Surfactant-Assisted Synthesis of Nanoporous

Nickel Sulfide Flakes and Their Hybridization

with Reduced Graphene Oxides for

Supercapacitor Applications

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Figure S1.



Figure S1 (a) SEM image and **(b)** TEM image of ZIF-8-derived carbon material. **(c)** Cyclic voltammograms (CVs) and **(d)** specific capacitances measured at various scan rate curves of ZIF-8-derived carbon. The CVs are measured in a KOH (3M) electrolyte using a three-electrode system.





Figure S2 Wide-angle XRD patterns of nickel sulfide samples prepared at different temperatures.



Figure S3 SEM and TEM images of a BNS sample prepared without surfactants.



Figure S4 HAADF-STEM image and elemental mapping for the detection of carbon, nickel, and sulfur in PNS/rGO40 composites. The scale bars are 500 nm in length.

Figure S5



Figure S5 Nitrogen adsorption-desorption isotherms of (a) PNS and BNS samples, and (b) different PNS/rGO composites. (c) Comparison of BET surface areas, and (d) pore size distribution of the PNS and PNS/rGO composites. (Please note that for data clarity, the isotherm and pore-size distribution curves for PNS are offset vertically by 40 cm³·g⁻¹ and 0.015 cm³·nm⁻¹·g⁻¹, respectively)



Figure S6 Zeta potentials for PNS, rGO, and PNS/rGO composite samples.



Figure S7 SEM images and the nitrogen adsorption-desorption isotherms of nickel sulfide samples at different temperatures [(a–b) 120 °C, (c–d) 150 °C, and (e–f) 180 °C].

Nickel sulfide materials							
Method	Nickel sulfide phase	Surface area (m²·g ⁻¹)	Ref.				
Hard template (KIT-6)	NiS ₂	77	S1				
Hydrothermal method	Mixed phase NiS	34.3	S2				
Solvothermal method	NiS	62	S3				
Solvothermal method	β-NiS	24.0	S4				
Solvothermal method	β-NiS	10.0	S5				
Dodocanothial complay	NiS nanorods 34.8		56				
Dodecariethiol complex	NiS nanowires	17.7					
	NiS ₂ nanocubes	12.0					
Microwave irradiation	NiS ₂ nanospheres	38.3	S7				
	NiS ₂ nanoparticles	25.1					
Soft template	NiS	85.7	Our work				
I	Nickel sulfide-based composites						
Mathad	Nickel sulfide based composites	Surface area	Ref				
Method	Nickel sulfide-based composites		Rof				
Method	Nickel sulfide-based composites	(m ² ·g ⁻¹)	Ref.				
Method MOF-74	Nickel sulfide-based composites Mixed-phase NiS with carbon	(m ² ·g ⁻¹) 112	Ref. \$8				
Method MOF-74	Nickel sulfide-based composites Mixed-phase NiS with carbon Carbon-coated Ni ₃ S ₂	(m ² ·g ⁻¹) 112 4.2	Ref. S8				
Method MOF-74 Solvothermal method	Nickel sulfide-based composites Mixed-phase NiS with carbon Carbon-coated Ni ₃ S ₂	(m ² ·g ⁻¹) 112 4.2	Ref. 58 59				
Method MOF-74 Solvothermal method	Nickel sulfide-based composites Mixed-phase NiS with carbon Carbon-coated Ni ₃ S ₂ Carbon-coated Ni ₃ S ₂ /RGO	(m ² ·g ⁻¹) 112 4.2 12.3	Ref. 58 59				
Method MOF-74 Solvothermal method Chemical method	Nickel sulfide-based composites Mixed-phase NiS with carbon Carbon-coated Ni ₃ S ₂ Carbon-coated Ni ₃ S ₂ /RGO Nickel sulfide with carbon rods	(m ² ·g ⁻¹) 112 4.2 12.3 30.8	Ref. 58 59 510				
Method MOF-74 Solvothermal method Chemical method	Nickel sulfide-based composites Mixed-phase NiS with carbon Carbon-coated Ni ₃ S ₂ Carbon-coated Ni ₃ S ₂ /RGO Nickel sulfide with carbon rods NiS/CNT	(m ² ·g ⁻¹) 112 4.2 12.3 30.8 16.4	Ref. 58 59 510				
Method MOF-74 Solvothermal method Chemical method Hydrothermal method	Nickel sulfide-based composites Mixed-phase NiS with carbon Carbon-coated Ni ₃ S ₂ Carbon-coated Ni ₃ S ₂ /RGO Nickel sulfide with carbon rods NiS/CNT NiS/rGO	(m ² ·g ⁻¹) 112 4.2 12.3 30.8 16.4 18.9	Ref. 58 59 510 511				
Method MOF-74 Solvothermal method Chemical method Hydrothermal method Biomolecule-assisted synthesis	Nickel sulfide-based composites Mixed-phase NiS with carbon Carbon-coated Ni ₃ S ₂ Carbon-coated Ni ₃ S ₂ /RGO Nickel sulfide with carbon rods NiS/CNT NiS/rGO NiS/rGO	(m ² ·g ⁻¹) 112 4.2 12.3 30.8 16.4 18.9 46.3	Ref. 58 59 510 511 512				

Table S1 Comparison of the BET surface areas of our samples with those of previous reports.

Table S2 Comparison of specific capacitance performance of our PNS and PNS/rGO composites with previous literature reports usinga standard three-electrode system.

Bare nickel sulfide materials								
No.	Materials	Morphology	Electrolyte	Specific capacitance	Scan rate	Current density	Ref	
				(F·g ⁻¹)	(mV·s⁻¹)	(A·g ⁻¹)	ner.	
1.	Mesoporous NiS	nanoflakes	КОН (ЗМ)	1205	5	-	Our work	
2.	NiS	nanoflakes	KOH (1M)	664	-	4	S13	
3.	NiS	hollow sphere	KOH (2M)	927	-	4.08	S14	
4.	NiS	nanoparticle	КОН (2М)	893	-	5	S15	
5.	eta-NiS	flower-like	KOH (2M)	857	-	2	S4	
6.	Co ₉ S ₈	nanorods	КОН (ЗМ)	783	5	-	S16	
7.	Co_3S_4	hollow nanosphere	KOH (2M)	522	-	0.5	S17	
8.	NiCo ₂ S ₄	Urchin-like	KOH (6M)	1149	-	1	S18	
9.	NiCo ₂ S ₄	Porous nanotube	KOH (6M)	933	-	1	S19	
Nickel sulfide-based composites								
10.	NiS/rGO40	nanoflakes	КОН (3М)	1312	5	-	Our work	
	composite							
11.	Ni ₃ S ₂ /MWCNT	nanoparticle	KOH (2M)	1024	-	0.8	S20	
	composite							

12.	Ni ₃ S ₂ /CNT	nanoparticle	кон (зм)	514	-	4	\$21
	composite						921
13.	Nickel sulfide/rGO	nanosphere	кон (2м)	1160	_	5	\$12
	composites		KOTT (ZWI)	1105		5	JIZ
14.	Graphene	nanostructure	кон (ем)	775	_	0.5	522
	nanosheets/NiS		KON (OW)	115		0.5	JLL
15.	Graphene/NiS ₂	nanostructure	KOH (6M)	478		0.5	S23
16.	Carbon/nickel	nanoparticle	кон (ЗМ)	860	5	_	50
	sulfide/rGO			500	5		55

Table S3 Comparison of our ASC cell, consisting of PNS/rGO40 as a positive and ZIF-derived carbon as negative electrode, with those of previous reports.

No.	Working electrode	Counter electrode	Electrolyte	Operating voltage	Specific energy	Specific power	Ref.
				(V)	(W∙h∙kg⁻¹)	(W∙kg⁻¹)	
1.	NiS/rGO40 composite	Nanoporous carbon	КОН (ЗМ)	1.6	17.01	10283.51	Our work
2.	MWCNT/NiS	graphene	KOH (6M)	1.4	17.0	7000	S24
3.	Ni ₃ S ₂ /MWCNT	AC	KOH (2M)	1.6	15.4	6400	S20
4.	NiCo ₂ S ₄	rGO	KOH (6M)	1.6	16.6	2348	S25
5.	Ni(OH)₂@Ni foam	a-MEGO	KOH (6M)	1.8	13.4	85000	S26
6.	Co(OH) ₂ nanorods	GO	KOH (1M)	1.2	11.94	2540	S27
7.	MnO ₂	AC	Na ₂ SO ₄ (0.5M)	1.8	10.4	14700	S28
8.	NiWO ₄	AC	KOH (2M)	1.6	15.1	4800	S29
9.	NiMoO ₄	rGO	KOH (3M)	1.1	12.31	274.91	S30

(AC: activated carbon; rGO: reduced graphene oxide; a-MEGO: activated microwave exfoliated graphite oxide; GO: graphene oxide)

References

- S1. B. T. Yonemoto, G. S. Hutchings and F. Jiao, J. Am. Chem. Soc., 2014, 136, 8895-8898.
- S2. Y. Wang, Q. Zhu, L. Tao and X. Su, J. Mater. Chem., 2011, 21, 9248-9254.
- **S3**. N. Chen, W. Zhang, W. Yu and Y. Qian, *Mater. Lett.*, 2002, **55**, 230-233.
- S4. J. Yang, X. Duan, Q. Qin and W. Zheng, J. Mater. Chem. A, 2013, 1, 7880-7884.
- S5. J. Yang, W. Guo, D. Li, C. Wei, H. Fan, L. Wu and W. Zheng, J. Power Sources, 2014, 268, 113-120.
- S6. Z. Wang, C. Nan, D. Wang and Y. Li, RSC Adv., 2014, 4, 47513-47516.
- S7. H. Pang, C. Wei, X. Li, G. Li, Y. Ma, S. Li, J. Chen and J. Zhang, Sci. Rep., 2014, 4, 3577.
- S8. Z. Wang, X. Li, Y. Yang, Y. Cui, H. Pan, Z. Wang, B. Chen and G. Qian, J. Mater. Chem. A, 2014, 2, 7912-7916.
- **S9**. L. Ma, X. Shen, Z. Ji, S. Wang, H. Zhou and G. Zhu, *Electrochim. Acta*, 2014, **146**, 525-532.
- S10. C. Sun, M. Ma, J. Yang, Y. Zhang, P. Chen, W. Huang and X. Dong, Sci. Reports, 2014, 4, 7054.
- S11. J. Yang, X. Duan, W. Guo, D. Li, H. Zhang and W. Zheng, Nano Energy, 2014, 5, 74-81.
- S12. Z. Xing, Q. Chu, X. Ren, J. Tian, A. Asiri, K. A. Alamry, A. O. A. Youbi and X. Sun, *Electrochem. Commun.*, 2013, 32, 9-13.
- **S13**. S. W. Chou and J. Y. Lin, J. Electrochem. Soc., 2013, 160, D178-182.
- S14. B. T. Zhu, Z. Wang, S. Ding, J. S. Chen and X. W. Lou, RSC Adv. 2011, 1, 397-400.
- S15. L. Hou, C. Yuan, D. Li, L. Yang, L. Shen, F. Zhang and X. Zhang, *Electrochim. Acta*, 2011, 56, 7454-7459.
- S16. J. Xu, Q. Wang, X. Wang, Q. Xiang, B. Liang, D. Chen and G. Shen, ACS Nano, 2013, 7, 5453-5462.
- S17. Q. Wang, L. Jiao, H. Du, Y. Si, Y. Wang and H. Yuan, J. Mater. Chem. 2012, 22, 21387-21391.
- S18. H. Chen, J. Jiang, L. Zhang, H. Wan, T. Qi and D. Xia, Nanoscale, 2013, 5, 8879-8883.
- S19. H. Wan, J. Jiang, J. Yu, K. Xu, L. Miao, L. Zhang, H. Chen and Y. Ruan, Cryst. Eng. Commun. 2013, 15, 7649-7651.
- S20. C. Dai, P. Y. Chien, J. Y. Lin, S. W. Chou, W. K. Wu, P. H. Li, K. Y. Wu and T. W. Lin, ACS Appl. Mater. Interfaces 2013, 5, 12168-12174.

- S21. T. Zhu, H. B. Wu, Y. Wang, R. Xu and X. W. Lou, Adv. Energy Mater., 2012, 2, 1497-1502.
- S22. Y. Li, K. Ye, K. Cheng, J. Yin, D. Cao and G. Wang, J. Power Sources, 2015, 274, 943-950.
- S23. X. Li, J. Shen, N. Li and M. Ye, Mater. Lett., 2015, 139, 81-85.
- S24. A. Singh, A. J. Roberts, R. C. T. Slade and A. Chandra, J. Mater. Chem. A, 2014, 2, 16723-16730.
- S25. H. Chen, J. Jiang, L. Zhang, D. Xia, Y. Zhao, D. Guo, T. Qi and H. Wan, J. Power Sources, 2014, 254, 249-257.
- S26. J. Ji, L. L. Zhang, H. Ji, Y. Li, X. Zhao, X. Bai, X. Fan, F. Zhang and R. S. Ruoff, ACS Nano, 2013, 7,6237-6243.
- S27. R. R. Salunkhe, B. P. Bastakoti, C. T. Hsu, N. Suzuki, J. H. Kim, S. X. Dou, C. C. Hu and Y. Yamauchi, *Chem. Eur. J.*, 2014, 20, 3084-3088.
- **S28**. Y. T. Wang, A. H. Lu, H. L. Zhang and W. C. Li, J. Phys. Chem. C, 2011, 115, 5413-5421.
- S29. L. Niu, Z. Li, Y. Xu, J. Sun, W. Hong, X. Liu, J. Wang and S. Yang, ACS Appl. Mater. Interfaces, 2013, 5, 8044-8052.
- S30. P. R. Jothi, K. Shanthi, R. R. Salunkhe, M. Pramanik, V. Malgras, S. M. Alshehri and Y. Yamauchi, *Eur. J. Inorg. Chem.*, 2015, 2015, 3694-3699.