Rational synthesis of CoFeP@nickel-manganese sulfide core-shell nanoarrays

for hybrid supercapacitor

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Fig. S1 (a,b) SEM images for the corresponding EDX mapping image of CoFeP@NiMnS/CC, (c) Fe elemental mapping, (d) Co elemental mapping, (e) P elemental mapping, (f) Ni elemental mapping, (g) Mn elemental mapping, and (h) S elemental mapping.



Fig. S2 The selected area electron diffraction (SEAD) pattern of CoFeP@NiMnS.



Fig. S3 (a) N_2 adsorption-desorption isotherms, and (b) pore size distributions of the CoFeP/CC, NiMnS/CC, and CoFeP@NiMnS/CC.



Fig. S4 XPS surveys of CoFeP/CC, NiMnS/CC, and CoFeP@NiMnS/CC.



Fig. S5 Comparison of CV curves of bare carbon cloth and CoFeP@NiMnS/CC electrodes at a scan rate of 5 mV s⁻¹.



Fig. S6 Electrochemical performance tested in a three-electrode system in 2.0 M KOH electrolyte: CV curves of (a) CoFeP/CC electrode and (b) NiMnS/CC electrode, and GCD curves of (c) CoFeP/CC electrode and (d) NiMnS/CC electrode.



Fig. S7 The linear relationship between the peak current and the scan rate during charge and discharge for (a) the CoFeP/CC and (b) NiMnS/CC electrodes.



Fig. S8 The diffusion-controlled and capacitive-controlled CV response at 5 mV s⁻¹ of (a) the CoFeP/CC and (b) NiMnS/CC electrode, and the percentages of capacitive contribution at different scan rates of 5-50 mV s⁻¹ for (c) CoFeP@NiMnS/CC, (d) CoFeP/CC, and (e) NiMnS/CC electrodes.



Fig. S9 SEM images of CoFeP@NiMnS/CC electrode after 5000 cycles at 5 A $\rm g^{-1}$ at

(a) low and (b) high magnifications.



Fig. S10 The cyclic performance and coulombic efficiency of the assembled CoFeP@NiMnS/CC//LPC-Cu HSC device over 10000 cycles at 5 A g⁻¹ (inset shows the first and last five GCD cycles).

CoFeP@NiMnS/CC.									
Samples	$\mathbf{S}_{\mathrm{BET}}$	S _{micro}	V _{total}	V _{micro}					
	$(m^2 g^{-1})^a$	$(m^2 g^{-1})^b$	$(cm^3 g^{-1})^c$	$(cm^3 g^{-1})$					
CoFeP/CC	38.6	1.02	0.102	0.008					
NiMnS/CC	61.3	4.73	0.137	0.031					
CoFeP@NiMnS/CC	89.7	6.36	0.169	0.082					

Table S1 Specific surface areas and pore parameters of CoFeP/CC, NiMnS/CC, and

 $^{\rm a}$ Specific surface area (S $_{\rm BET}$) was calculated via Brunauer-Emmett-Teller (BET) method.

 $^{\text{b}}$ Micropore surface area (S_{\text{mic}}) was calculated from t-plot method.

 $^{\rm c}$ Total pore volume (V_{total}) was obtained from the adsorbed amount at a relative pressure of 0.99.

in literature.						
Electrode	Synthesis method	Specific capacity (mAh g ⁻¹)	Rate performance	Maximum energy density (W kg ⁻¹)	Cycling stability	Ref.
NiCoP@CoS	Hydrothermal method and phosphorization	1796 F g ⁻¹ (2 A g ⁻¹)	68.3% (20 A g ⁻¹)	35.8 Wh kg ⁻¹ at 748.9 W kg ⁻¹	86.1% after 10000 cycles	1
NiCoP@MoSe ₂	Hydrothermal, phosphorization and CVD	2245.4 F g ⁻¹ (1 mA cm ⁻²)	91.6% (10 A g ⁻¹)	55.1 Wh kg ⁻¹ at 799.8 W kg ⁻¹	95.8% after 8000 cycles	2
CoP@NiCoP	Hydrothermal method and phosphorization	265.5 (2 A g ⁻¹)	61.68% (25 A g ⁻¹)	37.16 Wh kg ⁻ ¹ at 875 W kg ⁻¹	50% after 1000 cycles	3
NiCoP/NiCo- OH	Hydrothermal method and phosphorization	1100 (1 A g ⁻¹)	60% (10 A g ⁻¹)	34 Wh kg ⁻¹ at 775 W kg ⁻ 1	92% after 1000 cycles	4
CuCo-P@ Ni(OH) ₂	Solvotherma,pho sphorization and electrodeposition	230.6 (2 mA cm ⁻²)	86.3% (20 mA cm ⁻²)	40 Wh kg ⁻¹ at 319.6 W kg ⁻¹	73% after 6000 cycles	5
ZnCo ₂ O ₄ @ Ni-Co-S	Hydrothermal method and electrodeposition	1396.9 C g ⁻¹ (1 A g ⁻¹)	52.8% (10 A g ⁻¹)	53.1 Wh kg ⁻¹ at 3375 W kg ⁻¹	85.5% after 10000 cycles	6
Co- CH@NiCoMn -CH	Solvothermal method	3224 F g ⁻¹ (1 A g ⁻¹)	83.97% (5 A g ⁻¹)	20.31 Wh kg ⁻ ¹ at 748.46 W kg ⁻¹	90.4% after 6000 cycles	7
$\begin{array}{c} \text{Co-MoS}_2(a) \\ \text{Cu}_2\text{MoS}_4 \end{array}$	Hydrothermal method	220 (1 A g ⁻¹)	64% (10 A g ⁻¹)	41.6 Wh kg ⁻¹ at 6240 W kg ⁻¹	92.8% after 5000 cycles	8
CoFeP@ NiMnS/CC	Hydrothermal, phosphorization and electrodeposition	260.7 (1 A g ⁻¹)	65.9% (20 A g ⁻¹)	60.1 Wh kg ⁻¹ at 371.8 W kg ⁻¹	85.7% after 10000 cycles	This work

 Table S2 Comparison of the electrochemical performances of the as-fabricated

 CoFeP@NiMnS/CC electrode with previously reported core-shell electrode materials

References

[1] Z. Xu, C. Du, H. Yang, J. Huang, X. Zhang, J. Chen, NiCoP@CoS tree-like coreshell nanoarrays on nickel foam as battery-type electrodes for supercapacitors, Chem. Eng. J. (2021) 127871.

[2] X. Gao, L. Yin, L. Zhang, Y. Zhao, B. Zhang, Decoration of NiCoP nanowires with interlayer-expanded few-layer MoSe₂ nanosheets: A novel electrode material for asymmetric supercapacitors, Chem. Eng. J. 395 (2020) 125058.

[3] X. Wang, C. Jing, W. Zhang, X. Wang, X. Liu, B. Dong, Y. Zhang, One-step phosphorization synthesis of CoP@NiCoP nanowire/nanosheet composites hybrid arrays on Ni foam for high performance supercapacitors, Appl. Surf. Sci. 532 (2020) 147437.

[4] X. Li, H. Wu, A.M. Elshahawy, L. Wang, S.J. Pennycook, C. Guan, J. Wang, Cactus-like NiCoP/NiCo-OH 3D architecture with tunable composition for highperformance electrochemical capacitors, Adv. Funct. Mater. 28 (2018) 1800036.

[5] X. Li, J. Huang, L. Wang, J. Zhang, S. Song, G. Li, P. Wang, P. Sun, Y. Yang, Hierarchical honeycomb-like networks of CuCo-P@Ni(OH)₂ nanosheet arrays enabling high-performance hybrid supercapacitors, J. Alloys Compd. 838 (2020) 155626.

[6] M. Dai, D. Zhao, H. Liu, X. Zhu, X. Wu, B. Wang, Nanohybridization of Ni-Co-S nanosheets with ZnCo₂O₄ nanowires as supercapacitor electrodes with long cycling stabilities, ACS Appl. Energy Mater. 4 (2021) 2637–2643.

[7] Y. Zhong, X. Cao, Y. Liu, L. Cui, J. Liu, Nickel cobalt manganese ternary carbonate hydroxide nanoflakes branched on cobalt carbonate hydroxide nanowire arrays as novel electrode material for supercapacitors with outstanding performance, J. Colloid Interf. Sci. 581 (2021) 11–20. [8] S.K. Hussain, B.N.V. Krishna, G. Nagaraju, S.C. Sekhar, D. Narsimulu, J.S. Yu, Porous Co-MoS₂@Cu₂MoS₄ three-dimensional nanoflowers via in situ sulfurization of Cu₂O nanospheres for electrochemical hybrid capacitors, Chem. Eng. J. 403 (2021) 126319.