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# Supporting Information

#### Self-Sacrificial Template-Directed Synthesis of Metal– Organic Framework-Derived Porous Carbon for Energy-Storage Devices

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#### Supporting Information

#### **Experiment Sections**

*Preparation of ZnO spheres.* ZnO spheres were synthesized through hydrolysis of zinc acetate dihydrate in diethylene glycol as described in previous report.<sup>[S1]</sup> Typically, 1.97 g of zinc acetate dihydrate was added in 90 mL of diethylene glycol. The mixture was heated to 160 °C at a rapid heating of about 10 °C min<sup>-1</sup> and then reflux at this temperature for 16 h. The product was collected by centrifuged and washed by ethanol several times. Then the white product was annealed at 400 °C for 1 h in air.

*Preparation of hollow ZIF-8 derived carbon sphere*. 204 mg ZnO nanosheets was added to 80 mL N,N-dimethylformamide/H<sub>2</sub>O mixed solvent (v/v ratio of 3:1) and stirred for 1 h. Then 206 mg 2-methylimidazole (MeIM) was added to the dispersion under magnetic stirring. After 10 min stirring, the homogeneous dispersion was added to Teflon-lined stainless-steel autoclave (100 mL). The autoclave was transferred to an oven preheated to 70 °C. After the mixture reacted for 12 h, the white product was collected by centrifugation and washed by fresh DMF and ethanol for five times. The as-prepared ZnO@ZIF-8 composite was put into a ceramic boat and transferred into a temperature-programmed furnace, then heated to 200 °C for 6 h at a heating rate of 5 °C min<sup>-1</sup>. The further pyrolysis treatment was performed at 950 °C for 10 h.

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Figure S1. SEM images of ZnO@ZIF-8 composites prepared with (a) 4 h and (b) 12 h.



Figure S2. TGA curve of ZnO@ZIF-8 composite under N<sub>2</sub> conditions at a heating rate of  $5 \text{ }^{\circ}\text{C min}^{-1}$  (ZnO@ZIF-8 composite was prepared at 4 h).



Figure S3. (a) XRD pattern and (b) Raman spectrum of ZCNs-4.



Figure S4. SEM images of (a, b) ZCNs-4 and (c, d) ZCNs-12.



**Figure S5.** SEM images of (a, b) ZnO sphere, (c, d) core-shell nanostructured ZnO@ZIF-8 composite and (e, f) ZIF-8-derived hollow carbon sphere.



Figure S6. Typical survey scanned XPS spectrum of ZCNs-4.



Figure S7. (a) Nyquist plots and (b) bode plots of ZCNs-4 and ZCNs-12-based cell.



Figure S8. Raman spectra of elemental sulfur and ZCNs-4/S composite.



Figure S9. TG curves of elemental sulfur and ZCNs-4/S composite.



Figure S10. CV curve of ZCNs-4/S electrode.



Figure S11. (a) Cycling performance and (b) potential profiles of ZCNs-12/S electrode at 0.5C. (c) Potential profiles of ZCNs-4/S electrode at 0.5 C. (d) Capacity contribution from higher plateau, lower plateau and small sulfur molecule of ZCNs-4/S electrode.

Samples	$S_{BET}$ (m <sup>2</sup> g <sup>-1</sup> )	$\frac{\text{Micro-SSA}}{(\text{m}^2 \text{ g}^{-1})}$	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Micro volume (cm <sup>3</sup> g <sup>-1</sup> )	Meso+Macro Micro
ZCNs-4	1228	639	0.80	0.26	2.46
ZCNs-12	1023	565	0.74	0.23	2.22

Table S1. Porous characterizations of ZCNs-4 and ZCNs-12.

#### References

[S1] Q. Zhang, T. P. Chou, B. Russo, S. A. Jenekhe, G. Z. Cao, Adv. Funct. Mater. 2008, 18, 1654.