Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

Bimetallic organic framework nanocages enhance polysulfide trapping and redox kinetics in lithium-sulfur batteries†

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1. Experimental Section

Synthesis of Co-based zeolitic imidazolate framework-67 (ZIF-67). Typically, 292 mg of $Co(NO_3)_2 \cdot 6H_2O$ is added in 10 mL of aqueous solution with 4 mg of cetyltrimethylammonium bromide (CTAB). This solution is quickly injected into 70 mL of aqueous solution with 4.54 g of 2-methylimidazole (2-MIM). The mixture was allowed to stirred at 25 °C for a duration of 40 minutes. The resulting ZIF-67 is obtained by centrifugation, washed multiple times with ethanol, and dried.

Synthesis of hollow tannic acid-Co network (TA-Co). Typically, 60 mg of ZIF-67 is dissolved in 20 mL of ethanol, followed by adding 300 mL of an ethanol/deionized water (DIW) mixture (1:1, v/v) containing 1 mg mL^{-1} of tannic acid (TA). The mixture solution is stirred at room temperature for 15 minutes. The TA-Co is obtained by centrifugation, washed several times with ethanol, along with dried in an oven at 60°C.

Synthesis of hollow tannic acid-Co/Zn network (TA-CoZn). 40 mg of TA-Co is first dispersed into 30 mL of ethanol. Then 20 mL of aqueous solution containing 2.5 mM $Zn(CH_3COO)_2 \cdot 2H_2O$ is added to the above dispersion drop by drop, which is then stirred at 25 °C for 3 h. The product is obtained by centrifugation and washed with ethanol several times, then dried in an oven at 60 °C.

Synthesis of CoZn-based bimetal-organic framework (CoZn-HTP). The as-prepared TA-CoZn of 20 mg is dispersed into 20mL of DMF via ultrasonication for 15 min. Subsequently, 5 mL of 2 M sodium acetate solution and 5 mL of an aqueous solution with 12 mg of HTP ligands are added sequentially. The mixture is heated at 65°C for 2 hours, then cooled to room temperature while stirring. The CoZn-HTP is obtained by centrifugation, washed with ethanol for several times, and freeze-dried overnight.

Synthesis of Co-based metal-organic framework (Co-HTP). The Co-HTP is synthesized similarly to CoZn-HTP, using TA-Co as the precursor instead of TA-CoZn.

Preparation of CoZn-HTP@S and Co-HTP@S composites. CoZn-HTP@S and Co-HTP@S composites are fabricated using a melt-diffusion method. In details, the sulfur powder is uniformly grinded with CoZn-HTP or Co-HTP at a 3:1 mass ratio and placed into a Teflon-lined autoclave, following by heated at 155 °C for 24 h to obtain CoZn-HTP@S and Co-HTP@S cathode materials.

Li-S battery assembly and electrochemical measurements. The electrodes are producted by mixing the sulfur host (CoZn-HTP@S or Co-HTP@S), poly (vinylidene fluoride) binder (PVDF) as well as Super P with a quality ratio of 8:1:1 in the proper N-methylpyrrolidone (NMP). The slurry is deposited onto carbon paper with a diameter of 12 mm and subsequently dried at a temperature of 70 °C for a duration of 12 hours. The CR2032 coin cells are assembled in an argon-filled glove box, using the prepared electrodes as cathodes, a Celgard membrane as the separator, 12 mm lithium metal as the anode, and 1.0 M LiTFSI in a 1:1 (v/v) DME/DOL electrolyte with 2 wt% $LiNO_3$. The GCD measurements are performed on a LAND CT2001A test system within a voltage range of 1.6-2.8 V. The EIS is performed using a CHI760 electrochemical workstation, applying a 5.0 mV amplitude over a frequency spectrum ranging from 0.01 to 10^5 Hz. The CV tests are recorded over a voltage window of 1.6-2.8 V with the scan rates of 0.1-0.5 mV s^{-1} using a CHI660E electrochemical workstation. All measurements are carried out at 25°C.

Material characterizations. TEM (FEI Talos F200X G2, AEMC) and SEM (JEOL-JSM7500F) are employed to characterize the morphology and structure of CoZn-HTP and Co-HTP. The composition of CoZn-HTP is investigated using EDX spectroscopy. The XRD patterns of the as-prepared samples are obtained by a powder X-ray diffractometer (D-MAX 2500/PC, Cu Kα, λ = 1.5406 Å). Raman spectra (Renishaw inVia) employed to investigate the molecular structures of CoZn-HTP and Co-HTP. The FTIR spectra are obtained using a PerkinElmer FTIR spectrometer. TGA is carried out on a Shimadzu DRG-60 thermal analyzer under N_2 flow. N_2 adsorption-desorption isotherms are determined by Micromeritics ASAP 2460 analyzer at 77 K. The XPS (Thermo Scientific ESCALAB 250Xi) is performed to assess the chemical states and valence band spectra. UV-Vis spectroscopy (Shimadzu UV 2450 Spectrometer) is employed to analyze the adsorption degree of Li_2S_6 on the CoZn-HTP and Co-HTP.

Adsorption measurements of Li_2S_6. To obtain the 2 mM Li_2S_6 solution, S and Li_2S are dissolved in a 1:1 (v/v) mixture of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) with a molar ratio of 5:1 and stirred at 65°C for 24 hours. Equal masses of CoZn-HTP and Co-HTP are added to the prepared Li_2S_6 solution. The resulting supernatant and precipitate are analyzed by UV-Vis spectroscopy as well as X-ray photoelectron spectroscopy.

Symmetric cell measurements. Symmetric cells are assembled using the prepared electrodes as both cathode and anode. The anode electrolyte consisted of conventional Li-S battery electrolyte, while the cathode electrolyte is a 2 mM Li_2S_6 solution. The CV tests are performed on a CHI660E electrochemical workstation with a voltage range of -1.0 to 1.0 V and a sweep rate of 10 mV s^{-1}.

Li_2S nucleation and dissolution tests. Li_2S nucleation and dissolution experiments are used conventional 1 M LiTFSI electrolyte as anolyte and 2 mM Li_2S_8 electrolyte as catholyte. For the Li_2S nucleation experiments, the prepared batteries are galvanostatically discharged to 2.06 V at 0.112 mA, followed by potentiostatically discharged at 2.05 V until the current decreased to 10^{-5} A. For the Li_2S dissolution experiments, the prepared batteries are galvanostatically discharged to 1.7 V at 0.112 mA, and then potentiostatically charged at 2.4 V until the current dropped below 10^{-5} A.

2. Supplementary Figures

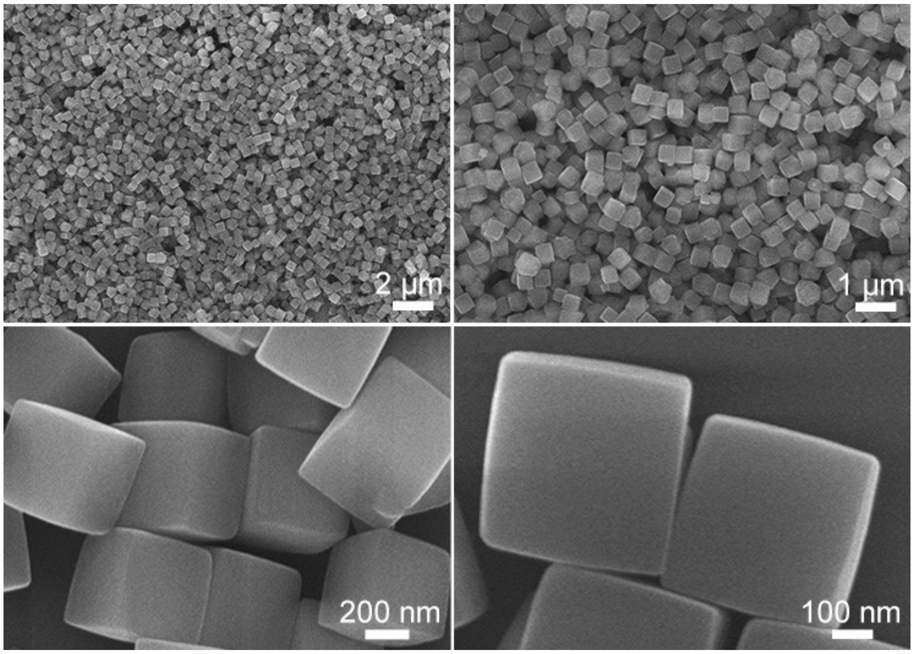

Figure S1. SEM images of ZIF-67 at different magnifications.

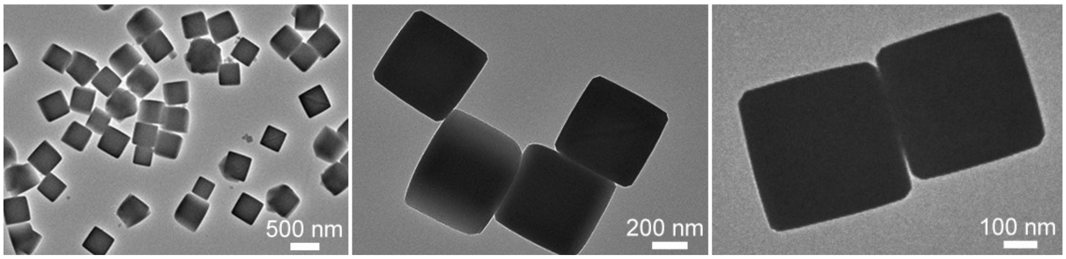

Figure S2. TEM images of ZIF-67 at different magnifications.

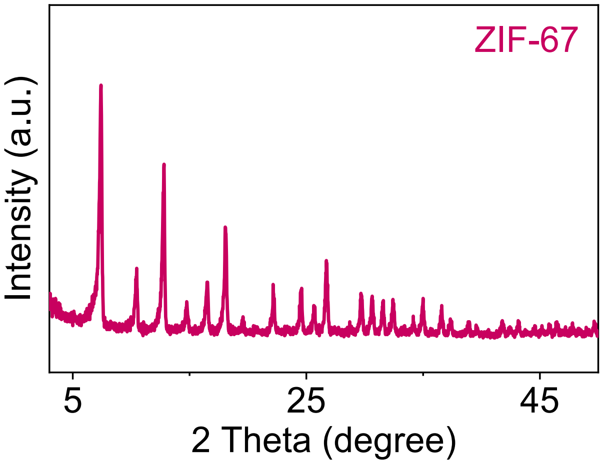

Figure S3. XRD pattern of ZIF-67.

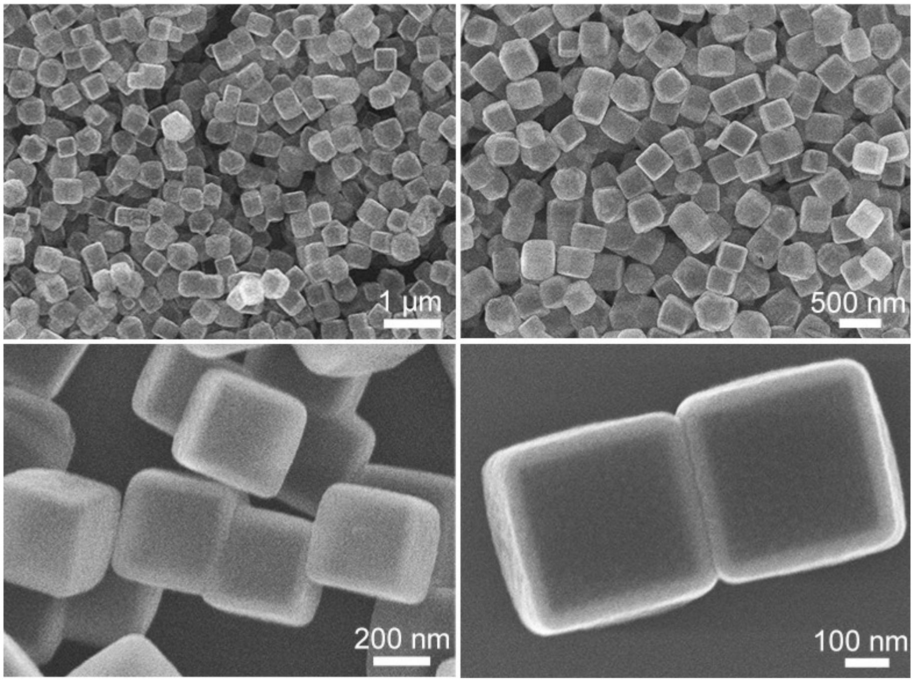

Figure S4. SEM images of TA-Co at different magnifications.

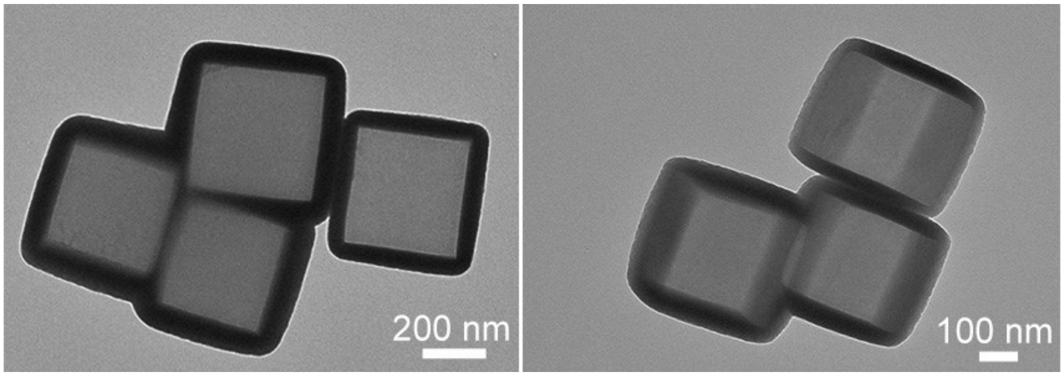

Figure S5. TEM images of TA-Co at different magnifications.

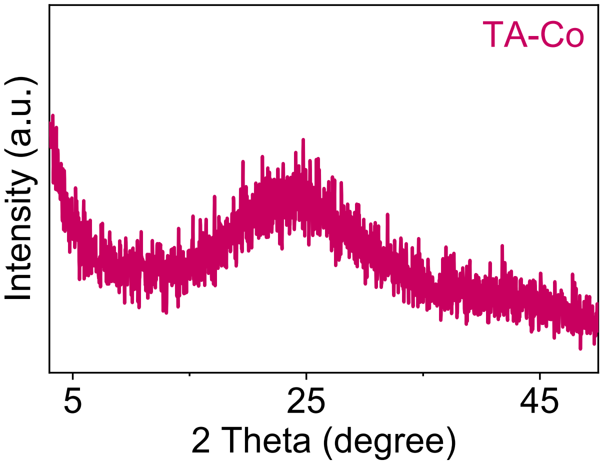

Figure S6. XRD pattern of TA-Co.

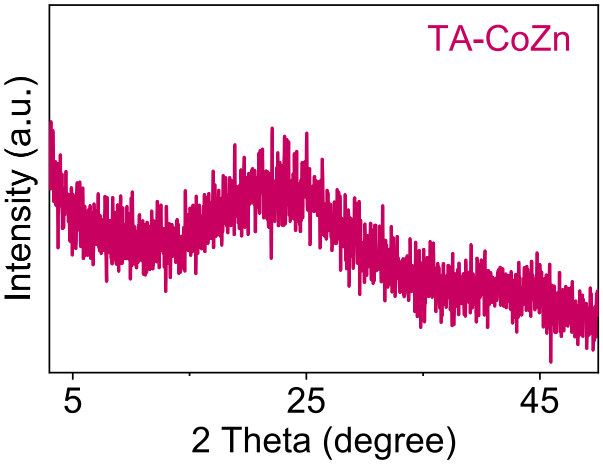

Figure S7. XRD pattern of TA-CoZn.

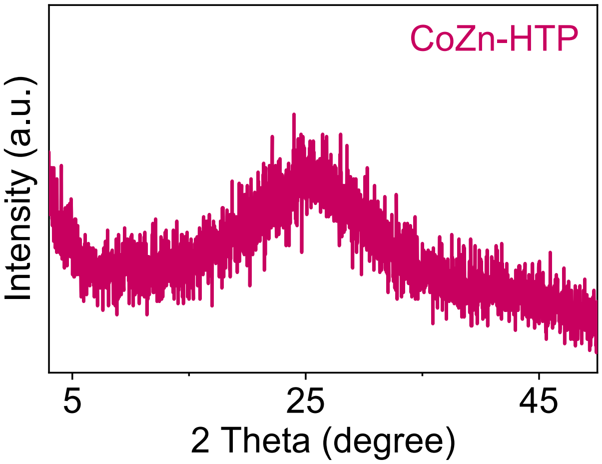

Figure S8. XRD pattern of CoZn-HTP.

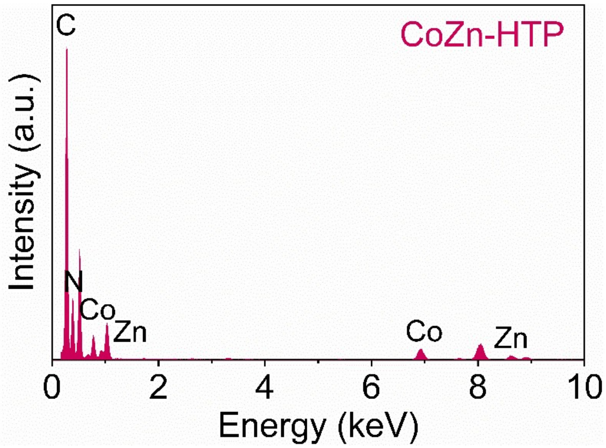

Figure S9. EDX spectrum of CoZn-HTP.

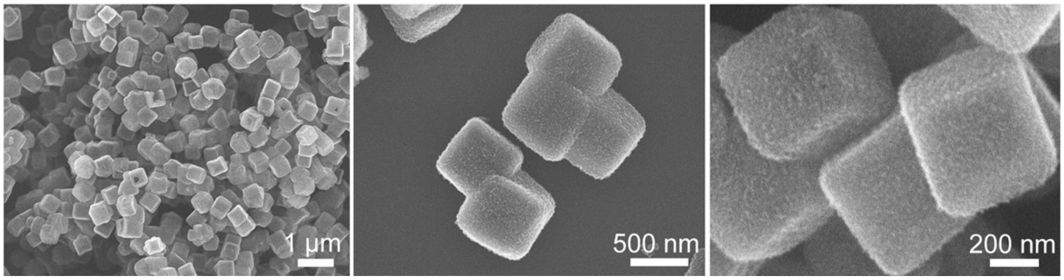

Figure S10. SEM images of Co-HTP at different magnifications.

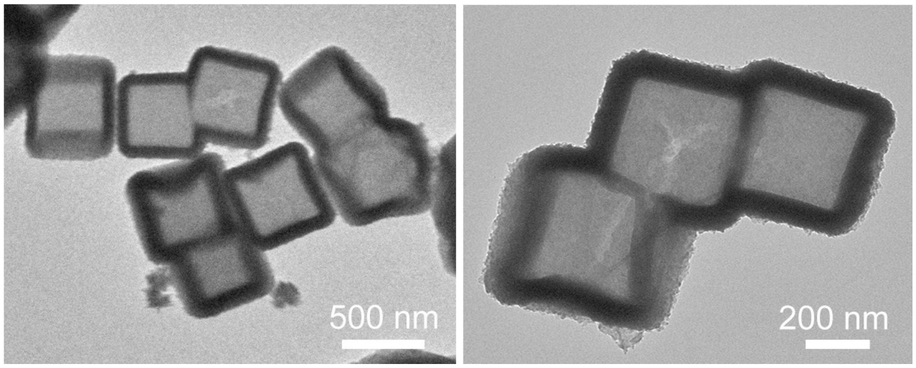

Figure S11. TEM images of Co-HTP at different magnifications.

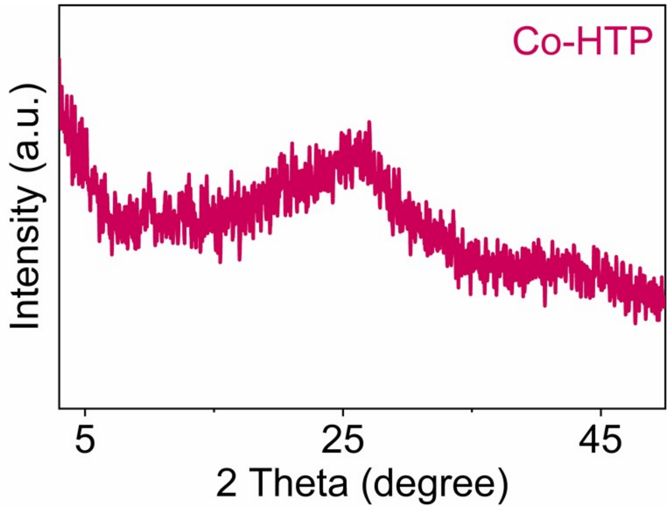

Figure S12. XRD pattern of Co-HTP.

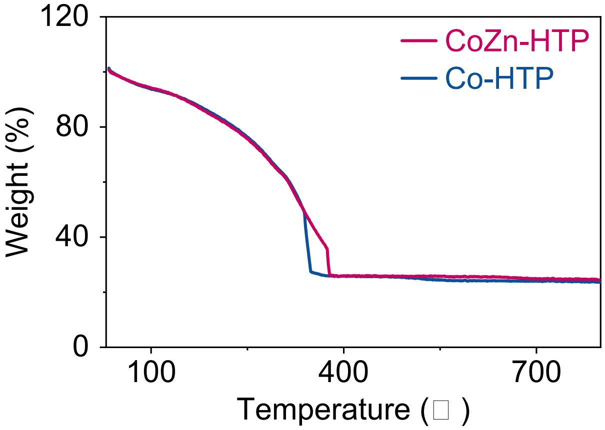

Figure S13. TGA curves of CoZn-HTP and Co-HTP in air atmosphere.

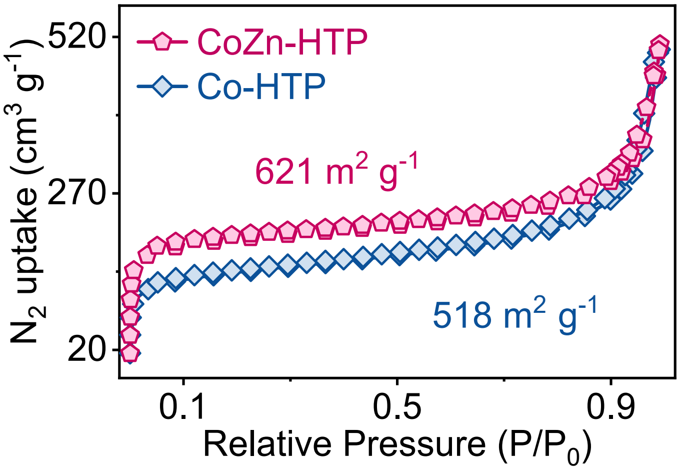

Figure S14. N_2 sorption isotherms for CoZn-HTP and Co-HTP at 77 K.

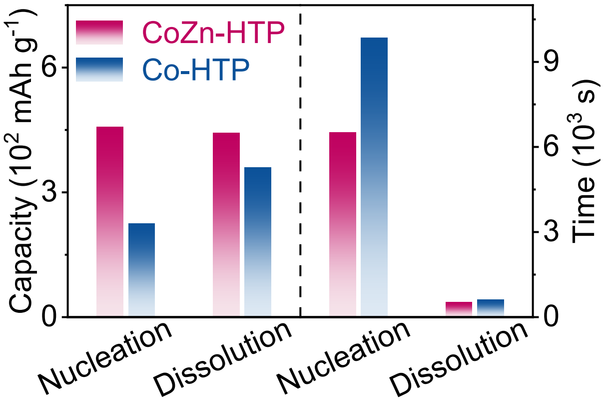

Figure S15. The comparison of Li_2S nucleation/dissolution capacity and time with different catalysts.

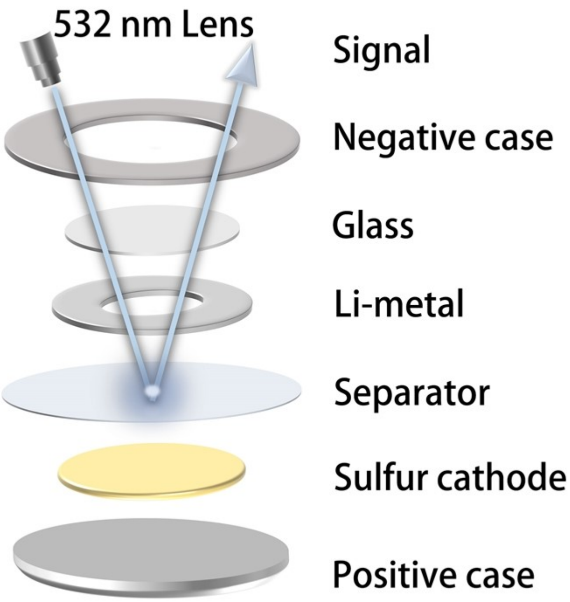

Figure S16. Schematic of the in-situ Raman testing of Li-S batteries.

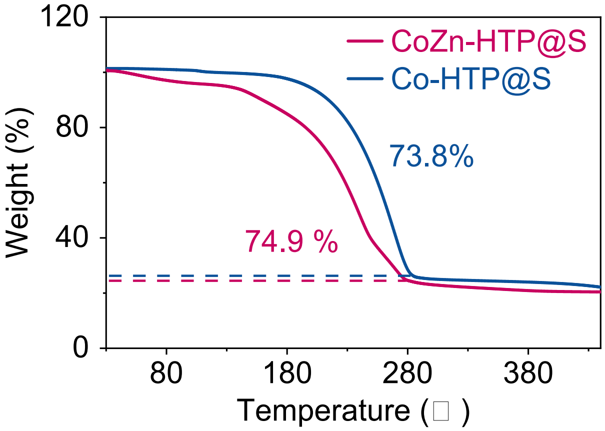

Figure S17. TGA curves of CoZn-HTP@S and Co-HTP@S.

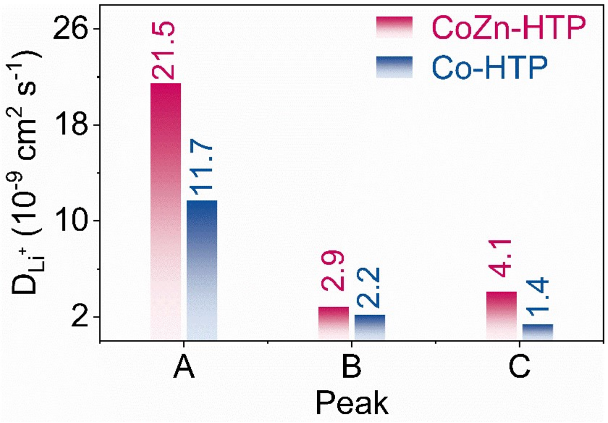

Figure S18. Li^+ diffusion coefficient of CoZn-HTP and Co-HTP electrodes.

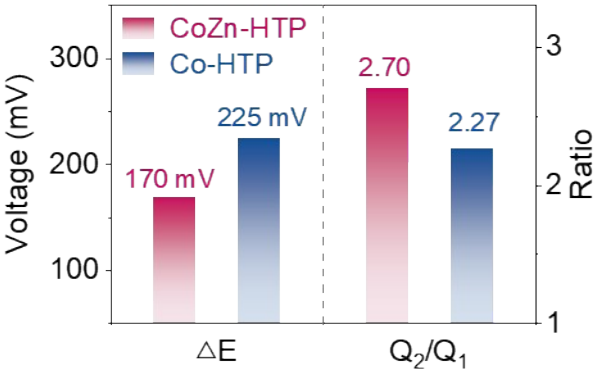

Figure S19. ΔE values and Q_2/Q_1 values of CoZn-HTP and Co-HTP electrodes.

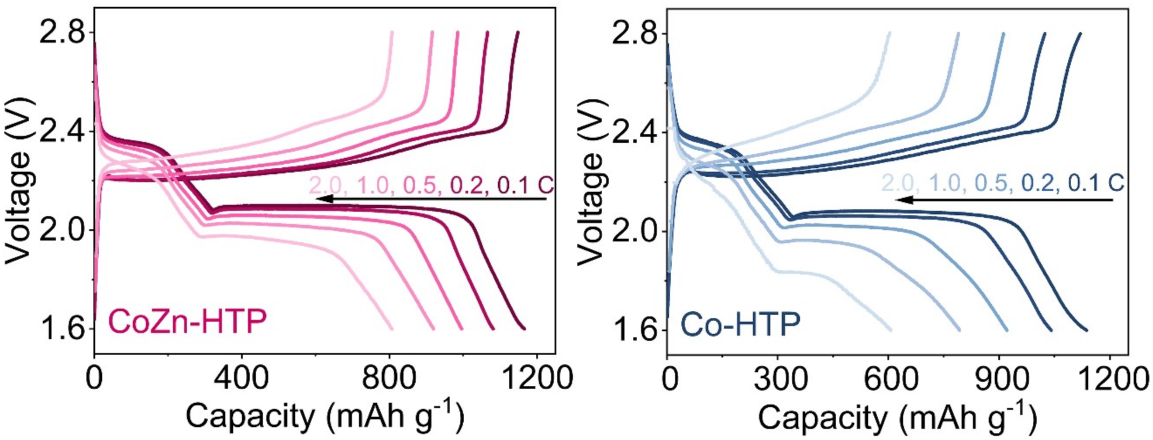

Figure S20. Voltage curves of the CoZn-HTP and Co-HTP electrodes at the current densities from 0.1 to 2.0 C.

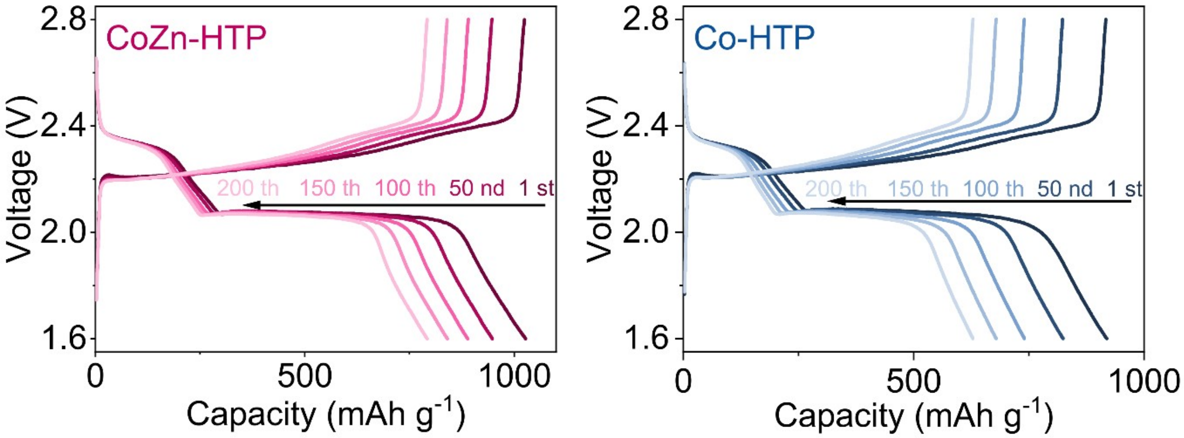

Figure S21. Cycle performance of the CoZn-HTP and Co-HTP electrodes at 0.5 C.

3. Supplementary Table

Table S1. Fitted impendence parameters of CoZn-HTP and Co-HTP electrodes.

Sample	*Rs* (Ω)	*Rct* (Ω)	W_0 (Ω)
CoZn-HTP	5.219	19.37	15.61
Co-HTP	7.946	27.26	16.04

Table S2. Comparison of electrochemical performance of CoZn-HTP@S with recently reported advanced electrocatalysts.

Catalysts	**Cycling stability**		**Capability stability**			***Ref.***
	Cycle number	**Fading rate**	**Capacity (mAh g^{-1})**			
			0.1 /0.2 /0.5 C	**1.0 C**	**2.0 C**	
Co-HTP/CG@S	500 (1 C)	0.0522%	1137 (0.1 C)	870	730	[1]
ZnCo-MOF@S	300 (1 C)	0.023%	1076 (0.1 C)	676	552	[2]
S@MOF-808	300 (1 C)	0.103%	1000 (0.1 C)	500	192	[3]
ZIF-67-600/N@S	1000 (2 C)	0.025%	1136 (0.1 C)	895	826	[4]
MOF-74-Ni-CNT/S	400 (2 C)	0.087%	878 (0.2 C)	733	667	[5]
S/TiO$_2$@MOF	500 (1 C)	0.133%	1000 (0.1 C)	650	600	[6]
S/ZIF-7	500 (1 C)	0.053%	880 (0.2 C)	600	550	[7]
S/3DOM ZIF-8	500 (2 C)	0.028%	1030 (0.2 C)	800	740	[8]
CNT@UIO66-S	900 (2 C)	0.022%	936 (0.5 C)	685	545	[9]
S@MOF-525(2H)	200 (1 C)	0.021%	950 (0.5 C)	520	410	[10]
Al/Cu-MOF-5-S	200 (0.1 C)	0.25%	974.2 (0.1 C)	400		[11]
CoZn-HTP@S	1000 (2 C)	0.019%	1184.9 (0.1 C)	916.2	826.1	*This work*

Notes and References

[1] Q. Lv, Y. Sun, B. Li, C. Li, Q. Zhang and L. Wang, *Adv. Energy Mater.*, 2024, 2403223. DOI: 10.1002/aenm.202403223

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