Supporting information

Design and construction of hollow metal sulfides/selenides core-shell heterostructure arrays for hybrid supercapacitor

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Experimental

Materials:

Commercial nickel foam (NF, thickness: 1.7 mm, pore diameter distribution: 0.2-0.5 mm), hydrochloric acid (HCl,35–38%), cobalt chloride hexahydrate (CoCl₂·6H₂O), nickel chloride hexahydrate (NiCl₂·6H₂O), urea (CO(NH₂)₂), sodium sulfide (Na₂S·9H₂O), Lithium chloride (LiCl) and selenium dioxide (SeO₂) were obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals in the experiments were of analytical grade and used as received without any further purification.

Characterization:

We scrape the synthetic sample from the NF and use a magnet to suck up the nickel chips for all characterization. Crystal information of the sample was characterized by an X-ray diffractometer (XRD, Bruker D8 Advance) with Cu Ka radiation. The microstructure was characterized by scanning electron microscopy (SEM, Hitachi S-4800) and transmission electron microscopy (TEM, FEI TalosF200x). Elements analysis and valence states on the surface of products were characterized by X-ray Photoelectron Spectroscopy. The specific surface area was obtained by nitrogen adsorption-desorption with the Brunauer–Emmett–Teller (BET) model, and the pore size

distribution was achieved by the Barrette-Joynere-Halenda (BJH) model. The types and contents of its elements are analyzed using energy dispersive spectroscopy (EDS) attached to a TEM device.



Fig. S1 SEM of (a) $NiSe_2$ and (b) $Co_{0.85}Se$.



Fig. S2 XRD of (a) CoCH and (b) Ni₃S₂.



Fig. S3 EDS spectrum of (a) $NiSe_2@Co_9S_8$ and (b) $Co_{0.85}Se@Co_9S_8$.



Fig. S4 XPS survey spectrum of NiSe₂@Co₉S₈, Co_{0.85}Se@Co₉S₈ and Co₉S₈.



Fig. S5 Nitrogen adsorption-desorption isotherms of (a) $NiSe_2@Co_9S_8$, (b) $Co_{0.85}Se@Co_9S_8$ and (c) Co_9S_8 : Pore diameter distribution of (d) $NiSe_2@Co_9S_8$, (e) $Co_{0.85}Se@Co_9S_8$ and (f) Co_9S_8 .



Fig. S6 CV curves of (a) NiSe₂@Co₉S₈, (b) Co_{0.85}Se@Co₉S₈, (c) Co₉S₈, (d) NiSe₂, and (e) Co_{0.85}Se at different scan rates.



Fig. S7 (a) CV curves of Ni_3S_2 NF at different scan rates from 5 to 50 mV s⁻¹, (b) GCD curves of Ni_3S_2 NF at different current densities from 2 to 20 mA cm⁻² and (c) areal capacity at different current densities of Ni_3S_2 NF.



Fig. S8 CP curves of (a) NiSe₂@Co₉S₈, (b) Co_{0.85}Se@Co₉S₈, (c) Co₉S₈, (d) NiSe₂, and (e) Co_{0.85}Se at different current densities.



Fig. S9 SEM images of (a) $NiSe_2@Co_9S_8$, (b) $Co_{0.85}Se@Co_9S_8$, (c) Co_9S_8 , (d) $NiSe_2$, and (e) $Co_{0.85}Se$ after 5000 cycles.



Fig. S10 CV curves of NiSe₂@Co₉S₈ with the capacitive and diffusion-controlled fraction shown by the shaded region at (a) 1 mv·s⁻¹, (b) 2 mv·s⁻¹, (c) 4 mv·s⁻¹ and (d) 5 mv·s⁻¹.



Fig. S11 CV curves of $Co_{0.85}Se@Co_9S_8$ with the capacitive and diffusion-controlled fraction shown by the shaded region at (a) 1 mv·s⁻¹, (b) 2 mv·s⁻¹, (c) 4 mv·s⁻¹ and (d) 5 mv·s⁻¹.



Fig. S12 (a) CV curves at different scan rates, (b) GCD curves at different current densities and (c) specific capacitance at different current densities of activated carbon.



Fig. S13 CV curves of AC and (a) $NiSe_2@Co_9S_8$ and (b) $Co_{0.85}Se@Co_9S_8$ at 10 mV s⁻¹ and CV curves of (c) $NiSe_2@Co_9S_8//AC$ and (d) $Co_{0.85}Se@Co_9S_8//AC$ in different potential windows at a scan rate of 50 mV s⁻¹.

Electrode materials	Capacitance	Current density	Electrolyte	<u>Ref</u>
CoSe ₂ @ZnS	953.3 F g ⁻¹	1 A g ⁻¹	3 М КОН	S1
Co _{0.85} Se@CoNi ₂ S ₄ /GF	5.25 F cm ⁻²	1 m A cm ⁻²	2 M KOH	S2
NiSe ₂ @CNT	980.5 F g ⁻¹	1 A g ⁻¹	6 M KOH	S3
Co ₉ S ₈ @MnO ₂	3.7 F cm^{-2}	1 m A cm^{-2}	1 M Na ₂ SO ₄	S4
Co ₉ S ₈ @NiMn oxide	5.34 F cm ⁻²	1 m A cm ⁻²	1 M LiOH	S5
NiSe/Ni(OH) ₂	2725.69 F g^{-1}	5 m A cm^{-2}	3 М КОН	S6
NiSe nanoarrays	1.55 F cm ⁻²	4 m A cm^{-2}	1 M KOH	S7
NiSe@NiCo(CO ₃)(OH) ₂	6.89 F cm ⁻²	4 m A cm^{-2}	1 M KOH	S 8
NiCo ₂ Se ₄	6.21 F cm ⁻²	1 m A cm^{-2}	6 M KOH	S9
$Ni_3S_2@Co_9S_8$ nanotubes	8.24 F cm^{-2}	2 m A cm^{-2}	6 M KOH	S10
Co ₃ O ₄ /carbon foam	106 F g ⁻¹	$0.1 \ V \ s^{-1}$	1 M NaOH	S11
Pr ₆ O ₁₁ @Ni-Co oxides	1635 F g ⁻¹	0.5 m A cm^{-2}	2 M KOH	S12
NiSe ₂ @Co ₉ S ₈	12.54 F cm^{-2}	2 m A cm^{-2}	2 М КОН	This work
Co _{0.85} Se@Co ₉ S ₈	9.61 F cm ⁻²			

Table S1 Performance comparison of supercapacitors.

References

- S1. S. A. Ahmad, M. Z. U. Shah, I. Hussain, M. Arif, P. Song, S. I. Al-Saeedi, M. Sajjad, I. Ahmad, J. Aftab, T. H. Huang and A. Shah, J. Energy Storage, 2023, 73, 109090.
- S2. C. Zhang, M. Hou, X. Cai, J. Lin, X. Liu, R. Wang, L. Zhou, J. Gao, B. Li and L. Lai, J. Mater. Chem. A, 2018, 6, 15630-15639.
- S3. Y. Y. Zheng, Y. R. Tian, S. Sarwar, J. J. Luo and X. Y. Zhang, J. Power Sources, 2020, 452, 227793.
- S4. Q. Li, M. Liu, F. Huang, X. Zuo, X. Wei, S. Li and H. Zhang, Chem. Eng. J., 2022, 437, 135494.
- S5. H. Qian, M. J. Liu, H. Zhang, X. Wei, H. Zhang, S. K. Li and F. Z. Huang, Electrochim. Acta, 2021, **399**, 139378.

- L. He, Y. Wang, Y. Guo, G. Li, X. Zhang and W. Cai, Nanotechnology, 2021, 32, 345706.
- S7. H. Chen, L. T. Wu, K. Y. Zhang, A. M. Qin and S. P. Chen, Int. J. Electrochem. Sci., 2018, 13, 12437-12449.
- S8. H. Gu, Y. Zeng, S. Wan, S. Zhang, Q. Zhong and Y. Bu, J. Mater. Chem. A, 2021, 9, 16099-16107.
- S9. R. Yang, Y. Zhang, X. Huang, H. Q. Yin, Y. Y. Mo, K. Y. Zhang, A. M. Qin, S. P. Chen and S. G. Dai, Ionics, 2023, 29, 3353-3363.
- S10.Y. Lin, X. Chen, P. Chang, Z. Liu, G. Ren and J. Tao, J. Alloys Compd., 2022, 900, 163503.
- S11.Z. Xu, A. Younis, D. Chu, Z. Ao, H. Xu and S. Li, J. Nanomater., 2014, 2014, 1-5.
- S12.N. Chen, A. Younis, S. Huang, D. Chu and S. Li, J. Alloys Compd., 2019, 783, 772-778.