## Supporting Information for

## Highly stable supercapacitors with MOF-derived Co<sub>9</sub>S<sub>8</sub>/carbon electrodes for high rate electrochemical energy storage

Shuo Zhang <sup>*a*</sup>, Daohao Li <sup>*a*</sup>, Shuai Chen <sup>*b*</sup>, Xianfeng Yang <sup>*c*</sup>, Xiaoliang Zhao <sup>*a*</sup>, Quansheng Zhao<sup>\*,*a*</sup>, Sridhar Komarneni <sup>*d*</sup> and Dongjiang Yang<sup>\*,*a*,*e*,*f*</sup>

<sup>*a*</sup>Collaborative Innovation Centre for Marine Biomass Fibres, Materials and Textiles of Shandong Province; College of Chemical and Environmental Engineering, Qingdao University, Qingdao, P R China.

<sup>b</sup>State Key Laboratory of Coal Conversion Institute of Coal Chemistry Chinese Academy of Science Taiyuan 030001, China.

<sup>*c*</sup>Analytical and Testing Centre South China University of Technology Guangzhou 510640, China.

<sup>*d*</sup>Department of Ecosystem Science and Management and Materials Research Institute, Materials Research Laboratory, The Pennsylvania State University, University Park, PA 16802, USA.

<sup>e</sup>Queensland Micro- and Nanotechnology Centre (QMNC), Griffith University, Nathan, Brisbane, Queensland 4111, Australia.

<sup>f</sup>Key Laboratory of Coal Science and Technology, Taiyuan University of Technology, Ministry of Education and Shanxi Province, Taiyuan 030024, P. R. China.

\*To whom correspondence should be addressed. E-mail: <u>zqs0811@sina.com</u>; <u>d.yang@qdu.edu.cn</u>.



Fig. S1. Experimental and simulated XRD patterns of DUT-58 (a) in the range of  $5 \sim 50^{\circ}$  and (b) in the range of  $10 \sim 50^{\circ}$  with amplified simulated data.



Fig. S2 XPS spectra of (a) C 1s and (b) O 1s for  $Co_9S_8/NS$ -C-1.5 h.



Fig. S3 EDX pattern of the as-prepared  $Co_9S_8/NS$ -C-1.5 h.



Fig. S4  $N_2$  sorption isotherms of DUT-58 (a) before and (b) after the confinement treatment. The insets are the corresponding pore size distributions for DUT-58 (a) before and (b) after the confinement of TAA.

The decomposition formula of TAA during the thermal pyrolysis is:  $CH_3CSNH_2 + 4H_2O \rightarrow H_2S + NH_3 + CO_2 + 4H_2$  (1)



**Fig. S5**  $N_2$  sorption isotherms of  $Co_9S_8/NS$ -C-1.5 h composite. The inset shows the corresponding pore size distribution.



Fig. S6 SEM images of DUT-58 and  $Co_9S_8/NS-C-t$ . (a) DUT-58, (b, c)  $Co_9S_8/NS-C-1.5$  h, (d)  $Co_9S_8/NS-C-0$  h, (e)  $Co_9S_8/NS-C-1$  h and (f)  $Co_9S_8/NS-C-2$  h.



Fig. S7 Raman spectra of Co<sub>9</sub>S<sub>8</sub>/NS-C-t composites.



Fig. S8 TG and the corresponding XRD patterns of Co<sub>9</sub>S<sub>8</sub>/NS-C-1.5 h.

To evaluate the amount of carbon in  $Co_9S_8/NS-C-1.5$  h material, the thermogravimetric (TG) analysis for  $Co_9S_8/NS-C-1.5$  h was carried out in air from 25 to 900 °C, and the corresponding TG curve is shown in Fig. S8. The sample  $Co_9S_8/NS-C-1.5$  h is very stable at temperatures below 200 °C. With increasing temperature, an obvious weight increase takes place from 268 °C to ~ 487 °C. This weight increase is mainly attributed to the partial oxidation of  $Co_9S_8$  NPs to form  $CoSO_4$ . Above 487 °C, the weight reduction is mainly due to the oxidation of  $CoSO_4$  to  $Co_3O_4$  and the removal of amorphous carbon from the composites. At higher than 670 °C, graphitic carbon of the composite gradually disappeared. When the testing temperature is higher than 858 °C, the weight becomes constant and the product is confirmed to be  $Co_3O_4$ . During the whole measurement range, the total weight loss is about 19.16%. From this final weight loss value, we estimated that the amount of carbon in  $Co_9S_8/NS-C-1.5$  h is about 12 wt %.



Fig. S9 CV curves of the  $Co_9S_8/NS$ -C composite electrodes. (a)  $Co_9S_8/NS$ -C-0 h, (b)  $Co_9S_8/NS$ -C-1 h and (c)  $Co_9S_8/NS$ -C-2 h at scan rates 5, 10, 20, 50 and 100 mV s<sup>-1</sup>.

![](_page_10_Figure_0.jpeg)

Fig. S10 Galvanostatic charge/discharge curves of the  $Co_9S_8/NS-C$  electrodes. (a)  $Co_9S_8/NS-C$ -t at 1 A g<sup>-1</sup>. (b)  $Co_9S_8/NS-C$ -0 h, (c)  $Co_9S_8/NS-C$ -1 h and (d)  $Co_9S_8/NS-C$ -2 h at different current densities.

![](_page_11_Figure_0.jpeg)

Fig. S11 EIS Nyquist plots of  $Co_9S_8/NS$ -C-t electrodes. Inset: EIS Nyquist plots withzoomeddataatthehighfrequencyregion.

![](_page_12_Figure_0.jpeg)

Fig. S12 Ragone plots of  $Co_9S_8/NS$ -C-1.5 h and other related electrodes.

![](_page_13_Figure_0.jpeg)

Fig. S13 The cycling performance at the current density of 10 A  $g^{-1}$  of  $Co_9S_8/NS-C-t$  electrodes.

![](_page_14_Figure_0.jpeg)

Fig. S14 (a) CV curves and (b) Galvanostatic charge/discharge curves of the AC electrode.

![](_page_15_Figure_0.jpeg)

Fig. S15 Cyclic voltammograms of optimized  $Co_9S_8/NS-C-1.5h//AC$  asymmetric hybrid supercapacitor at different potential windows at a scan rate of 10 mV s<sup>-1</sup>.

![](_page_16_Figure_0.jpeg)

Fig. S16 Ragone plots of  $Co_9S_8/NS-C-1.5h//AC$  and other related asymmetric hybrid supercapacitors.

![](_page_17_Figure_0.jpeg)

Fig. S17 EIS Nyquist plot of  $Co_9S_8/NS-C-1.5h//AC$  asymmetric hybrid supercapacitor. (The inset shows EIS Nyquist plot with zoomed data at the high frequency region).

Electrode	Electrolyte	Stability	Specific capacitances	Rate	Refs
				capability	
Co <sub>9</sub> S <sub>8</sub> /NS-C		140000	734.09 F g <sup>-1</sup> @1 A g <sup>-1</sup>	89 %	
		cycles	653.64 F g <sup>-1</sup> @10 A g <sup>-1</sup>		
	6.0 M	99.8%			This
Co <sub>9</sub> S <sub>8</sub> /NS-C-1.5h//AC	КОН	2000	75.6 F g <sup>-1</sup> @1 A g <sup>-1</sup>	42.87%	work
		cycles	32.41 F g <sup>-1</sup> @10 A g <sup>-1</sup>		
		99.5%	(AHS)		
C0 <sub>9</sub> S <sub>8</sub> @	2.0 M	2000	1620 F g <sup>-1</sup> @0.5 A g <sup>-1</sup>	75.78 %	1
Ni(OH) <sub>2</sub>	КОН	cycles	1227 F g <sup>-1</sup> @20 A g <sup>-1</sup>		
		100%			
Co <sub>9</sub> S <sub>8</sub> /NF	2.0 M	2000	1645 F g <sup>-1</sup> @3 A g <sup>-1</sup>	80 %	2
	КОН	cycles	1309 F g <sup>-1</sup> @45 A g <sup>-1</sup>		
		94.4%			
C09S8	3.0 M	2000	1775 F g <sup>-1</sup> @4 A g <sup>-1</sup>	83.5 %	3
	КОН	cycles	1483 F g <sup>-1</sup> @24 A g <sup>-1</sup>		
		91.4%			
C0988	6.0 M	60 cycles	306.1 F g <sup>-1</sup> @0.1 A g <sup>-1</sup>	73.2 %	4
	КОН	100%	224 F g <sup>-1</sup> @1 A g <sup>-1</sup>		
C0988		1500	520 F g <sup>-1</sup> @0.5 A g <sup>-1</sup>	56 %	
		cycles	291.2 F g <sup>-1</sup> @8 A g <sup>-1</sup>		
	2.0 M	100%			5
	КОН	2000	55 F g <sup>-1</sup> @0.5 A g <sup>-1</sup>	80 %	5
AC//Co <sub>9</sub> S <sub>8</sub>		cycles	44 F g <sup>-1</sup> @5 A g <sup>-1</sup> (AHS)		
		100%			
Co <sub>9</sub> S <sub>8</sub> @S,N-doped	6.0 M	2000	429 F g <sup>-1</sup> @1 A g <sup>-1</sup>	78.32 %	6
carbon cuboid	КОН	cycles	336 F g <sup>-1</sup> @50 A g <sup>-1</sup>		
		98%			
C@C0988	2.0 M	3000	654 F g <sup>-1</sup> @2 A g <sup>-1</sup>	75.08 %	7
	КОН	cycles	491 F g <sup>-1</sup> @8 A g <sup>-1</sup>		
		88.5%			
C0988	6.0 M	1000	273.7 F g <sup>-1</sup> @1 A g <sup>-1</sup>		8
	КОН	cycles			
		90.4%			
C0988	30%	5000	82.9 F g <sup>-1</sup> @1.25 A g <sup>-1</sup>	89%	9
nanoflakes//AC	КОН	cycles	73.92F g <sup>-1</sup> @5 A g <sup>-1</sup>		
		90%	(AHS)		

**Table S1** Comparison of various  $Co_9S_8$ -based electrodes and asymmetric hybridsupercapacitor (AHS) in recent years as supercapacitors.

## References

- 1 J. Wen, S. Z. Li, B. Li, Z. C. Song, H. N. Wang, R. Xiong and G. J. Fang, *J. Power Sources*, 2015, **284**, 279-286.
- 2 H. Li, Y. H. Gao, Y. D. Shao, Y. T. Su and X. W. Wang, *Nano lett.*, 2015, **15**, 6689-6695.
- 3 J. Pu, Z. H. Wang, K. L. Wu, N. Yu and E. H. Sheng, *Phys. Chem. Chem. Phys.*, 2014, 16, 785-791.
- 4 L. P. Zhang, Y. R. Wang, W. Zhou, G. S. Song and S. Q. Cheng, *Int. J. Electrochem. Sci.*, 2016, **11**, 1541-1548.
- 5 B. Li, Y. X. Hu, J. J. Li, M. C. Liu, L. B. Kong, Y. M. Hu and L. Kang, *Metals*, 2016, 6, 142.
- 6 S. W. Liu, M. Y. Tong, G. Q. Liu, X. Zhang, Z. M. Wang, G. Z. Wang, W. P. Cai, H. M. Zhang and H. J. Zhao, *Inorg. Chem. Front.*, 2017, 4, 491-498.
- 7 T.Wu, X. L. Ma, T. Zhu, Mater. Lett., 2016, 183, 290-295.
- 8 L. Yin, L. Q. Wang, X. H. Liu, Y. S. Gai, L. H. Su, B. H. Qu and L. Y. Gong, *Eur. J. Inorg. Chem.*, 2015, 2015, 2457-2462.
- 9 R. B. Rakhi, N. A. Alhebshi. D. H. Anjum and H. N. Alshareef, J. Mater. Chem. A., 2014, 2, 16190-16198.