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## **Supplementary Information**

## LiFePO<sub>4</sub>/Li<sub>2</sub>S<sub>n</sub> hybrid system with enhanced Li-ion storage performance

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## Figures



**Fig. S1**<sup>†</sup> High resolution XPS spectrum of S 2p for  $Li_2S_n$  (a) and LFP/ $Li_2S_n$  hybrid system (b) after the cycling test (at fully discharged state). It can be seen the obvious shifts of the peak positions of  $Li_2S$  between LFP/ $Li_2S_n$  hybrid system and  $Li_2S_n$  system, indicative of the interaction between LFP and  $Li_2S_n$ .<sup>1,2</sup>

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**Fig. S2**<sup>†</sup> (a) Low- and (b) high-magnification SEM images of commercial LFP powder, revealing that the particles are in irregular shape with particle size ranging from tens of nanometer to micrometer. Severe particle agglomeration can also be seen. The BET surface area of the commercial LFP powder was measured to be 9.3  $m^2 \cdot g^{-1}$  without pores existence.<sup>3</sup>

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Fig. S3<sup>†</sup> XRD pattern of the commercial LFP powder and the standard for LFP (JCPDS card no. 81–1173).

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**Fig. S4**<sup>†</sup> (a) and (b) SEM images of LFP electrode in LFP/Li<sub>2</sub>S<sub>n</sub> hybrid system after the cycling test (at fully discharged state) with different magnification. It can be seen that the integrality of the electrode was kept well and a Li<sub>2</sub>S layer was uniformly deposited on the surface of LFP electrode, suggested a good structural stability of the electrode during the cycling process.

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**Fig. S5**<sup>†</sup> The equivalent circuits for the Nyquist plots of LFP/Li<sub>2</sub>S<sub>n</sub> hybrid system (a), LFP system (b) and Li<sub>2</sub>S<sub>n</sub> system (c). In the equivalent circuit,  $R_0$  represents the ohmic resistance corresponding to the intersection with the  $Z_{re}$  axis at the high frequency region of the Nyquist plot,  $R_1$  and  $Q_1$  represent the resistance of the solid electrolyte interphase (SEI) film and the relax capacitance corresponding to the high-frequency region in the semicircle of the Nyquist plot,  $R_2$  and  $Q_2$  represented the charge transfer resistance and double-layer capacitance corresponding to the electrochemical reaction of LFP (the 1<sup>st</sup> semicircle of the Nyquist plots),  $R_3$  and  $Q_3$  represented the charge transfer resistance corresponding to the electrochemical reaction of LFP (the 1<sup>st</sup> semicircle of the Nyquist plots),  $R_3$  and  $Q_3$  represented the charge transfer resistance and double-layer capacitance corresponding to the electrochemical reaction of Li<sub>2</sub>S<sub>n</sub> (the 2<sup>nd</sup> semicircle of the Nyquist plots), and W represents the Warburg resistance related to the lithium ion diffusion process corresponding to the straight line in the low-frequency region of the Nyquist plot.<sup>4-6</sup> Here, a constant phase element Q is employed taking into account the non-ideal frequency response of the displayed data.

**Table S1**<sup>†</sup> The fitting values of the resistance components in the equivalent circuits. Based on the fitting data, the higher conductivity  $(1/R_{sum})$  and lower charge-transfer resistance corresponding to each electrochemical process of LFP/Li<sub>2</sub>S<sub>n</sub> hybrid system were confirmed, beneficial from the synergistic effect for energy-storage between LFP component and Li<sub>2</sub>S<sub>n</sub> component.

	$R_{0}(\Omega)$	$R_{I}(\Omega)$	$R_2(\Omega)$	$R_3(\Omega)$	$R_{sum^{a}}(\Omega)$
LFP	4.23	96.64	63.34	-	164.21
$Li_2S_n$	4.09	154.20	-	47.19	205.48
LFP- $Li_2S_n$	9.60	70.77	31.98	10.70	123.05

<sup>a</sup>  $R_{sum} = R_0 + R_1 + R_2 + R_3$ 

## References

[1] Y., Zhang, Y. Ma, Y. Chen, L. Zhao, L. Huang, H. Luo, W. Jiang, X. Zhang, S. Niu, D. Gao, J. Bi, G. Fan and J. Hu, *ACS Appl. Mater. Interfaces*, 2017, **9**, 36857-36864.

[2] X. Yan, C. Xue, B. Yang and G. Yang, *Applied Surface Science*, 2017, **394**, 248-257.

[3] B. Wang, W. Al Abdulla, D. Wang and X. S. Zhao, *Energy Environ. Sci.*, 2015, **8**, 869-875.

[4] B. Wang, T. Liu, A. Liu, G. Liu, L. Wang, T. Gao, D. Wang and X. S. Zhao, *Adv. Energy Mater.*, 2016, **6**, 1600426;

[5] B. Wang, Q. Wang, B. Xu, T. Liu, D. Wang and G. Zhao, *RSC Adv.*, 2013, **3**, 20024-20033

[6] B. Wang, Y. Xie, T. Liu, H. Luo, B. Wang, C. Wang, L. Wang, D. Wang, S. Dou and Y. Zhou, *Nano Energy*, 2017, **42**, 363-372.