

Synthesis of iron doped nickel sulfide/rGO as an electroactive material for asymmetric supercapacitors

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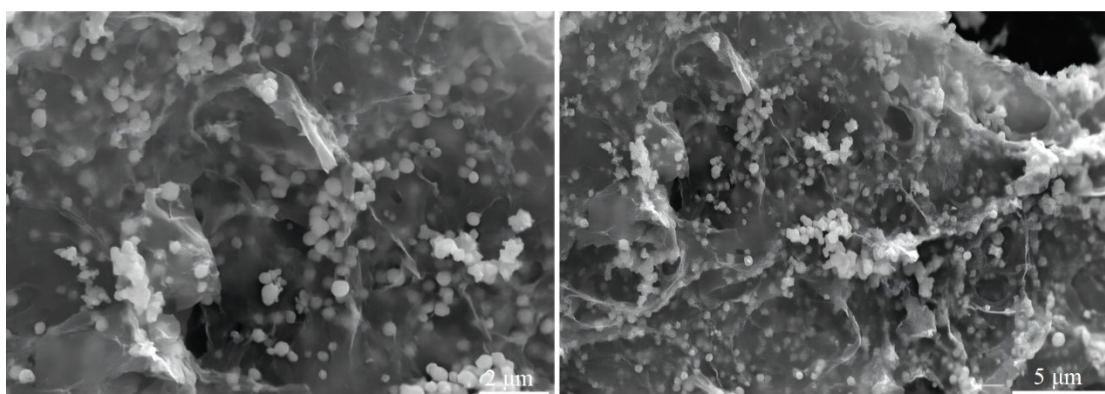


Figure S1 SEM images of Ni-S/rGO.

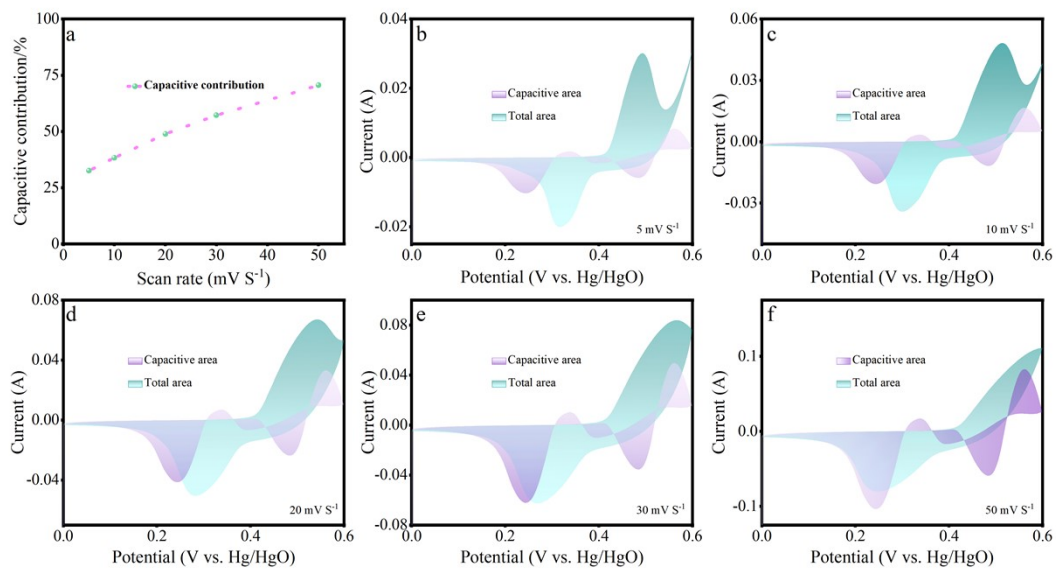


Figure S2 capacitive contributions to the total current at different scan rates.

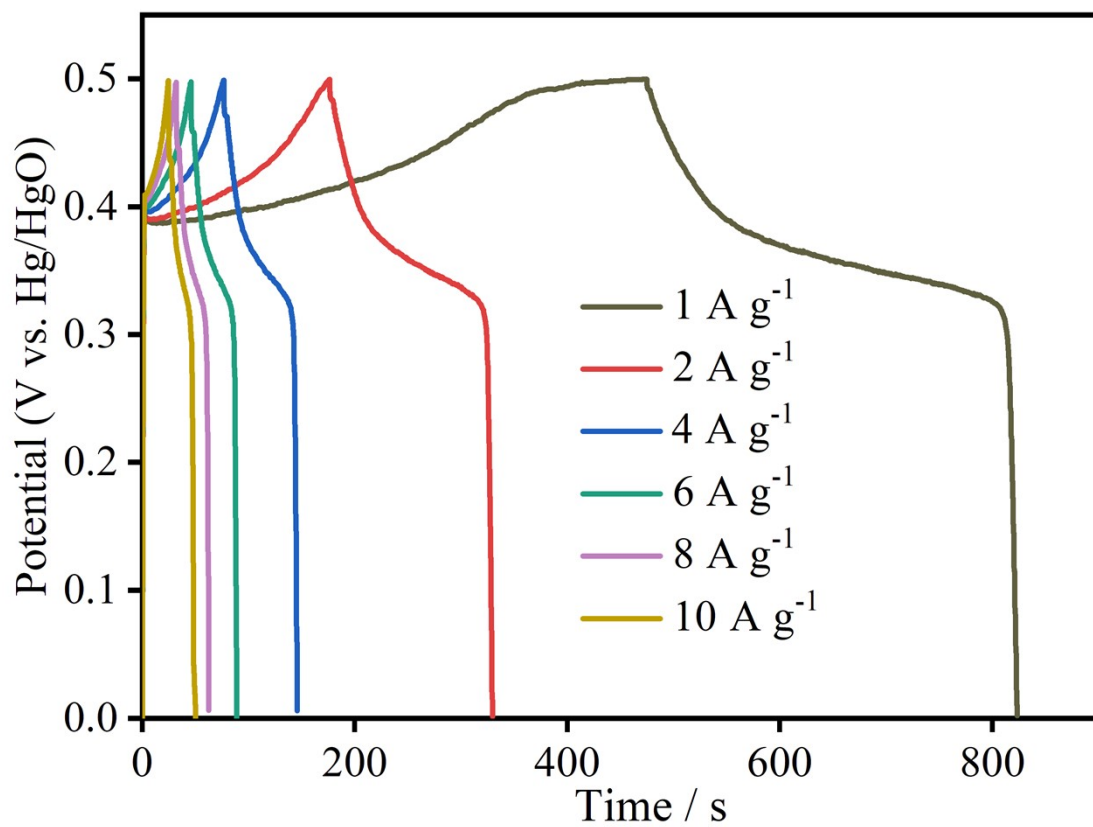


Figure S3 GCD curves at varied current densities for Fe-Ni-S

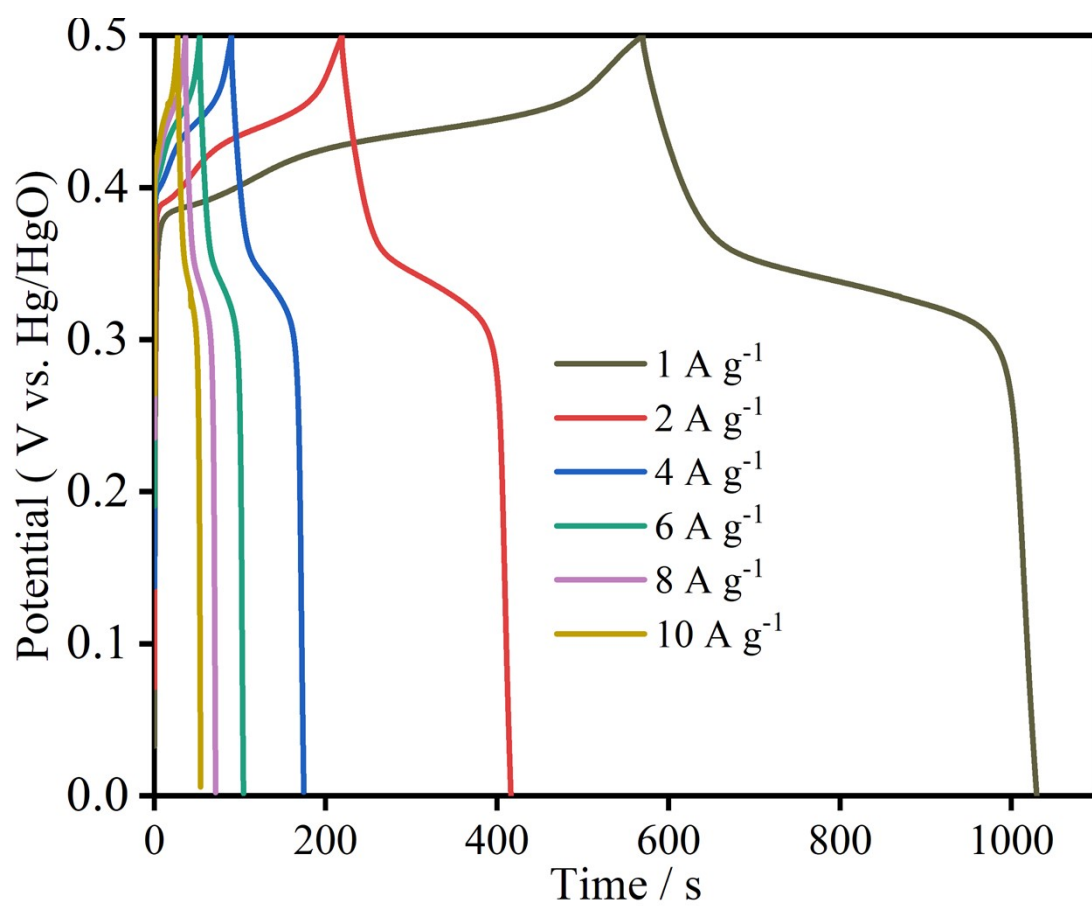


Figure S4 GCD curves at varied current densities for Ni-S/rGO

Table S1 The 2 θ values observed in the XRD patterns of Fe-Ni-S/rGO and Ni-S/rGO.

Fe-Ni-S/rGO	Ni-S/rGO	
2 θ (degree)	2 θ (degree)	Description
30.1	30.1	Ni _{0.96} S(100)
34.5	34.6	Ni _{0.96} S(101)
45.7	45.8	Ni _{0.96} S(102)
53.5	53.6	Ni _{0.96} S(110)
21.3	21.3	Ni ₃ S ₂ (101)
73.0	73.1	Ni ₃ S ₂ (214)
31.5	31.6	NiS ₂ (200)
38.9	39.0	NiS ₂ (211)

Table. S2. Comparison of electrochemical performance for NiS based electrode.

Materials	Electrolyte	Max. SC	Rate Performance	Refs.
NiS	3 M KOH	1122.7 F·g ⁻¹ /1 A·g ⁻¹	28%/30 A·g ⁻¹	1
NiS/NHCS	2 M KOH	1150 F·g ⁻¹ /1 A·g ⁻¹	52.2%/20 A·g ⁻¹	2
NiS	3 M KOH	1315.4 F·g ⁻¹ /1 A·g ⁻¹	24.2%/30 A·g ⁻¹	3
NiS	2 M KOH	515.98 C·g ⁻¹ /1 A·g ⁻¹	37.6%/50 A·g ⁻¹	4
P-NiS	2 M KOH	727.79 C·g ⁻¹ /1 A·g ⁻¹	50.6%/50 A·g ⁻¹	4
r-FeNi ₂ S ₄ -rGO	6 M KOH	746.8 C g ⁻¹ /1 A g ⁻¹	49.01%/10 A g ⁻¹	5
NiFe-S/NF	6 M KOH	884.9 F g ⁻¹ /1 A g ⁻¹	73.79%/10 A g ⁻¹	6
NiS ₂ /GO	2 M KOH	1020 F g ⁻¹ /1 A g ⁻¹	55.68%/5 A g ⁻¹	7
NiS/NF	3 M KOH	1279.8 F g ⁻¹ /7.5 A g ⁻¹	70.5%/12.5 A g ⁻¹	8
NiCo ₂ S ₄ /CNF	3 M KOH	757.97 C g ⁻¹ /1 A g ⁻¹	86%/ 20 A g ⁻¹	9
Fe-NiS@MWCNTs/NF	1.5 M KOH	662 C g ⁻¹ /5 mV s ⁻¹	70.2%/100 mV s ⁻¹	10
NiS/NF	3 M KOH	613 F g ⁻¹ /1.1 A g ⁻¹	80%/2.8 A g ⁻¹	11
SS-NiS@3DNF	3 M KOH	694 F g ⁻¹ /1 A g ⁻¹	41.5%/6 A g ⁻¹	12
NiS/CF@NiS	6 M KOH	1691.1 F g ⁻¹ /1 A g ⁻¹	60.3%/10 A g ⁻¹	13
carbon sphere@NiS	3 M KOH	1022 F g ⁻¹ /1A g ⁻¹	61.7%/10 A g ⁻¹	14
NiS hollow cubes	2 M KOH	874.5 F g ⁻¹ /1 A g ⁻¹	60.3%/10 A g ⁻¹	15
NiS/TC-g-C ₃ N ₄	6 M KOH	1162 F g ⁻¹ /1 A g ⁻¹		16
NiS	2 M KOH	529 F g ⁻¹ /2 A g ⁻¹	23.06%/30 A g ⁻¹	17
NiS-CFs	2 M KOH	635.1 F g ⁻¹ /1 A g ⁻¹	67.88%/10 A g ⁻¹	18
NiS/RGO	6 M KOH	302 F g ⁻¹ /1.1 A g ⁻¹		19
NiS@NF	6 M KOH	603.9 F g ⁻¹ /1 A g ⁻¹	30.65%/10 A g ⁻¹	20
rGO- Ni ₃ S ₂	6 M KOH	616 C g ⁻¹ /1 A g ⁻¹	52.27%/20 A g ⁻¹	21
NiO/NiS	3 M KOH	386.7 F g ⁻¹ /1 A g ⁻¹	45%/10 A g ⁻¹	22
SS-NiS@3DNF-E-3	2 M KOH	694 F g ⁻¹ /1A g ⁻¹	41.5%/6 A g ⁻¹	23
NiS	2 M KOH	964 F g ⁻¹ /1 A g ⁻¹	49.6%/10 A g ⁻¹	24
rGO@Ni ₃ S ₂ /CC	1 M KOH	501.23 C g ⁻¹	78.2%/10 A g ⁻¹	25
Fe-Ni-S/rGO	3 M KOH	1220 F g ⁻¹ /1 A g ⁻¹	75.4%/10 A g ⁻¹	This work

Table S3 A comparison of the Ni@CNTs@Co₉S₈/NCNTs asymmetric supercapacitor device with those of advanced supercapacitors recently reported.

Supercapacitor devices	Energy density (Wh kg ⁻¹)	Power density (W kg ⁻¹)	Cyclic stability	Ref.
Ni-Co-S//AC	30.1 16.89	800.2 7800	82%, 30 A g ⁻¹ 10000 cycles	26
NiCo ₂ S ₄ /Co ₉ S ₈ //AC	33.5 17.5	150 3375	70%, 3 A g ⁻¹ 5000 cycles	27
CC/h-Co ₉ S ₈ /NiCo-Mo//AC	37.6	228.7	87.7%, 20 mA cm ⁻² 10000 cycles	28
NiS/NF//NiS/NF	27.58	1320	97%, 10 A g ⁻¹ 5000 cycles	11
NiS@CoS//AC	24.1	752.15	80%, 5000 cycles	29
Mn-NiS NSs//ONAC	44.2	825	90%, 8 A g ⁻¹ 5000 cycles	30
Ni-Mn-S//AC	27.3	505.2	75.3%, 8 mA cm ⁻² 6000 cycles	31
NiMn-S//AC	82.2	800	81.1%, 10 A g ⁻¹ 10000 cycles	32
MnCo ₂ S ₄ /CC//PCP/rGO	43	801	87%, 10 A g ⁻¹ 10000 cycles	33
FeNi ₂ S ₄ -rGO//AC	43.4	800	87.1%, 4 A g ⁻¹ 1000 cycles	5
Ni ₃ S ₂ //pen ink	8.2	214.6	93.1%, 2.4 A g ⁻¹ 3000 cycles	34
ppy@Ni ₃ S ₂ //AC	17.5	179.3	100.1%, 30 mA cm ⁻² 3000 cycles	35
rGO/Ni ₃ S ₂ (rGO)	29.1	390	86.1%, 5 A g ⁻¹ 5000 cycles	36
Ni ₃ S ₂ @NF//AC@NF	32	210.8	83.9%, 8 mA cm ⁻² 2000 cycles	37
NiS-C@rGO//AC	44.1	755	93.5, 1 A g ⁻¹ 10000 cycles	38
NiS _{NF} /CF@NiS _{NP} //AC	31.2	400.1	87.8%, 5 A g ⁻¹	13

			5000 cycles	
NiS hollow cubes//AC	34.9	387.5	82.8, 4 A g ⁻¹ 10000 cycles	15
TC-g-C ₃ N ₄ /NiS//AC	27	379	87.9%, 5 A g ⁻¹ 8000 cycles	16
NiS@C//C	21.6	400	84%, 5 A g ⁻¹ 5000 cycles	39
NiS@C QDs-CNTs-rGO/GH	21	811	82%, 2 A g ⁻¹ 5000 cycles	40
NiS//NiS	16.5	250	None	24
NiS-CFs CNFs	13.8	373.9	96.4% , 1A g ⁻¹ 5000 cycles	18
rGO@Ni ₃ S ₂ //AC	17.2	2752	79%, 1 A g ⁻¹ 1000 cycles	25
Ni@CNTs@Co ₉ S ₈ //NCNTs	30.5	800	82%, 3 A g ⁻¹ 10000 cycles	This work

References :

1. B. Guan, Y. Li, B. Yin, K. Liu, D. Wang, H. Zhang and C. Cheng, Synthesis of hierarchical NiS microflowers for high performance asymmetric supercapacitor, *Chem. Eng. J.*, 2017, **308**, 1165-1173.
2. T. Liu, C. Jiang, B. Cheng, W. You and J. Yu, Hierarchical NiS/N-doped carbon composite hollow spheres with excellent supercapacitor performance, *J. Mater. Chem. A*, 2017, **5**, 21257-21265.
3. J. Zhao, B. Guan, B. Hu, Z. Xu, D. Wang and H. Zhang, Vulcanizing time controlled synthesis of NiS microflowers and its application in asymmetric supercapacitors, *Electrochim. Acta*, 2017, **230**, 428-437.
4. L. a. Peng, Y. Tuo, Y. Lin, C. Jia, S. Wang, Y. Zhou and J. Zhang, Synthesis of P-doped NiS as an electrode material for supercapacitors with enhanced rate capability and cycling stability, *New J. Chem.*, 2022, **46**, 6461-6469.
5. Y. Tao, J. Yuan, X. Qian, Q. Meng, J. Zhu, G. He and H. Chen, Spinel-type FeNi₂S₄ with rich sulfur vacancies grown on reduced graphene oxide toward enhanced supercapacitive performance, *Inorganic Chemistry Frontiers*, 2021, **8**, 2271-2279.
6. M. Naseri, M. Moradi, S. Hajati, J. P. Espinos and M. A. Kiani, Comparative studies on electrochemical energy storage of NiFe-S nanoflake and NiFe-OH towards aqueous supercapacitor, *J Mater Sci: Mater Electron*, 2019, **30**, 4499-4510.
7. M. Lu, M.-y. Sun, X.-h. Guan, X.-m. Chen and G.-S. Wang, Controllable synthesis of hollow spherical nickel chalcogenide (NiS₂ and NiSe₂) decorated with graphene for efficient supercapacitor electrodes, *Rsc Adv*, 2021, **11**, 11786-11792.
8. K. D. Ikkurthi, S. Srinivasa Rao, J.-W. Ahn, C. D. Sunesh and H.-J. Kim, A cabbage leaf like nanostructure of a NiS@ZnS composite on Ni foam with excellent electrochemical performance for supercapacitors, *Dalton Trans*, 2019, **48**, 578-586.
9. F. Xie, H. Zhu, Y. Qu, J. Hu, H. Tan, K. Wang and L. Sun, Promoted OH⁻ adsorption and electron-transfer kinetics by electrospinning mono-disperse NiCo₂S₄ nanocrystals within porous CNFs for solid asymmetric supercapacitors, *J. Colloid Interface Sci.*, 2024, **657**, 63-74.
10. P. O. Agboola, I. Shakir, Z. A. Almutairi, S. S. Shar and M. F. Aly Aboud, Synergistic effect of Fe (III) doping and MWCNTs integration on the electrochemical performance of nickel sulfide

nanoparticles for hybrid supercapacitor applications, *Physica B: Condensed Matter*, 2023, **659**, 414866.

11. S. Nayak, A. A. Kittur, S. Nayak and B. Murgunde, Binderless nano marigold flower like structure of nickel sulfide electrode for sustainable supercapacitor energy storage applications, *J Energy Storage*, 2023, **62**, 106963.

12. B. T. Al-Abawi, N. Parveen and S. A. Ansari, Controllable synthesis of sphere-shaped interconnected interlinked binder-free nickel sulfide@nickel foam for high-performance supercapacitor applications, *Scientific Reports*, 2022, **12**, 14413.

13. D. Wu, X. Xie, J. Zhang, Y. Ma, C. Hou, X. Sun, X. Yang, Y. Zhang, H. Kimura and W. Du, Embedding NiS nanoflakes in electrospun carbon fibers containing NiS nanoparticles for hybrid supercapacitors, *Chem. Eng. J.*, 2022, **446**, 137262.

14. A. Simon Justin, P. Vickraman and B. Joji Reddy, Carbon Sphere@Nickel sulfide core-shell nanocomposite for high performance supercapacitor application, *Current Applied Physics*, 2019, **19**, 295-302.

15. X. Ma, L. Zhang, G. Xu, C. Zhang, H. Song, Y. He, C. Zhang and D. Jia, Facile synthesis of NiS hierarchical hollow cubes via Ni formate frameworks for high performance supercapacitors, *Chem. Eng. J.*, 2017, **320**, 22-28.

16. X. Sun, H. Yang, H. Zhu, L. Wang, Z. Fu, Q. Zhang and H. Zhu, Synthesis and enhanced supercapacitor performance of carbon self-doping graphitic carbon nitride/NiS electrode material, *J. Am. Ceram. Soc.*, 2021, **104**, 1554-1567.

17. S. Nandhini and G. Muralidharan, 2018.

18. F. Tong, X. Wu, W. Jia, J. Guo, Y. Pan, Y. Lv, D. Jia and X. Zhao, NiS nanosheets with novel structure anchored on coal-based carbon fibers prepared by electrospinning for flexible supercapacitors, *CrystEngComm*, 2020, **22**, 1625-1632.

19. N. A. Marand, S. M. Masoudpanah, S. Alamolhoda and M. S. Bafghi, Solution combustion synthesis of nickel sulfide/reduced graphene oxide composite powders as electrode materials for high-performance supercapacitors, *J Energy Storage*, 2021, **39**.

20. N. Parveen, S. A. Ansari, S. G. Ansari, H. Fouad, N. M. Abd El-Salam and M. H. Cho, Solid-state symmetrical supercapacitor based on hierarchical flower-like nickel sulfide with shape-controlled morphological evolution, *Electrochim. Acta*, 2018, **268**, 82-93.

21. A. Namdarian, A. G. Tabrizi, A. Maselena, A. Mohammadi and S. E. Moosavifard, One step synthesis of rGO-Ni₃S₂ nano-cubes composite for high-performance supercapacitor electrodes, *Int. J. Hydrogen Energy*, 2018, **43**, 17780-17787.
22. S.-Y. Kim, C. V. V. M. Gopi, A. E. Reddy and H.-J. Kim, Facile synthesis of a NiO/NiS hybrid and its use as an efficient electrode material for supercapacitor applications, *New J. Chem.*, 2018, **42**, 5309-5313.
23. B. T. Al-Abawi, N. Parveen and S. A. Ansari, Controllable synthesis of sphere-shaped interconnected interlinked binder-free nickel sulfide@nickel foam for high-performance supercapacitor applications, *Scientific Reports*, 2022, **12**.
24. N. S, J. C. M. A and M. G, Facile microwave-hydrothermal synthesis of NiS nanostructures for supercapacitor applications, *Appl. Surf. Sci.*, 2018, **449**, 485-491.
25. Z. Tian, J. Yin, X. Wang and Y. Wang, Construction of Ni₃S₂ wrapped by rGO on carbon cloth for flexible supercapacitor application, *J. Alloys Compd.*, 2019, **777**, 806-811.
26. W. Zhao, Y. Zheng, L. Cui, D. Jia, D. Wei, R. Zheng, C. Barrow, W. Yang and J. Liu, MOF derived Ni-Co-S nanosheets on electrochemically activated carbon cloth via an etching/ion exchange method for wearable hybrid supercapacitors, *Chem. Eng. J.*, 2019, **371**, 461-469.
27. L. Hou, Y. Shi, S. Zhu, M. Rehan, G. Pang, X. Zhang and C. Yuan, Hollow mesoporous hetero-NiCo₂S₄/Co₉S₈ submicro-spindles: unusual formation and excellent pseudocapitance towards hybrid supercapacitors, *J. Mater. Chem. A*, 2017, **5**, 133-144.
28. Y. Pan, J. Wei, D. Han, Q. Xu, D. Gao, Y. Yang and Y. Wei, Hetero-nanostructures constructed by 2D porous metal oxide/hydroxide nanosheets supported on 1D hollow Co₉S₈ nanowires for hybrid supercapacitors with high areal capacity, *Inorganic Chemistry Frontiers*, 2021, **8**, 4676-4684.
29. Y. Miao, X. Zhang, J. Zhan, Y. Sui, J. Qi, F. Wei, Q. Meng, Y. He, Y. Ren, Z. Zhan and Z. Sun, Hierarchical NiS@CoS with Controllable Core-Shell Structure by Two-Step Strategy for Supercapacitor Electrodes, *Advanced Materials Interfaces*, 2020, **7**, 1901618.
30. R. K. Devi, M. Ganesan, T.-W. Chen, S.-M. Chen, M. Akilarasan, S.-P. Rwei, J. Yu, T. Elayappan and A. Shaju, A facile strategy for the synthesis of manganese-doped nickel sulfide nanosheets and oxygen, nitrogen-enriched 3D-graphene-like porous carbon for hybrid supercapacitor, *J. Alloys Compd.*, 2023, **944**, 169261.

31. H. Cai, X. Li, G. Li, H. Xia, P. Wang, P. Sun, J. Huang, L. Wang and Y. Yang, Synthesis of honeycomb-like nickel-manganese sulfide composite nanosheets as advanced battery-type electrodes for hybrid supercapacitor, *Mater. Lett.*, 2019, **255**, 126505.
32. X. Wang, C. Hao, J. Zhang, C. Ni, X. Wang and Y. Shen, Reasonable design and synthesis of nickel manganese sulfide nanoparticles derived from metal organic frameworks as electrode materials for supercapacitors, *J. Power Sources*, 2022, **539**, 231594.
33. A. M. Elshahawy, X. Li, H. Zhang, Y. Hu, K. H. Ho, C. Guan and J. Wang, Controllable MnCo_2S_4 nanostructures for high performance hybrid supercapacitors, *J. Mater. Chem. A*, 2017, **5**, 7494-7506.
34. J. Wen, S. Li, K. Zhou, Z. Song, B. Li, Z. Chen, T. Chen, Y. Guo and G. Fang, Flexible coaxial-type fiber solid-state asymmetrical supercapacitor based on Ni_3S_2 nanorod array and pen ink electrodes, *Journal of Power Sources*, 2016, **324**, 325-333.
35. L. Long, Y. Yao, M. Yan, H. Wang, G. Zhang, M. Kong, L. Yang, X. Liao, G. Yin and Z. Huang, Ni_3S_2 @polypyrrole composite supported on nickel foam with improved rate capability and cycling durability for asymmetric supercapacitor device applications, *Journal of Materials Science*, 2016, **52**, 3642-3656.
36. N. Wang, G. Han, Y. Chang, W. Hou, Y. Xiao and H. Li, Preparing Ni_3S_2 composite with neural network-like structure for high-performance flexible asymmetric supercapacitors, *Electrochim. Acta*, 2019, **317**, 322-332.
37. M. Shen, J. Liu, T. Liu, C. Yang, Y. He, Z. Li, J. Li and D. Qian, Oxidant-assisted direct-sulfidization of nickel foam toward a self-supported hierarchical Ni_3S_2 @Ni electrode for asymmetric all-solid-state supercapacitors, *J. Power Sources*, 2020, **448**.
38. M. Beemarao, P. Periyannan and K. Ravichandran, High-performance supercapacitor electrode obtained by directly bonding 2D materials: hierarchal NiS_2 on reduced graphene oxide, *Journal of Materials Science: Materials in Electronics*, 2023, **34**.
39. J. Wu, F. Wei, Y. Sui, J. Qi and X. Zhang, Interconnected NiS -nanosheets@porous carbon derived from Zeolitic-imidazolate frameworks (ZIFs) as electrode materials for high-performance hybrid supercapacitors, *Int. J. Hydrogen Energy*, 2020, **45**, 19237-19245.

40. R. Zhang, C. Lu, Z. Shi, T. Liu, T. Zhai and W. Zhou, Hexagonal phase NiS octahedrons co-modified by 0D-, 1D-, and 2D carbon materials for high-performance supercapacitor, *Electrochim. Acta*, 2019, **311**, 83-91.