M KOH	96.2% 10000	This work

**Table S6.** Electrochemical properties comparison with recently reported literatures.

Reported Devised	Electrolyte	Device Window (V)	Energy density (Wh kg <sup>-1</sup> )	Power Density (W kg <sup>-1</sup> )	Stability (Cycles)	Ref.
FeCo <sub>2</sub> S <sub>4</sub> @Ni@Gr//AC	3M KOH	0-1.6	65.8	849	89.2% 6000	2
NiCo <sub>2</sub> S <sub>4</sub> /rGO//AC	6M KOH	0-1.7	41.52	1067	82% 3000	3
NiCoS@PPy//AC	2M KOH	0-1.6	34.4	799	84% 8500	4
NiCo <sub>2</sub> S <sub>4</sub> @HCs//AC	2M KOH	0-1.6	69.6	847	90.2% 10000	6
ZnCo <sub>2</sub> S <sub>4</sub> @ppy//AC	3M KOH	0-1.6	33.78	800.05	90% 5000	7
NiCo <sub>2</sub> S <sub>4</sub> @NiMoS <sub>4</sub> /Fe <sub>2</sub> O <sub>3</sub> /NG	KOH/PVA	0-1.6	72.3	460	90.5% 10000	13
MnCo <sub>2</sub> S <sub>4</sub> NSs/Fe <sub>2</sub> O <sub>3</sub> @rGO	KOH/PVA	0-1.6	61.4	244	90.4 % 10000	14
MnCo <sub>2</sub> S <sub>4</sub> /Co <sub>9</sub> S <sub>8</sub> //AC	6M KOH	0-1.6	45.8	800	94.8% 5000	15
CoMoS <sub>4</sub> @Ni-Co-S//AC	3M KOH	0-1.6	49.1	800	90.3% 10000	16
MoS <sub>2</sub> /NiCo <sub>2</sub> S <sub>4</sub> @C HMSs//AC	6M KOH	0-1.6	53.01	4200	90.1% 10000	17
MnCo <sub>2</sub> S <sub>4</sub> /Co <sub>9</sub> S <sub>8</sub> //AC	6M KOH	0-1.6	45.8	800	94.8% 5000	18
NiCo <sub>2</sub> S <sub>4</sub> /BPC//BPC	3M KOH	0-1.6	38.5	738.1	89% 4000	19
NiCo <sub>2</sub> S <sub>4</sub> //ARHC	2M KOH	0-1.6	41.1	400	62% 10000	20
CoMoS <sub>4</sub> /RGO//AC	1M KOH	0-1.5	59.4	1125	99.3% 6000	21
Mn-NiS NSs//ONAC	KOH/PVA	0-1.65	44.2	825	90% 5000	22
NiCo <sub>2</sub> S <sub>4</sub> -Ni <sub>9</sub> S <sub>8</sub> -C DYMs//rGO gel	6M KOH	0-1.6	51.0	1399.4	84.5% 5000	23
C/NiCo <sub>2</sub> S <sub>4</sub> //AC	6M KOH	0-1.6	34.1	160	78.9% 4000	24
NiCo <sub>2</sub> S <sub>4</sub> /CNT//Fe <sub>2</sub> O <sub>3</sub> /CNT	3M KOH	0-1.7	41.6	800	82% 5000	25
Mn-Mo-S NSs//Fe <sub>2</sub> O <sub>3</sub> @rGO	KOH/PVA	0-1.6	72.9	516.8	94.6% 10000	This work

## References

- 1 S. Anand, A. Choudhury, *Mater. Chem. Phys.*, 2023, **299**, 127517.
- 2 X. Zheng, J. Jiang, T. Bi, F. Jin, M. Li, *ACS Appl. Energy Mater.*, 2021, **4**, 3288-3296.
- 3 A. I. A. Salam, S. Y. Attia, F. I. E. I. Hosiny, M. A. Sadek, S. G. Mohamed, M. M. Rashad, *Mater. Chem. Phys.*, 2022, **277**, 125554.
- 4 X. Zhao, Q. Ma, K. Tao, L. Han, *ACS Appl. Energy Mater.*, 2021, **4**, 4199-4207.
- 5 R. Xiong, X. Zhang, X. Xu, Z. Zhang, X. Tian, C. Wang, *Diam. Relat. Mater.*, 2022, **127**, 109183.
- 6 J. Zhao, Y. Wang, Y. Qian, H. Jin, X. Tang, Z. Huang, J. Lou, Q. Zhang, Y. Lei, S. Wang, *Adv. Funct. Mater.*, 2023, **33**, 2210238.
- 7 Y. Wang, C. Xiang, Y. Zou, F. Xu, L. Sun, J. Zhang, *J. Energy Storage*, 2021, **41**, 102838.
- 8 K. V. G. Raghavendra, C. V. V. M. Gopi, R. Vinodh, S. S. Rao, I. M. Obaidat, H. J. Kim, *J. Energy Storage*, 2020, **27**, 101159.
- 9 L. Abbasi, M. Arvand, S. E. Moosavifard, *Carbon*, 2020, **161**, 299-308.
- 10 X. Wang, C. Hao, J. Zhang, C. Ni, X. Wang, Y. Shen, *J. Power Sources*, 2022, **539**, 231594.
- 11 J. Zhu, C. Han, X. Song, *Mater. Chem. Phys.*, 2022, **283**, 126038.
- 12 A. M. Zardkhoshoui, M. M. Ashtiani, M. Sarparast, S. S. H. Davarani, *J. Power Sources*, 2020, **450**, 227691.
- 13 K. R. Shrestha, S. Kandula, N. H. Kim, J. H. Lee, *Chem. Eng. J.*, 2021, **405**, 127046.
- 14 C. Li, T. Zhao, X. Feng, S. Liu, L. Li, R. Zha, Y. Zhang, Z. Zhang, *J. Alloys Compd.*, 2021, **859**, 157815.
- 15 H. Jia, J. Wang, W. Fu, J. Hu, Y. Liu, *Chem. Eng. J.*, 2020, **391**, 123541.
- 16 F. Ma, X. Dai, J. Jin, N. Tie, Y. Dai, *Electrochim. Acta*, 2020, **331**, 135459.
- 17 Q. Li, W. Lu, Z. Li, J. Ning, Y. Zhong, Y. Hu, *Chem. Eng. J.*, 2020, **380**, 122544.
- 18 H. Jia, J. Wang, W. Fu, J. Hu, Y. Liu, *Chem. Eng. J.*, 2020, **391**, 123541.

- 19 J. Feng, X. Zhang, Q. Lu, E. Guo, M. Wei, *Energy Fuels*, 2022, **36**, 5424-5432.
- 20 Y. Gao, B. Wu, J. Hei, D. Gao, X. Xu, Z. Wei, H. Wu, *Electrochim. Acta*, 2020, **347**, 136314.
- 21 Z. Zhang, X. Zhang, X. Xu, R. Xiong, X. Tian, C. Wang, *Colloid. Surface. A*, 2022, **652**, 129762.
- 22 R. K. Devi, M. Ganesan, T. W. Chen, S. M. Chen, M. Akilarasan, S. P. Rwei, J. Yu, T. Elayappan, A. Shaju, *J. Alloy Compd.*, 2023, **944**, 169261.
- 23 Y. Yan, A. Li, C. Lu, T. Zhai, S. Lu, W. Li, W. Zhou, *Chem. Eng. J.*, 2020, **396**, 125316.
- 24 W. Lu, M. Yang, X. Jiang, Y. Yu, X. Liu, Y. Xing, *Chem. Eng. J.*, 2020, **382**, 122943.
- 25 X. Yang, X. He, Q. Li, J. Sun, Z. Lei, Z. H. Liu, *Energy Fuels*, 2021, **35**, 3449-3458.