Supporting information for

## Covalent Organic Framework with 3D Ordered Channel and Multi-

## Functional Groups Endows Zn Anode with Superior Stability

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## **Supplementary Figures and Table**



Fig. S1 Element mapping images of COF-S-F



Fig. S2 TEM images of COF-S-F at (a) low magnification and (b) high magnification



Fig. S3 XRD pattern of COF-S-F



Fig. S4 High-resolution XPS spectra of COF-S-F for (a) S 2p, (b) C 1s and (c) N 1s



Fig. S5 linear polarization curve of Zn@PVDF symmetric cell



Fig. S6 SEM images of bare Zn (a-c) and Zn@COF-S-F (d-f) after 3-day-immersion in 2 M ZnSO<sub>4</sub> electrolyte



Fig. S7 The geometric model of the multi-physical simulation



Fig. S8 CV curves of bare Zn|Ti and Zn@COF-S-F|Ti cells



**Fig. S9 (a-c)** Galvanostatic charge/discharge cycling voltage profiles of bare Zn and Zn@COF-S-F symmetric cells at current density of 0.3 mA cm<sup>-2</sup>



Fig. S10 Capacity voltage curves for bare Zn and Zn@COF-S-F symmetric cells at current density of  $1.5 \text{ mA cm}^{-2}$ 



Fig. S11 Rate performance of bare Zn, Zn@COF-S-F and Zn@PVDF symmetrical cells



Fig. S12 Chronoamperometry profiles of Zn@PVDF symmetric cells at the overpotential of -200 mV



Fig. S13 Nucleation overpotentials of Zn@PVDF|Cu asymmetric cell



Fig. S14 SEM images of (a, b) bare Zn and (c, d) Zn@COF-S-F after 500 h of cycling



Fig. S15 XRD patterns of bare Zn and Zn@COF-S-F after 500 h of cycling



Fig. S16 (a) SEM image and (b) XRD pattern of MnO<sub>2</sub> cathode material



**Fig. S17** Charge/discharge profiles of  $Zn|MnO_2$  full cells with (**a**) bare Zn and (**b**) Zn@COF-S-F anodes at stepped current density ranging from 0.1 to 4.0 A g<sup>-1</sup>



**Fig. S18** Charge/discharge profiles of  $Zn|MnO_2$  full cells with (**a**) bare Zn and (**b**) Zn@COF-S-F anode at current density of 0.3 A  $g^{-1}$  at different cycles



Fig. S19 Charge/discharge profiles of the rest test at  $100^{\text{th}}$  cycle at current density of 0.5 A g<sup>-1</sup>



Fig. S20 Cross-sectional SEM images of the bare Zn and Zn@COF-S-F after 800 cycles at current density of  $1.2 \text{ A g}^{-1}$ 

Work	Current density	Area specific capacity	Cycling time
	$(mA cm^{-2})$	(mAh cm <sup>-2</sup> )	(hour)
This work	1.5	0.75	1000
Ref.30	0.5	0.25	500
Ref.48	1.0	1.0	350
Ref.18	2.0	2.0	500
Ref.47	0.3	0.15	200
Ref.13	0.5	1.0	700
Ref.44	2.0	1.0	500
Ref.45	0.25	0.25	800
Ref.17	1.0	1.0	890
Ref.29	1.0	0.5	900
Ref.9	1.0	1.0	500
Ref.16	0.1	0.1	350

Table S1 Cycling performance comparison of this work and other previous reports