## **Supporting Information**

## Dual Electrocatalytic Heterostructures for Efficient Immobilization and Conversion of Polysulfides in Li-S Batteries

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Sample	Specific surface area (m <sup>2</sup> g <sup>-1</sup> )		
Co-Zn/Zn-C-700	13		
Co-Zn/Zn-C-800	131		
Co-Zn/Zn-C-900	676		
Co-Zn/Zn-C-800-1	137		
Co-Zn/Zn-C-800-3	76		

 Table S1 The specific surface areas of different samples.

 Table S2 The real contents of Zn and Co in different samples achieved by ICP.

Sample	Co (wt%)	Zn (wt%)
Co-Zn/Zn-C-700	0.99	23.6
Co-Zn/Zn-C-800	1.76	14.2
Co-Zn/Zn-C-900	2.79	2.08

Sample	Rate	Cycle number	Reversible capacity (mAh g <sup>-1</sup> )	Ref.
CoP@HPCN/S	0.2 C	300	630	1
S/PCMSs	0.5 C	700	489	2
CNT@TiO <sub>2-x</sub> -S	1 C	500	590	3
S@TiO2@HCNBs	0.5 C	600	508	4
CF/FeP@C@S	1 C	200	500	5
CNT/CdS-QDs/S	0.5 C	150	820.6	6
CGPE	1 C	200	580	7
S-SAV@NG	0.5 C	400	551	8
B/2D MOF-Co	1 C	600	450	9
Sph-Ox-S	0.2 C	300	700	10
V <sub>2</sub> O <sub>5</sub> -S-CNG	0.5 C	150	713.3	11
Co-Zn/Zn-C-800/S	1 C	500	590	This work

 Table S3 Comparison of electrochemical performances among Co-Zn/Zn-C-800/S

 electrode and the literature reported sulfur cathodes.<sup>1-11</sup>



Fig. S1 SEM images of (a) Zn/Co-ZIF and (b)Zn/Co-ZIF@PZS.



Fig. S2 (a) XRD pattern and (b)  $N_2$  adsorption-desorption isotherm of the Co-Zn/Zn-C-800. The inset is the pore size distribution.



Fig. S3 SEM images of (a) Co-Zn/Zn-C-700 and (b) Co-Zn/Zn-C-900.



Fig. S4 XRD patterns of (a) Co-Zn/Zn-C-700, (b) Co-Zn/Zn-C-900, (c) Co-C-800 and

(d) Zn-C-800.



Fig. S5  $N_2$  adsorption-desorption isotherms of (a) Co-Zn/Zn-C-700 and (b) Co-Zn/Zn-C-900. The inset is pore size distribution.



Fig. S6 Full XPS spectra of Co-Zn/Zn-C-800 (a) before (b) after 250 s etching.



**Fig. S7** (a and c) The stable adsorption configurations of  $\text{Li}_2\text{S}_n$  (n = 8 and 4) clusters on Co<sub>2</sub>P (121) plane, ZnS (100) plane and Co<sub>2</sub>P-ZnS heterostructure interface, together with (b and d) the comparison of calculated adsorption energies. Pink, purple, gray, yellow and green balls represent P, Co, Zn, S and Li atoms, respectively.



Fig. S8 TGA curve of Co-Zn/Zn-C-800/S achieved under  $N_2$  atmosphere at heating rate of 10 °C min<sup>-1</sup>.



**Fig. S9** (a) TEM image, (b) HRTEM image and the corresponding elemental mapping analysis of (c-h) of Co-Zn/Zn-C-800/S.



Fig. S10 Stability test of Co-Zn/Zn-C-800  $\mid$  Li control cell at 340 mA g^-1.



Fig. S11 Schematic illustration of the interface contact and the possible catalytic mechanism of  $Co_2P$ -ZnS heterostructure.



Fig. S12 TEM images of Co-Zn/Zn-C-800/S after 500 cycles at 1 C.



**Fig. S13** Comparison of electrochemical performances among Co-Zn/Zn-C-800/S electrode and the literature reported sulfur cathodes.



Fig. S14 Optical image of blank  $Li_2S_6$  solution and after adsorbing with Co-C-800 and Zn-C-800, respectively.



**Fig. S15** (a) CV curves of  $\text{Li}_2\text{S}_6$  symmetric cells from -0.8 to 0.8 V at 10 mV s<sup>-1</sup> of Co-C-800 and Zn-C-800. (b and c) CV curves of different electrodes at various scanning rates; (d-f) The kinetic plots and diffusion coefficient ( $D_{\text{Li}^+}$ ) of Li<sup>+</sup> ion corresponding peak 1 and 2 on Co-C-800/S and Zn-C-800/S cathodes.



Fig. S16 (a) N<sub>2</sub> adsorption-desorption isotherms and (b) pore size distributions.



Fig. S17 XRD patterns of (a) Co-Zn/Zn-C-800-1 and (b) Co-Zn/Zn-C-800-3.



**Fig. S18** (a) Galvanostatic charge–discharge curves, (b) CV curves, (c) EIS spectra, (d) cycling performance at 1 C, and (e) rate performance of different samples.



Fig. S19 CV curves of Li<sub>2</sub>S<sub>6</sub> symmetric cells from -0.8 to 0.8 V at 10 mV s<sup>-1</sup>.

## **Supporting References:**

- 1 Z. Ye, Y. Jiang, J. Qian, W. Li, T. Feng, L. Li, F. Wu and R. Chen, *Nano Energy*, 2019, **64**, 103965.
- S. Liu, T. Zhao, X. Tan, L. Guo, J. Wu, X. Kang, H. Wang, L. Sun and W. Chu, *Nano Energy*, 2019, 63, 103894.
- Y. Wang, R. Zhang, J. Chen, H. Wu, S. Lu, K. Wang, H. Li, C. J. Harris, K.
   Xi, R. V. Kumar and S. Ding, *Adv. Energy Mater.*, 2019, 9, 1900953.
- H. Gu, H. Wang, R. Zhang, T. Yao, T. Liu, J. Wang, X. Han and Y. Cheng,
   *Ind. Eng. Chem. Res.*, 2019, 58, 18197-18204.
- J. Shen, X. Xu, J. Liu, Z. Liu, F. Li, R. Hu, J. Liu, X. Hou, Y. Feng, Y. Yu and
   M. Zhu, ACS Nano, 2019, 13, 8986-8996.
- 6 D. Cai, L. Wang, L. Li, Y. Zhang, J. Li, D. Chen, H. Tu and W. Han, *J. Mater. Chem. A*, 2019, **7**, 806-815.
- 7 D. Yang, L. He, Y. Liu, W. Yan, S. Liang, Y. Zhu, L. Fu, Y. Chen and Y. Wu, S12

J. Mater. Chem. A, 2019, 7, 13679-13686.

- G. Zhou, S. Zhao, T. Wang, S.-Z. Yang, B. Johannessen, H. Chen, C. Liu, Y.
  Ye, Y. Wu, Y. Peng, C. Liu, S. P. Jiang, Q. Zhang and Y. Cui, *Nano Lett.*, 2020, 20, 1252-1261.
- Y. Li, S. Lin, D. Wang, T. Gao, J. Song, P. Zhou, Z. Xu, Z. Yang, N. Xiao and
   S. Guo, *Adv. Mater.*, 2020, **32**, 1906722.
- 10 Y. Liu, Z. Ge, Z. Sun, Y. Zhang, C. Dong, M. Zhang, Z. Li and Y. Chen, *Nano Energy*, 2020, **67**, 104216.
- C. Wang, Y. Yi, H. Li, P. Wu, M. Li, W. Jiang, Z. Chen, H. Li, W. Zhu and S. Dai, *Nano Energy*, 2020, 67, 104253.