Supporting Information

Rational construction of core-shell Ni₃S₂@Ni(OH)₂ nanostructure as the

battery-like electrode for supercapacitors

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Fig. S1 SEM images of $Ni_3S_2@Ni(OH)_2$ samples with different immersion time: (a) 5 min, (b) 10min, (c) 15 min, (d) 20 min.



Fig. S2 CV and GCD curves of Ni₃S₂@Ni(OH)₂ samples with different immersion time: (a, b)
5min, (c, d) 10 min and (e, f) 20min. (g) The GCD curves at a current density of 2 mA cm⁻² for Ni₃S₂@Ni(OH)₂ samples with different immersion time. (h) The areal capacitance of Ni₃S₂@Ni(OH)₂ samples with different immersion time at 2 mA cm⁻².

For comparison, $Ni_3S_2@Ni(OH)_2$ samples with different immersion time (5, 10, 15, 20 min) also prepared. Firstly, the electrochemical performances of $Ni_3S_2@Ni(OH)_2$ samples with different immersion time (5, 10, 15, 20 min) were compared. Fig. S1 shows the SEM images of Ni₃S₂@Ni(OH)₂ samples with different immersion time. As the immersion time increases, the surface of Ni₃S₂ nanorods is gradually covered by Ni(OH)₂ nanosheets. Undoubtedly, the size of Ni(OH)₂ nanosheets as shell can be adjusted by controlling the immersion time. Fig. S2g shows the GCD curves of Ni₃S₂@Ni(OH)₂ with different immersion samples time. Obviously, $Ni_3S_2@Ni(OH)_2$ -15min electrode showed the longest discharge time at 2 mA cm⁻², indicating the highest specific capacitance. According to the above results, the following performance tests and discussion were focused on the Ni₃S₂@Ni(OH)₂ obtained with 15 min immersion time.



Fig. S3 The corresponding current density $(i)-v^{1/2}$ (scan rate^{1/2}) plots of Ni₃S₂@Ni(OH)₂



Fig. S4 CV and GCD curves of (a, b) Ni₃S₂ and (c, d) Ni(OH)₂.



Fig. S5 SEM images of Ni₃S₂@Ni(OH)₂ after 10000 cycles.



Fig. S6 The relationship between Z' and $\omega^{-1/2}$ in the low-frequency region of Ni₃S₂@Ni(OH)₂ and Ni₃S₂.

According to previous researches [1-4], the OH⁻ ion diffusion coefficient (D_{OH} , cm² s⁻¹) was calculated by following equation:

$$D_{OH} = (RT)^2 / 2 (A n^2 F^2 C_{OH} \sigma)^2$$

where *R*, T, *A*, *n*, *F*, C_{OH}^{-} and σ represent the gas constant, absolute temperature, electrode area, number of electrons transfer, Faraday constant, the OH⁻ concentration and Warburg factor. And σ could be calculated by the slope of line in the low frequency region, according to the following equation [4,5]:

$$Z' = R_e + R_{ct} + \sigma$$

Based on above equation, the D_{OH} has been calculated and the results are shown in Fig. S6. As a results, the calculated D_{OH} of Ni₃S₂@Ni(OH)₂ is larger than that of pristine Ni₃S₂, suggesting the faster ion transport.



Fig. S7 (a,b) SEM images of Ni₃S₂@Ni(OH)₂-Ar. (c) XRD pattern of Ni₃S₂@Ni(OH)₂-Ar. (d-f) CV, GCD curves and corresponding areal capacitance of Ni₃S₂@Ni(OH)₂-Ar.

In order to investigate influence of crystallinity on the electrochemical performances, the obtained Ni₃S₂@Ni(OH)₂ was annealed at Ar atmosphere in 150 °C for 2h (labeled as Ni₃S₂@Ni(OH)₂-Ar). As shown in Fig. S7a-b, SEM images suggested that the morphology and structure of Ni₃S₂@Ni(OH)₂-Ar show no obvious changes. As shown in Fig. S7c, XRD result shows that the peaks of Ni(OH)₂ become obvious and sharp after annealing process, suggesting the improvement of crystallinity of the Ni(OH)₂. Fig. S7d-S7f show the electrochemical performance of Ni₃S₂@Ni(OH)₂-Ar. As a results, Ni₃S₂@Ni(OH)₂-Ar shows the lower capacitance than that of pristine Ni₃S₂@Ni(OH)₂, only 2.37 F cm⁻² at 2 mA cm⁻². According to previous results [6-8], electrodes with low crystallinity could be able to achieve better electrochemical performances than that of crystalline counterparts, due to more structure disorder and defects.



Fig. S8 (a and b) CV and GCD curves of AC at various scan rate and (b) corresponding specific capacitance



Fig. S9 (a) The specific capacitance vs. current density of $Ni_3S_2@Ni(OH)_2//AC$, (b) Cycling performance of $Ni_3S_2@Ni(OH)_2//AC$, which was determined by GCD tests at the current density of 10 A g⁻¹ for 5000 cycles.

Electrode materials	Electrolyte	Specific capacitance	Potential	
			Windows	Reference
			(V)	
Surface-enriched Ni-Co-S/Graphene	6 M KOH	1436 F g ⁻¹	-0.05-0.55	9
Ni ₃ S ₂ @β-NiS	6 M KOH	1158 F g ⁻¹	-0.2-0.5	10
nickel sulfides/MoS ₂ -CNT	3 М КОН	757 F g ⁻¹	0-0.55	11
NiS ₂ hollow sphere	2 M KOH	1643 F g ⁻¹	0-0.7	12
Ni ₃ S ₂ @CdS	3 М КОН	3.15 F cm^{-2}	0-0.5	13
NiS nanosheets array	1 M NaOH	1325 F g ⁻¹	0-0.8	14
NiS/carbon aerogle	2 M KOH	1606 F g ⁻¹	0-0.5	15
graphene-wrapped nickel sul-	2 М КОН	1495 F g^{-1}	0-0.5	16
fide nanoprisms		-		
NiMoO ₄ @Ni-Co-S	2 M KOH	2.27 F cm^{-2}	0-0.65	17
Co ₃ O ₄ @CdS	3 М КОН	1539 F g ⁻¹	0-0.6	18
hierarchical carbon@Ni ₃ S ₂ @MoS2	6 M KOH	1544 F g^{-1}	0-0.4	19
Ni ₃ S ₂ @Ni(OH) ₂	6M KOH	1775 F g ⁻¹	0-0.5	This work
		$(3.55 \mathrm{F} \mathrm{cm}^{-2})$		

Table S1 The specific capacitance of various electrodes in the three-electrode system in references

Reference:

- X. Zhao, W. Cai, Y. Yang, X. Song, Z. Neale, H. Wang, J. Sui and G. Cao, *Nano Energy*, 2018, 47, 224-234.
- 2. X. Zhao, H. Wang, J. Cao, W. Cai and J. Sui, Chem. Commun., 2017, 53, 10723-10726.
- 3. C. Liu, R. Mass é, X. Nan and G. Cao, Energy Storage Mater., 2016, 4, 15-58.
- 4. T. F. Yi, Y. Xie, L.J. Jiang, J. Shu, C. B. Yue, A. N. Zhou and M. F. Y, *RSC Adv.*, 2012, 2, 3541-3547.
- 5. S. Sarkar, H. Banda, and S. Mitra, *Electrochim. Acta*, 2013, 99, 242-252.
- 6. J. Lang, L. Kong, W. Wu, Y. Luo and L. Kang, Chem. Commun., 2008, 4213-4215.
- 7. J. Chen, H. Wang, J. Deng, C. Xu and Y. Wang, J. Mater. Chem. A, 2018, 6, 8986-8991.
- 8. K. A. Owusu, L. Qu, J. Li, Z. Wang, K. Zhao, C. Yang, K. M. Hercule, C. Lin, C. Shi, Q. Wei, L.
- Zhou and L. Mai, Nat. Commun., 2017, 8, 14264–14275.
- 9. X. Wang, S. Zhao, L. Dong, Q. Lu, J. Zhu and C. Nan, *Energy Storage Mater.*, 2017, 6, 180-187.
- 10. W. Li, S. Wang, L. Xin, M. Wu and X. Lou, J. Mater. Chem. A, 2016, 4, 7700-7709.
- 11. X. Yang, L. Zhao and J. Lian, J. Power Sources, 2017, 343, 373-382.
- 12. M. Lu, X. Yuan, X. Guan and G. Wang, J. Mater. Chem. A, 2017, 5, 3621-3627.
- 13. X. Wang, B. Shi, Y. Fang, F. Rong, F. Huang, R. Que and M. Shao, *J. Mater. Chem. A*, 2017, **5**, 7165–7172.
- 14. N. Nair and B.R. Sankapal, New J. Chem., 2016, 40, 10144-10152.
- 15. L. Zuo, W. Fan, Y. Zhang, Y. Huang, W. Gao and T. Liu, Nanoscale, 2017, 9, 4445-4455.
- 16. A. A. AbdelHamid, X. Yang, J. Yang, X. Chen and J. Y. Ying, *Nano Energy*, 2016, **26**, 425-437.
- 17. C. Chen, D. Yan, X. Luo, W. Gao, G. Huang, Z. Han, Y. Zeng and Z. Zhu, ACS Appl. Mater. Interfaces, 2018, **10**, 4662-4671.
- 18. D. S. Patil, S. A. Pawar and J. C. Shin, Chem. Eng. J., 2018, 335, 693-702.
- L. Li, H. Yang, J. Yang, L. Zhang, J. Miao, Y. Zhang, C. Sun, W. Huang, X. Dong and B. Liu, J. Mater. Chem. A, 2016, 4, 1319–1325.