

Supporting Information

Nitrogen-doped graphene encapsulated cobalt iron sulfide as an advanced electrode for high-performance asymmetric supercapacitors

Yazan Al Haj,^a Jayaraman Balamurugan,^a Nam Hoon Kim,^{a*} Joong Hee Lee^{a,b*}

^aAdvanced Materials Institute of BIN Convergence Technology (BK21 Plus Global) & Department of BIN Convergence Technology, Chonbuk National University, Jeonju, Jeonbuk, 54896, Republic of Korea

^bCarbon Composite Research Centre, Department of Polymer - Nano Science and Technology, Chonbuk National University, Jeonju, Jeonbuk, 54896, Republic of Korea

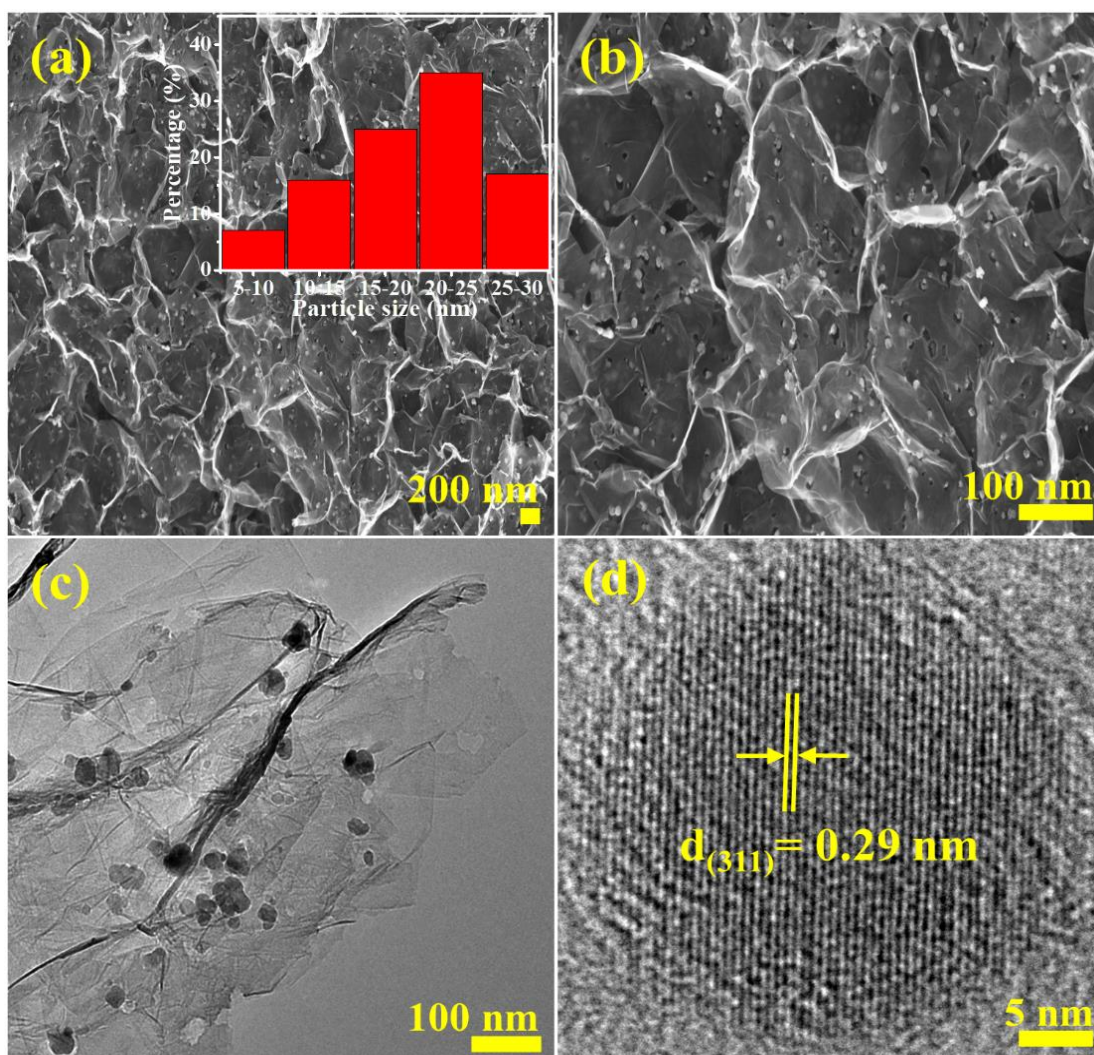


Fig. S1 (a and b) FE-SEM images with different magnifications (inset shows the particle size distribution), (c) TEM image, and (d) HR-TEM image of $\text{Co}_8\text{FeS}_8/\text{NG}$.

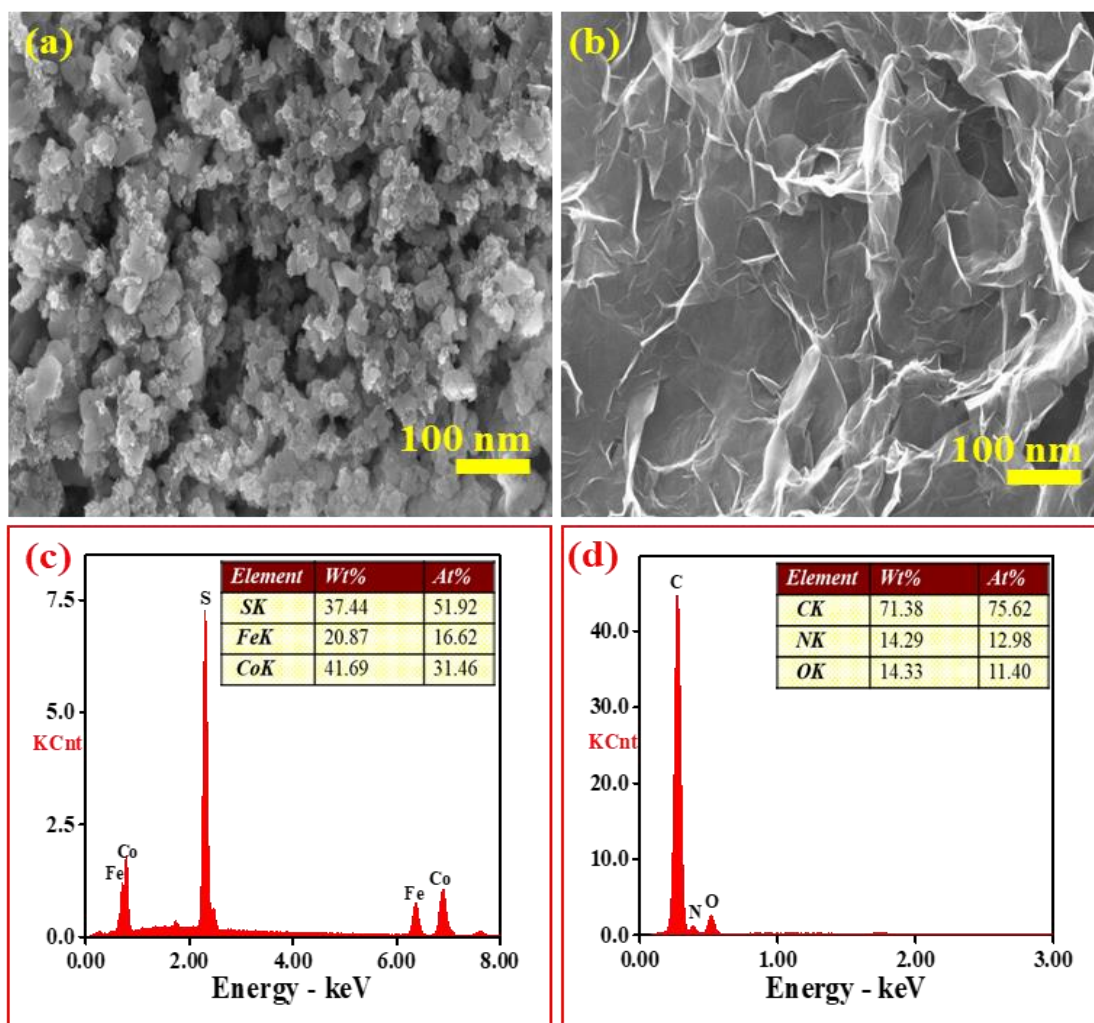


Fig. S2 (a and b) FE-SEM images, and (c and d) EDAX spectra of pristine Co_8FeS_8 and pristine NG, respectively.

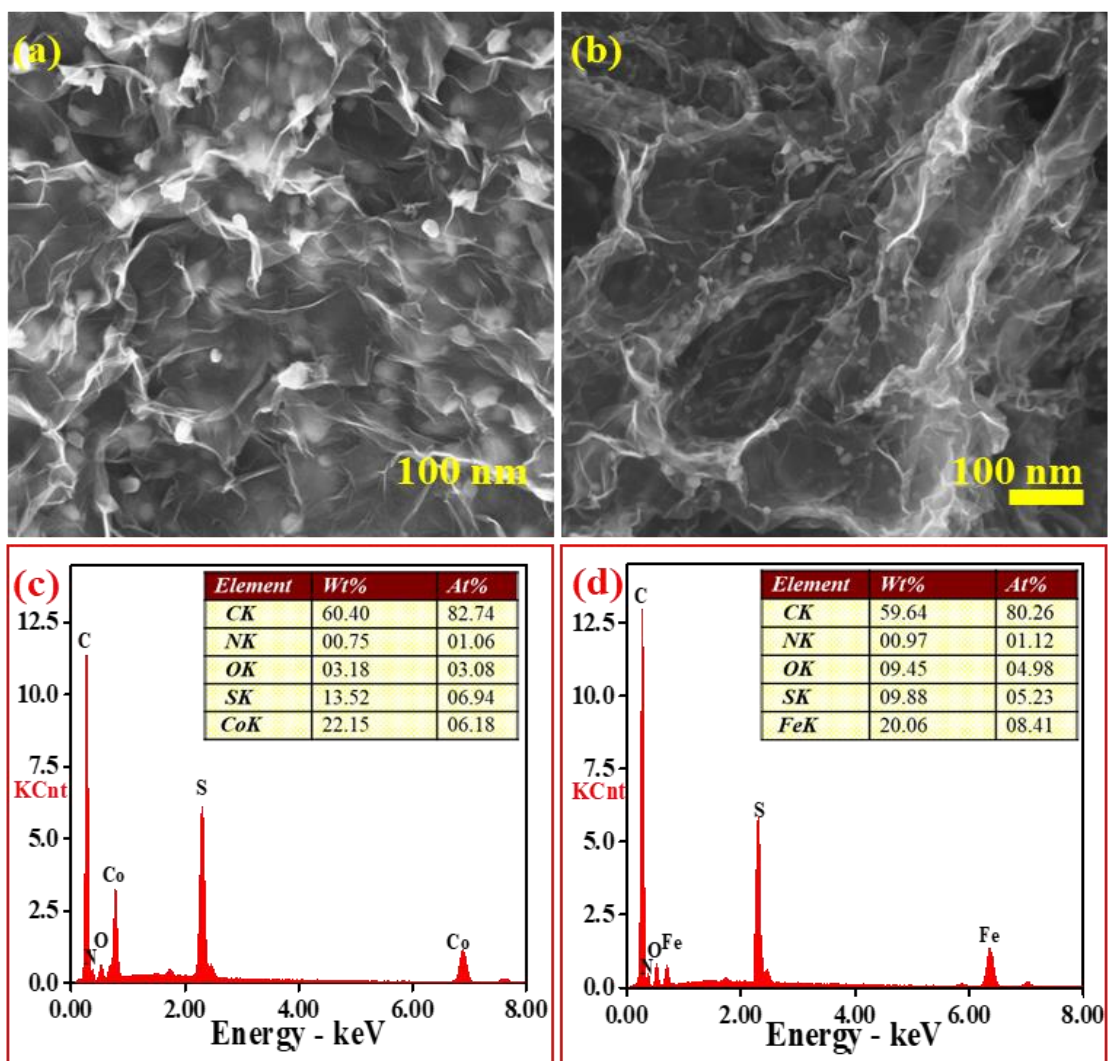


Fig. S3 (a and b) FE-SEM images, and (c and d) EDAX spectra of pristine $\text{Co}_9\text{S}_8@\text{NG}$ and $\text{FeS}@\text{NG}$, respectively.

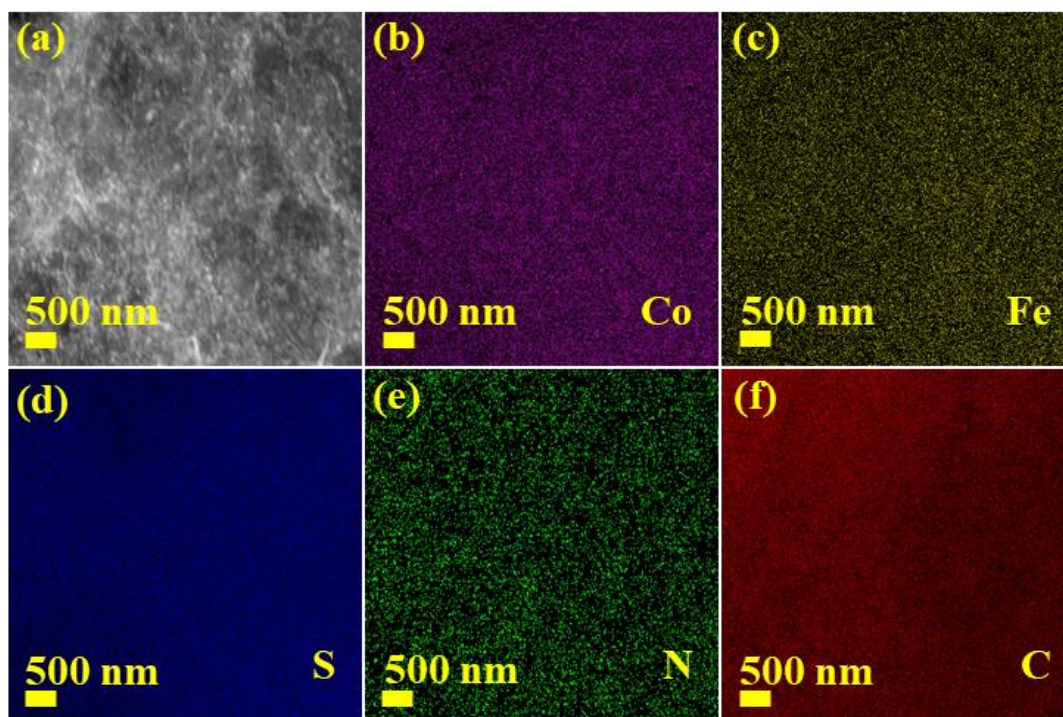


Fig. S4 SEM-EDS color mapping of cobalt, iron, sulfur, nitrogen, and carbon in the core-shell $\text{Co}_8\text{FeS}_8@\text{NG}$ hybrid.

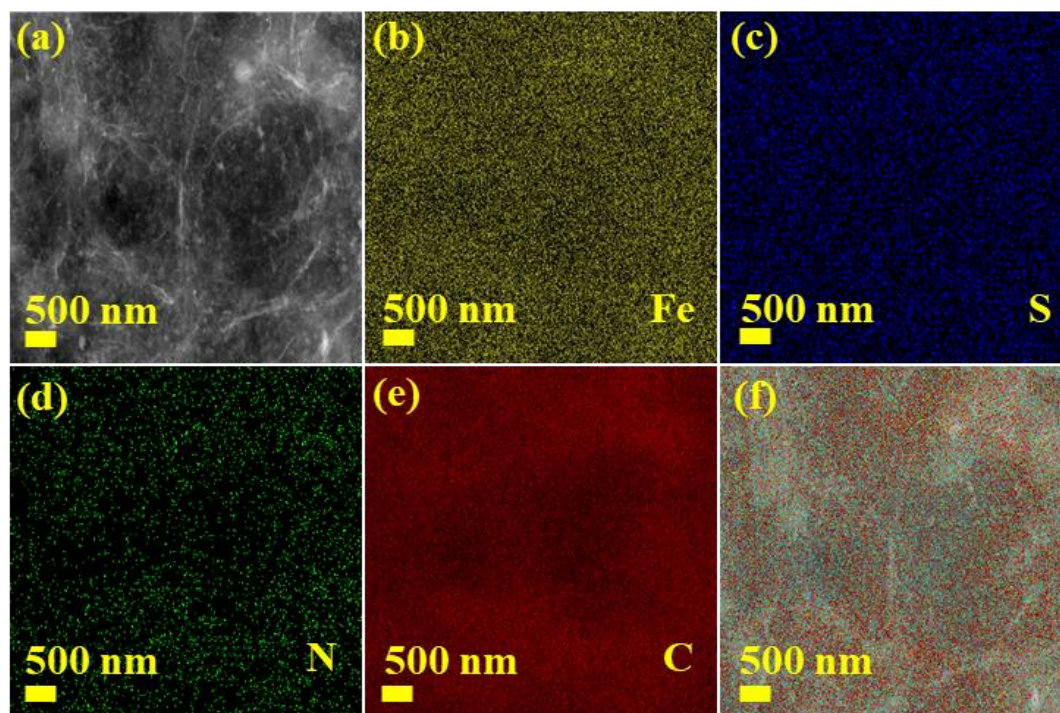


Fig. S5 SEM-EDS color mapping of iron, sulfur, nitrogen, and carbon, in the $\text{FeS}@\text{NG}$ hybrid.

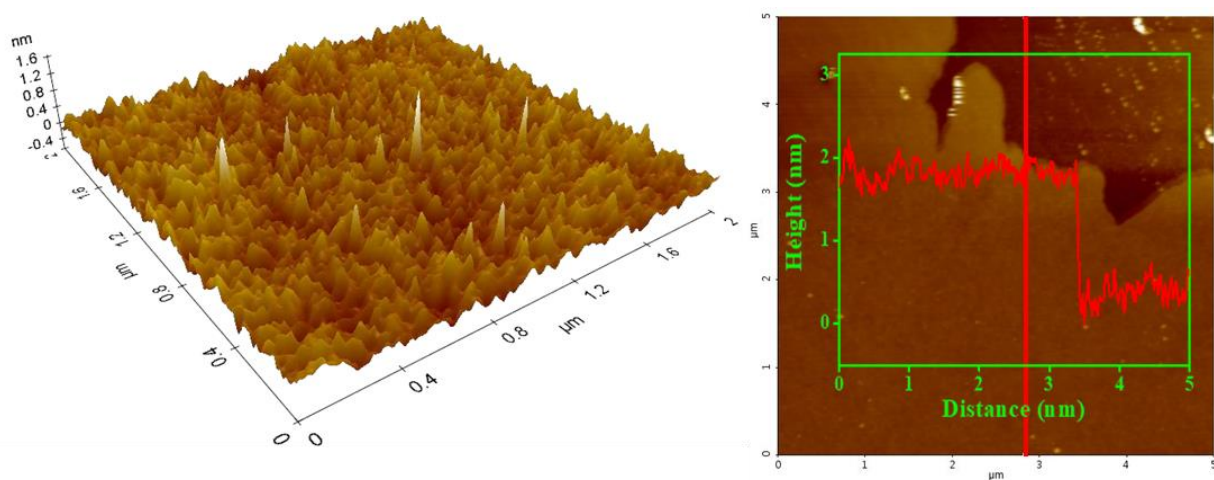


Fig. S6 AFM images of the core-shell Co₈FeS₈@NG hybrid.

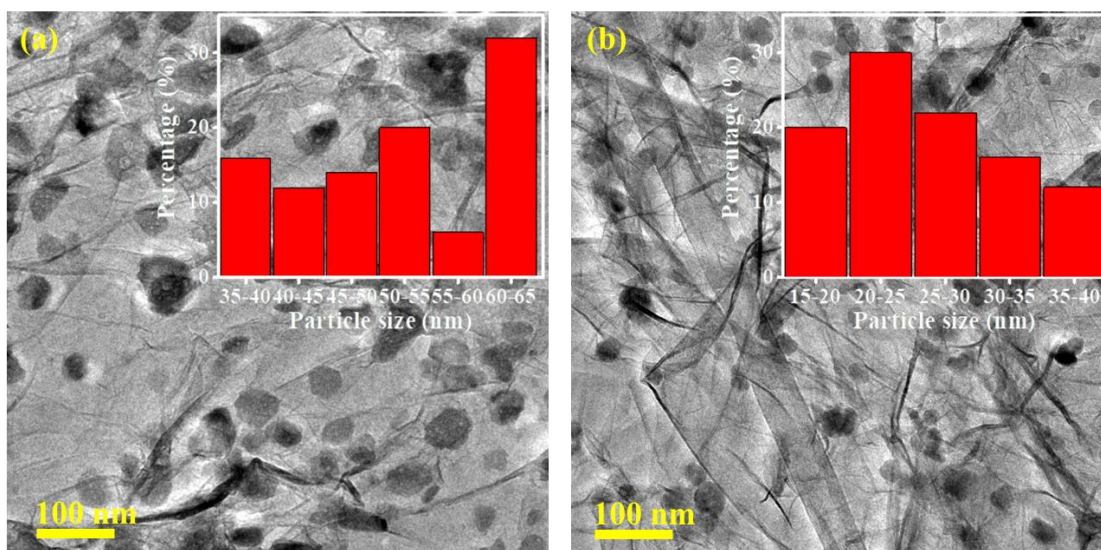


Fig. S7 (a and b) TEM images of the Co₉S₈@NG and FeS@NG hybrids (inset shows their corresponding particle size distributions).

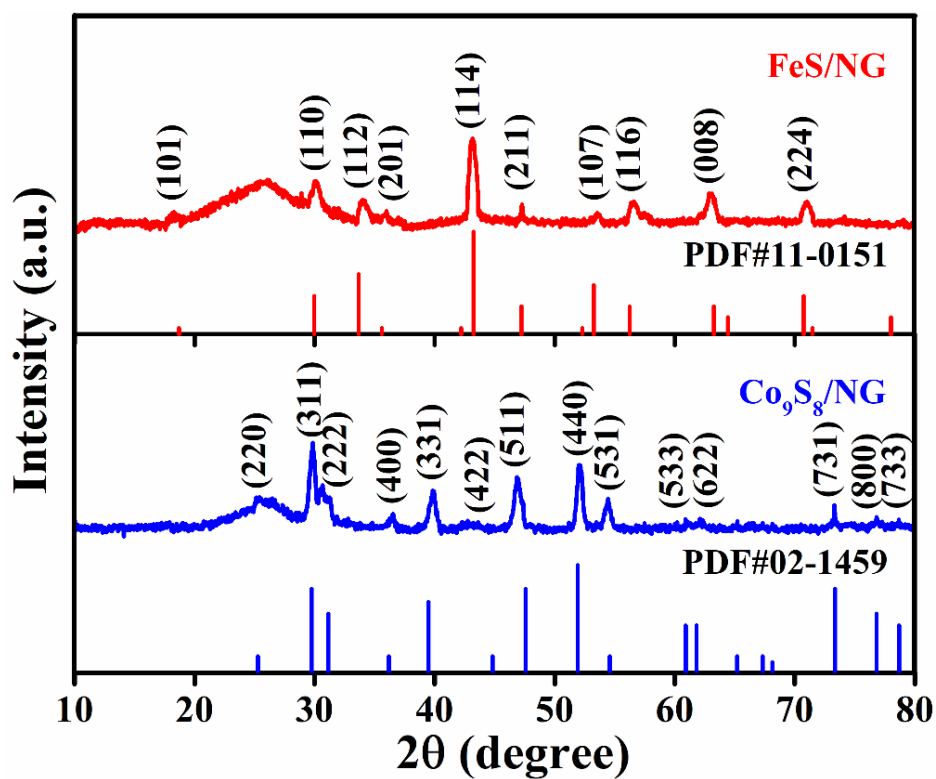


Fig. S8 XRD pattern of the Co₉S₈@NG and FeS@NG hybrids.

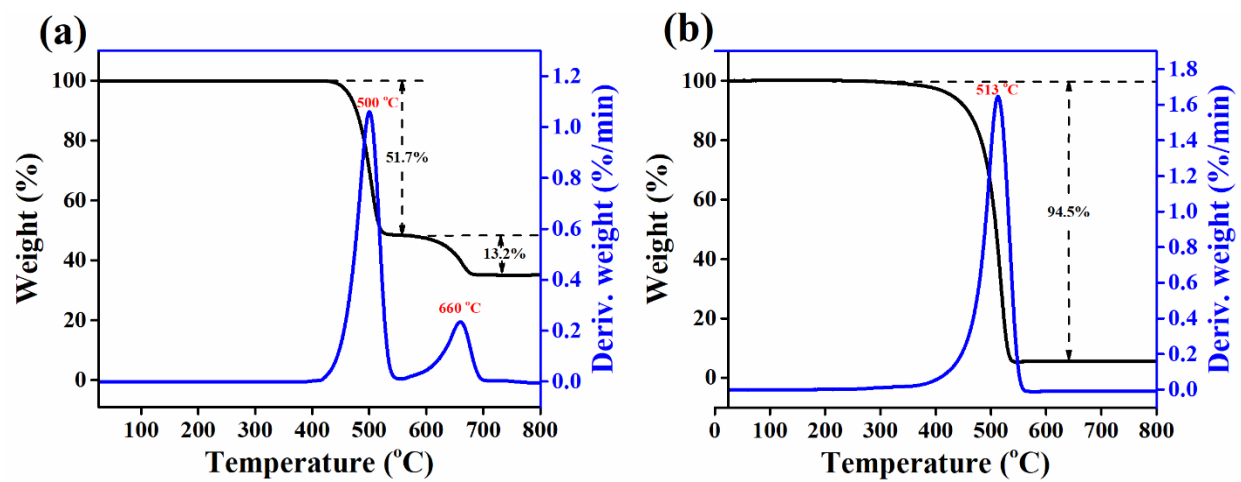


Fig. S9 TGA-DTA analysis curves of (a) the core-shell $\text{Co}_8\text{FeS}_8@\text{NG}$ hybrid and (b) Pristine NG.

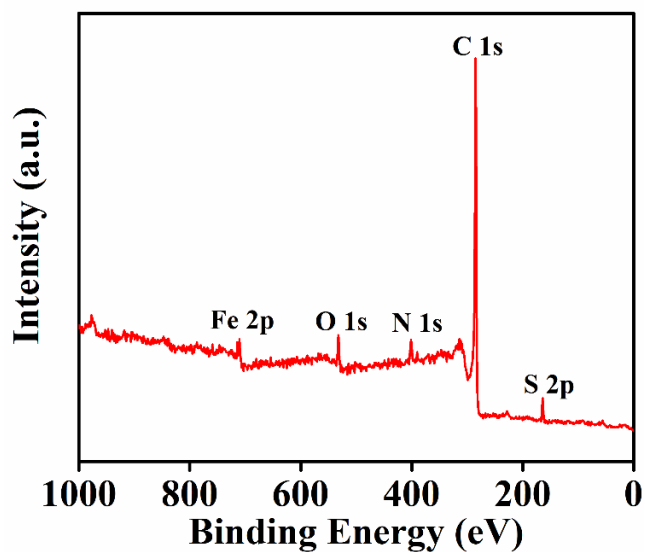


Fig. S10 XPS survey spectra of the FeS@NG hybrid (negative electrode).

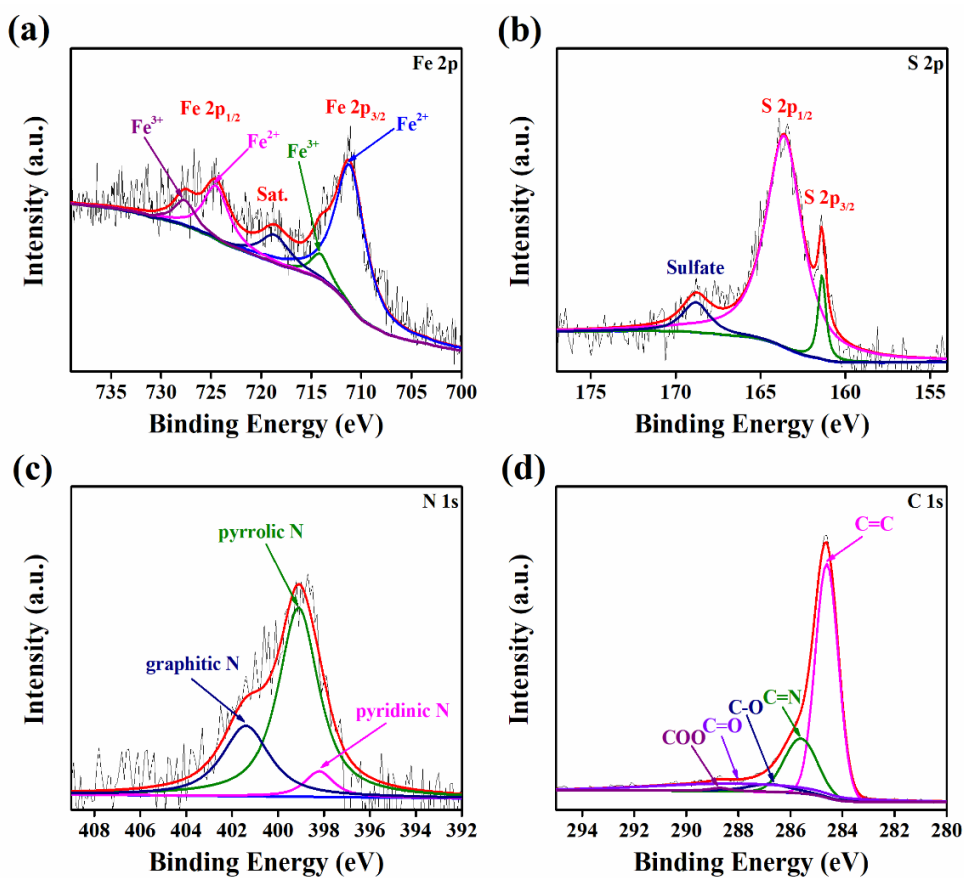


Fig. S11 High-resolution XPS spectra of a) Fe 2p, b) S 2p, c) N 1s, and c) C 1s, for the FeS@NG hybrid (negative electrode).

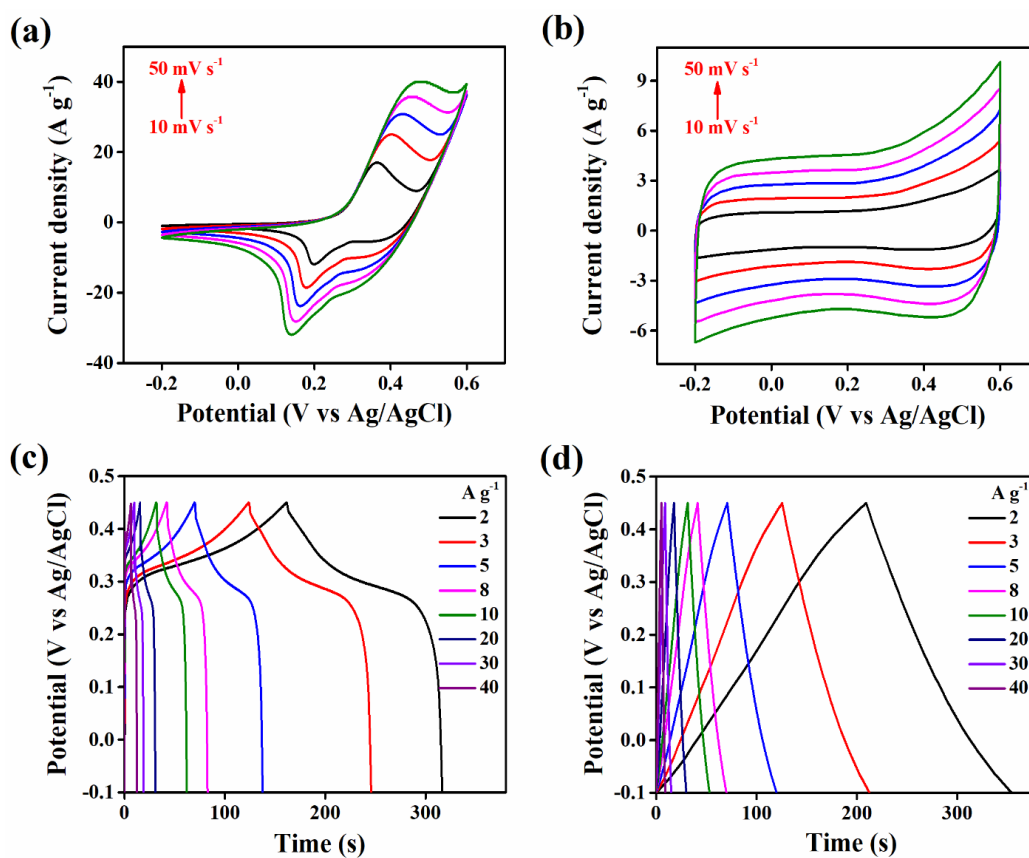


Fig. S12 CV curves of (a) Pristine Co_8FeS_8 and (b) Pristine NG electrodes with different scan rates from 10 to 50 mV s^{-1} . GCD curves of (c) Pristine Co_8FeS_8 and (d) Pristine NG electrodes with various current densities from 2 to 40 A g^{-1} .

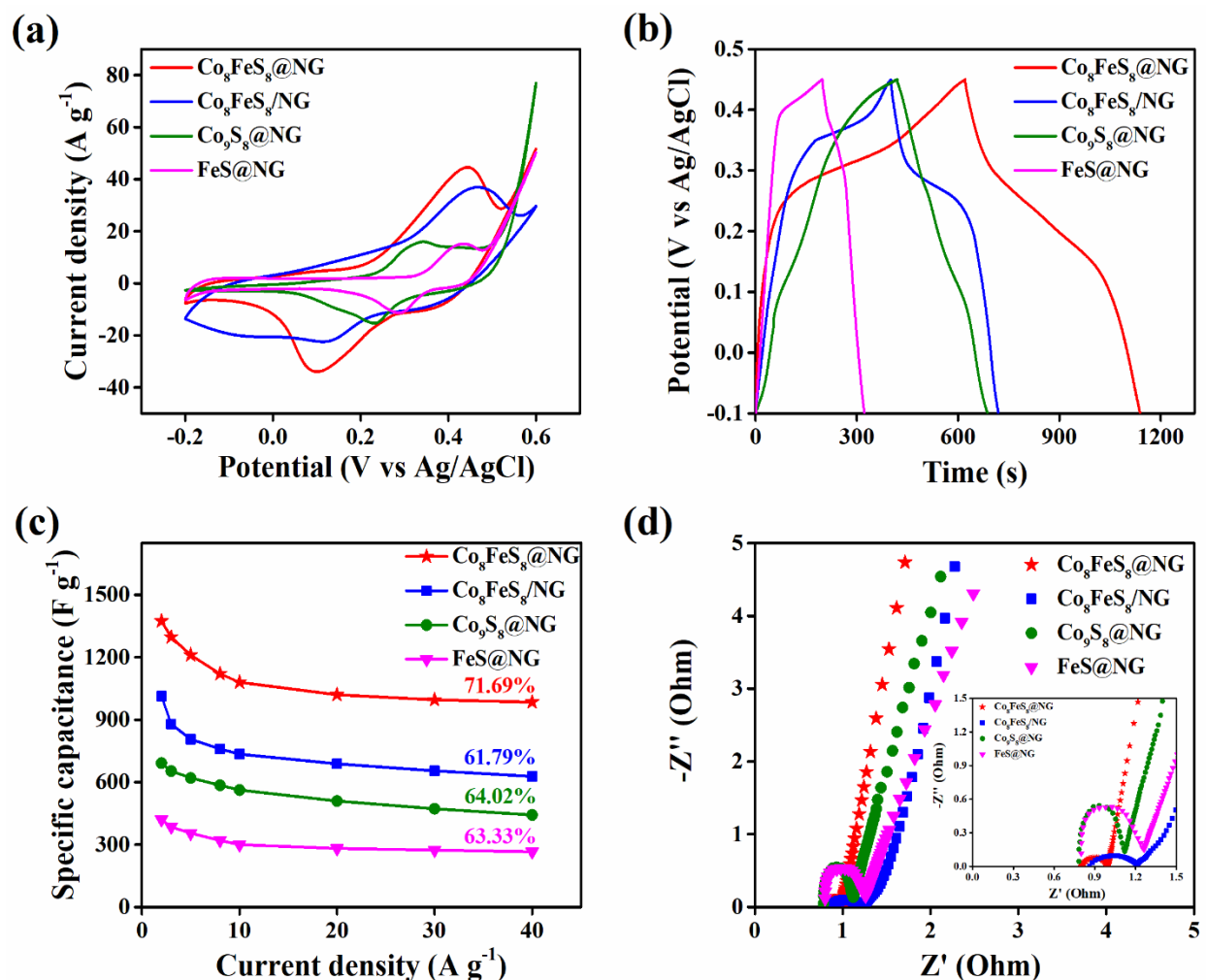


Fig. S13 (a) CV curves of $\text{Co}_8\text{FeS}_8@\text{NG}$, $\text{Co}_8\text{FeS}_8/\text{NG}$, $\text{Co}_9\text{S}_8@\text{NG}$, and $\text{FeS}@\text{NG}$ electrodes at a scan rate of 20 mV s^{-1} , (b) GCD curves of $\text{Co}_8\text{FeS}_8@\text{NG}$, $\text{Co}_8\text{FeS}_8/\text{NG}$, $\text{Co}_9\text{S}_8@\text{NG}$, and $\text{FeS}@\text{NG}$ electrodes at a current density of 2 A g^{-1} , (c) Specific capacitance vs. current density of $\text{Co}_8\text{FeS}_8@\text{NG}$, $\text{Co}_8\text{FeS}_8/\text{NG}$, $\text{Co}_9\text{S}_8@\text{NG}$, and $\text{FeS}@\text{NG}$ electrodes, and (d) EIS spectrum of $\text{Co}_8\text{FeS}_8@\text{NG}$, $\text{Co}_8\text{FeS}_8/\text{NG}$, $\text{Co}_9\text{S}_8@\text{NG}$, and $\text{FeS}@\text{NG}$ electrodes.

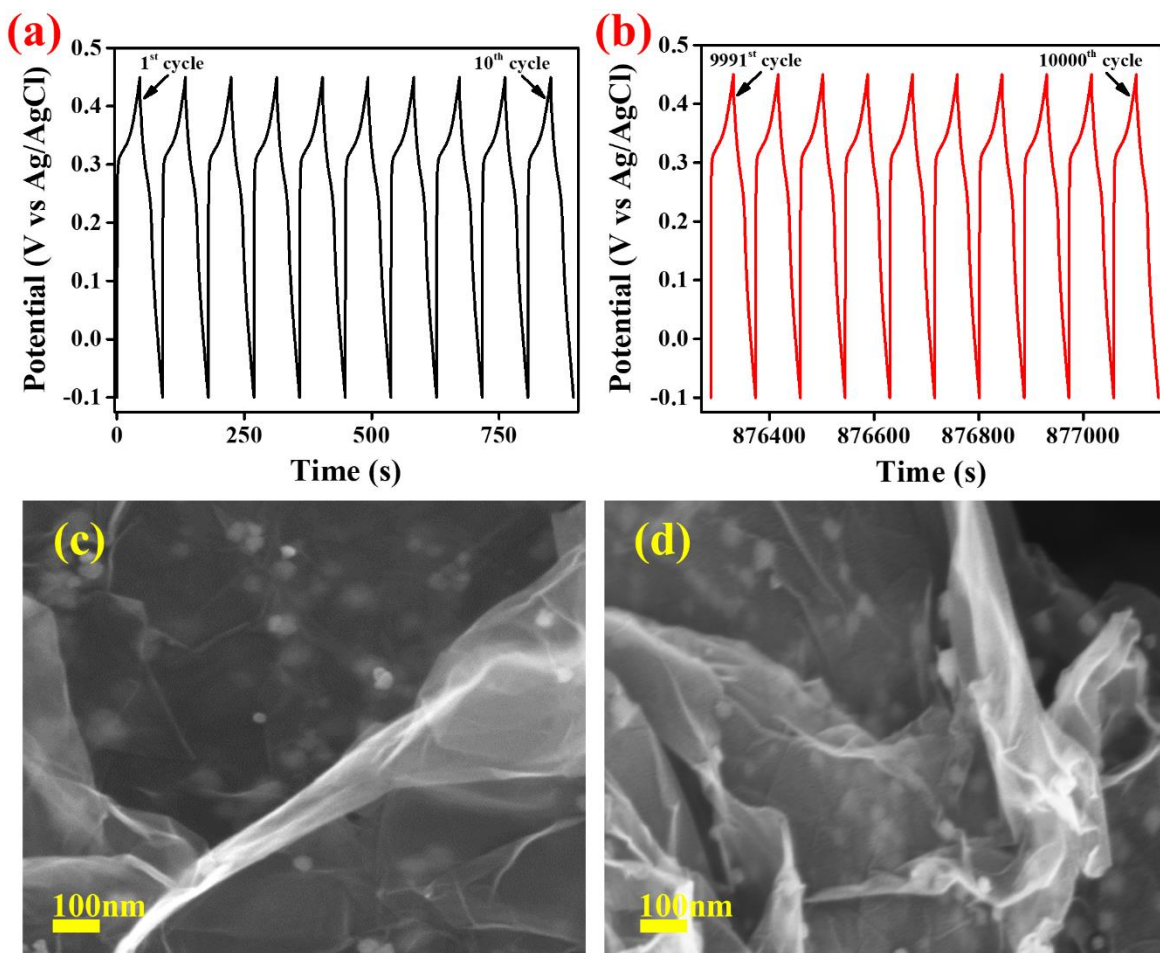


Fig. S14 GCD curves of Co₈FeS₈@NG electrode: (a) From 1st to 10th cycle, (b) From 9991st to 10 000th cycle, and (c and d) FE-SEM image of core-shell Co₈FeS₈@NG hybrid before and after 10 000 GCD cycles test, respectively.

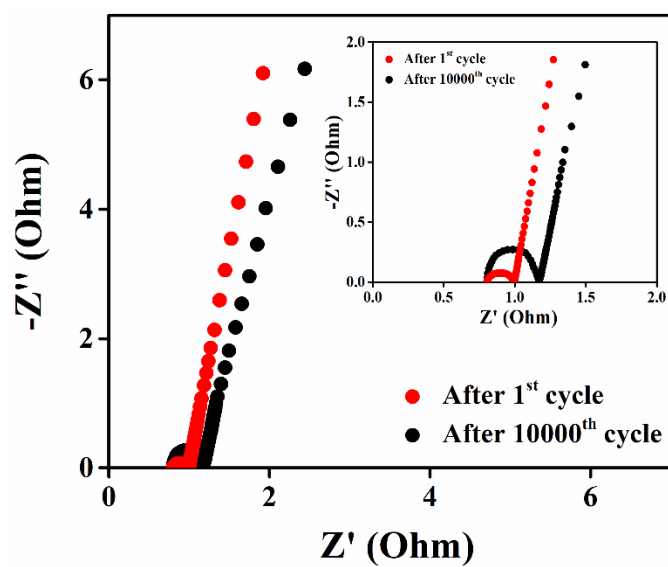


Fig. S15 EIS spectrum of the $\text{Co}_8\text{FeS}_8@\text{NG}$ electrode after 1st GCD cycle and after the 10 000th GCD cycle.

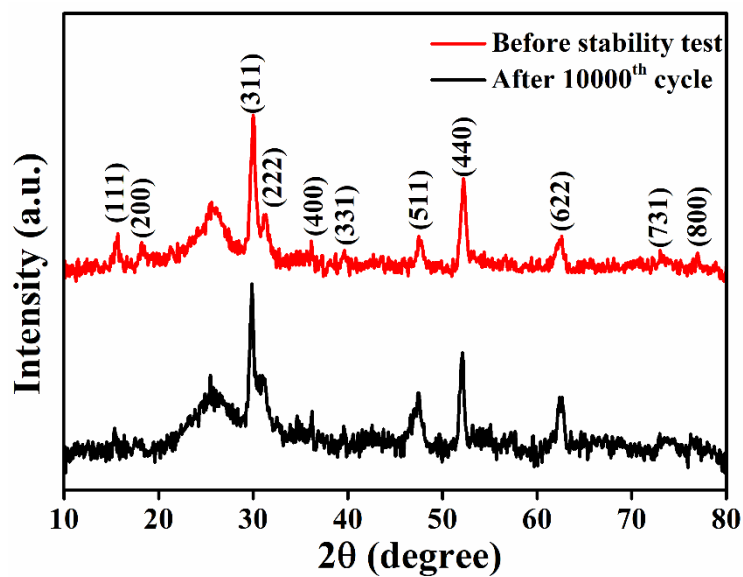


Fig. S16 XRD pattern of the core-shell $\text{Co}_8\text{FeS}_8@\text{NG}$ hybrid before and after cyclic stability test.

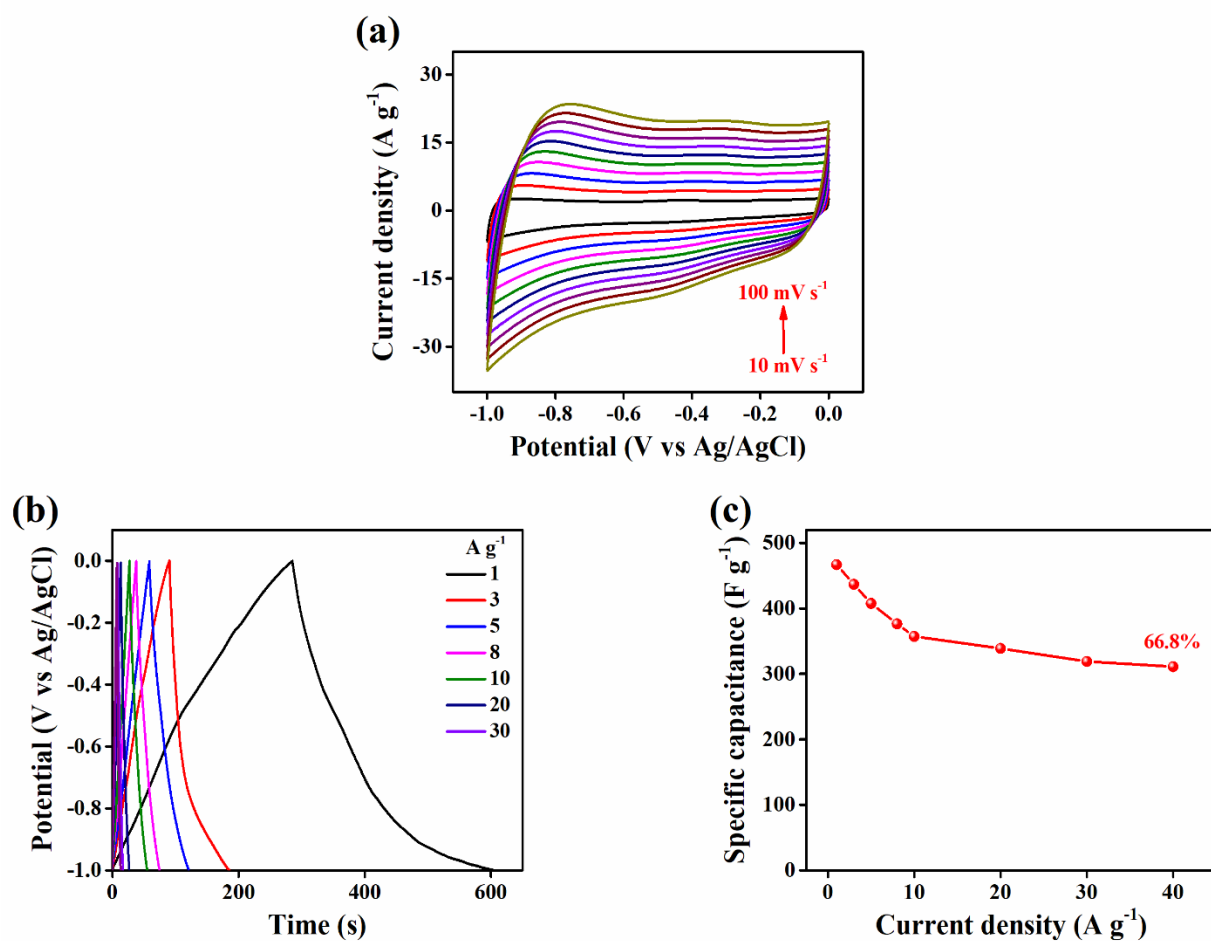


Fig. S17 (a) CV curves of the FeS@NG electrode at different scan rates from 10 to 100 mV s^{-1} , (b) GCD curves of FeS@NG electrode at various current densities from 1 to 30 A g^{-1} , and (c) Specific capacitance vs. current density of FeS@NG electrode.

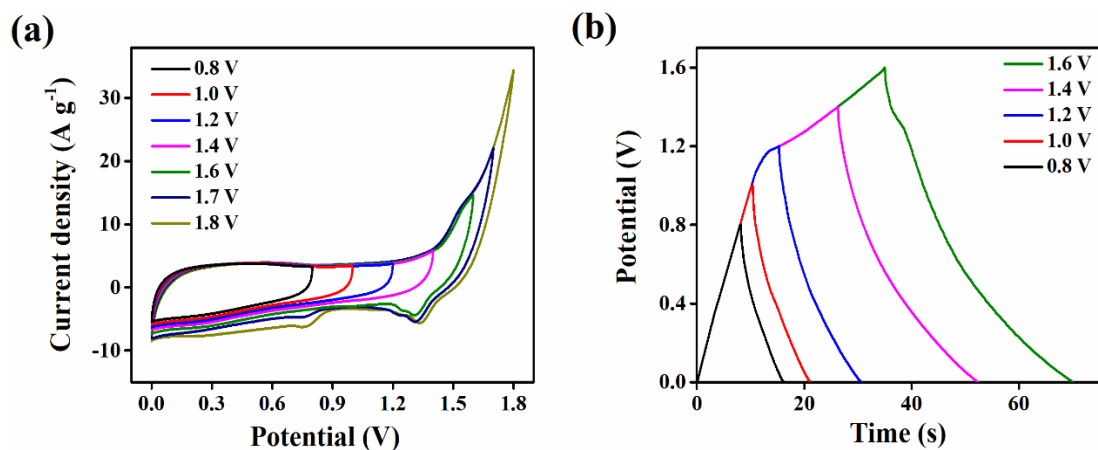


Fig. S18 (a) CV curves (at a sweep rate of 20 mV s^{-1}) of the $\text{Co}_8\text{FeS}_8@\text{NG}//\text{FeS}@\text{NG}$ ASC device with different operating potential window from 0.8 to 1.8 V and (b) GCD curves (at a current density of 10 A g^{-1}) of the $\text{Co}_8\text{FeS}_8@\text{NG}//\text{FeS}@\text{NG}$ ASC device at different operating potential window from 0.8 to 1.6 V.

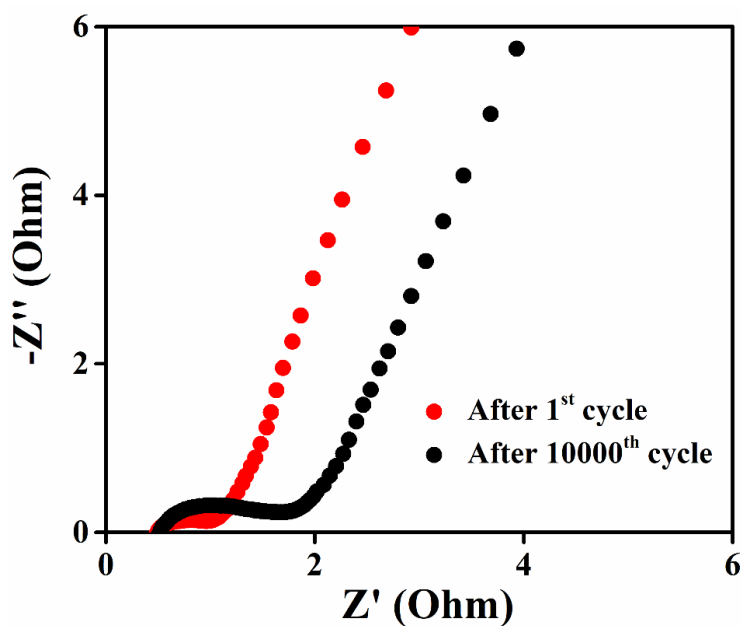


Fig. S19 EIS spectrum of the $\text{Co}_8\text{FeS}_8@\text{NG}//\text{FeS}@\text{NG}$ ASC after the 1st and 10 000th cycles test.

Table S1. Elemental composition of the core-shell Co₈FeS₈@NG and FeS@NG hybrids measured by XPS analysis.

Sample	Co (at. %)	Fe (at. %)	S (at. %)	N (at. %)	C (at. %)	O (at. %)
Co ₈ FeS ₈ @NG	4.11	1.12	5.49	6.26	76.10	6.92
FeS@NG	-	3.88	3.41	6.12	79.2	7.39

Table S2. Electrochemical properties of the Co₈FeS₈@NG electrode comparison with reported literature.

Materials	Specific capacitance (F g ⁻¹)	Current density	Electrolyte	Potential window (V)	Stability (Cycles)	References
Co ₈ FeS ₈ @NG	1374	2 A g ⁻¹	2 M KOH	−0.1-0.45	96.1% (10 000)	This work
GNS/NiS	775	0.5 A g ⁻¹	6 M KOH	0.0-0.4	88.1% (1000)	1
NiCo ₂ S ₄ -g-MoS ₂	1002	5 A g ⁻¹	6 M KOH	0-0.3	94.8% (4000)	2
GN-CoMoS ₄ @rGO	774	1 A g ⁻¹	3 M KOH	0.0-0.55	94.49% (6000)	3
Ni _x Co _{1-x} S _{1.987} microspheres/rGO	1152	0.5 A g ⁻¹	2 M KOH	0.0-0.5	-	4
CGH	564	1 A g ⁻¹	6 M KOH	−0.05-0.4	94.8% (2000)	5
CoMoS ₄	661	1 A g ⁻¹	1 M KOH	0.0-0.6	86% (10 000)	6
ZnCo _{1-x} S nanoartichokes	486	2 A g ⁻¹	1 M KOH	0.0-0.45	86.4% (2000)	7
CdS/NF	909	2 mA cm ⁻²	6 M KOH	0.0-0.4	104% (5000)	8
Co ₂ CuS ₄ /NG	1005	1 A g ⁻¹	6 M KOH	−0.1-0.5	96.3% (5000)	9
Ni ₃ S ₂ @Ni(OH) ₂ /3D GN	1277	5.1 A g ⁻¹	3 M KOH	−0.15-0.55	99.1 (2000)	10

CGH: 3D CoS/graphene composite hydrogel

Table S3. ASCs device performance comparison with previously reported literature.

Reported ASC Devices	Electrolyte	Device window (V)	Energy density (Wh kg ⁻¹)	Power density (kW kg ⁻¹)	Stability (Cycles)	References
Co ₈ FeS ₈ @NG//FeS@NG	PVA-KOH	0-1.6	70.4	0.59	93.7% (10 000)	This work
Ni-Co-S/G//PCNS	KOH	0-1.6	43.3	0.8	85% (10000)	11
ZICO//NG	PVA-KOH	0-1.5	40.5	0.75	95% (5000)	12
GN-CoMoS ₄ @rGO//AC	PVA-KOH	0-1.8	42.8	0.9	93.2% (8000)	3
CuCo ₂ S ₄ @NiMn-LDH//AC	KOH	0-1.5	45.8	1.49	87.6% (10 000)	13
Fe ₃ O ₄ @Fe ₂ O ₃ //Fe ₃ O ₄ @MnO ₂	Na ₂ SO ₄	0-2.0	26.6	0.5	92% (5000)	14
CC@CoMoO ₄ @NiCo-LDH	PVA-KOH	0-1.6	59.5	0.8	89.7% (5000)	15
MnO ₂ NS-CC//FeOOH NS-CC	Li ₂ SO ₄	0-1.85	37.4	16	-	16
MoO ₂ @NC//CuCo ₂ S ₄	PVA-KOH	0-1.6	65.1	0.8	90.6% (5000)	17
Co ₂ CuS ₄ /NG//NG	KOH	0-1.6	53.3	0.79	92.2% (4000)	9
NiNTAs@MnO ₂ //NiN TAs@Fe ₂ O ₃	PVA-Na ₂ SO ₄	0-1.6	34.1	3.19	79.3% (5000)	18
NiCo ₂ S ₄ //AC	KOH	0-1.5	28.3	0.24	91.7% (5000)	19

Notes and References

- 1 Y. Li, K. Ye, K. Cheng, J. Yin, D. Cao and G. Wang, *J. Power Sources*, 2015, **274**, 943–950.
- 2 J. Shen, P. Dong, R. Baines, X. Xu, Z. Zhang, P. M. Ajayan and M. Ye, *Chem. Commun.*, 2016, **52**, 9251–9254.
- 3 M. Wei, C. Wang, Y. Yao, S. Yu, W. H. Liao, J. Ren, R. Sun and C. P. Wong, *Chem. Eng. J.*, 2019, **355**, 891–900.
- 4 Y. Gao, L. Mi, W. Wei, S. Cui, Z. Zheng, H. Hou and W. Chen, *ACS Appl. Mater. Interfaces*, 2015, **7**, 4311–4319.
- 5 X. Meng, J. Deng, J. Zhu, H. Bi, E. Kan and X. Wang, *Sci. Rep.*, 2016, **6**, 1–9.
- 6 X. Xu, Y. Song, R. Xue, J. Zhou, J. Gao and F. Xing, *Chem. Eng. J.*, 2016, **301**, 266–275.
- 7 J. Yang, Y. Zhang, C. Sun, G. Guo, W. Sun, W. Huang, Q. Yan and X. Dong, *J. Mater. Chem. A*, 2015, **3**, 11462–11470.
- 8 P. Xu, J. Liu, P. Yan, C. Miao, K. Ye, K. Cheng, J. Yin, D. Cao, K. Li and G. Wang, *J. Mater. Chem. A*, 2016, **4**, 4920–4928.
- 9 M. Guo, J. Balamurugan, T. D. Thanh, N. H. Kim and J. H. Lee, *J. Mater. Chem. A*, 2016, **4**, 17560–17571.
- 10 W. Zhou, X. Cao, Z. Zeng, W. Shi, Y. Zhu, Q. Yan, H. Liu, J. Wang and H. Zhang, *Energy Environ. Sci.*, 2013, **6**, 2216–2221.
- 11 J. Yang, C. Yu, X. Fan, S. Liang, S. Li, H. Huang, Z. Ling, C. Hao and J. Qiu, *Energy Environ. Sci.*, 2016, **9**, 1299–1307.
- 12 A. Maitra, A. K. Das, R. Bera, S. K. Karan, S. Paria, S. K. Si and B. B. Khatua, *ACS Appl. Mater. Interfaces*, 2017, **9**, 5947–5958.
- 13 J. Lin, H. Jia, H. Liang, S. Chen, Y. Cai, J. Qi, C. Qu, J. Cao, W. Fei and J. Feng, *Chem. Eng. J.*, 2018, **336**, 562–569.
- 14 X. Tang, R. Jia, T. Zhai and H. Xia, *ACS Appl. Mater. Interfaces*, 2015, **7**, 27518–27525.

- 15 Y. Zhao, X. He, R. Chen, Q. Liu, J. Liu, J. Yu, J. Li, H. Zhang, H. Dong, M. Zhang and J. Wang, *Chem. Eng. J.*, 2018, **352**, 29–38.
- 16 Y.-C. Chen, Y.-G. Lin, Y.-K. Hsu, S.-C. Yen, K.-H. Chen and L.-C. Chen, *Small*, 2014, **10**, 3803–3810.
- 17 S. Liu, Y. Yin, K. S. Hui, K. N. Hui, S. C. Lee and S. C. Jun, *Adv. Sci.*, 2018, **5**, 1800733.
- 18 Y. Li, J. Xu, T. Feng, Q. Yao, J. Xie and H. Xia, *Adv. Funct. Mater.*, 2017, **27**, 26–28.
- 19 Y. Zhu, Z. Wu, M. Jing, X. Yang, W. Song and X. Ji, *J. Power Sources*, 2015, **273**, 584–590.