

## Supporting Information

### **Inspired by “tip effect”: a novel structure design strategy of the cathode in advanced lithium-sulfur batteries**

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# 1. Experimental Section

## *1.1 Materials synthesis*

Synthesis of hollow cupric oxide spheres (HCOS): 2.416 g of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  was dissolved in pure ethanol solvent. Then 70 mL ammonia solution (28%) was added to the above solution. The solution became clear and dark blue. After that, 5 mL of 1.0 M NaOH solution was added drop-by-drop; the solution was still kept clear. Afterwards 5 g of  $\text{NaNO}_3$  was added. The mixture was then transferred to a hermetic container and kept inside an oil bath at  $100^\circ\text{C}$  with constant stirring for 48 h. The products were washed several times with DI water and pure ethanol and collected by centrifugation. The washed precipitates were dried in an electric oven at  $50^\circ\text{C}$  overnight.

Synthesis of the HCOS-S and Graphene-S (GP-S) composites: HCOS-S composites were prepared via a well-established melt-diffusion method. Commercial sulfur (Alfa Aesar, >99.5%, 100 mesh) was used as received. The sulfur and hollow CuO microspheres with weight ratio of 4:1 were ground together in the agate mortar, and the mixture was first heated at  $155^\circ\text{C}$  for 12 h in an oven. Then, the product was heated at  $200^\circ\text{C}$  for 2 h under Ar protection in the tube furnace to remove redundant sulfur to prepare HCOS-S composites. As a comparison, GP-S composites were prepared by the same method as HCOS-S. Commercialized graphene was obtained from Ningbo Morsh Technology Co. Ltd.

## *1.2 Materials characterization*

The crystal structure of the samples was determined by X-ray powder diffraction (XRD, Rigaku Ultima IV, Cu K $\alpha$  radiation, 40 kV, 40 mA). Diffraction patterns were taken at room temperature in the range from 10° to 80° at intervals of 0.02°. Thermalgravimetric analysis (TGA) was measured with a thermo gravimetric analyzer in nitrogen from room temperature to 450 °C under a heating rate of 10 °C min<sup>-1</sup>. The morphologies were obtained using scanning electron microscopy (SEM, Quanta FEG 250) and transmission electron microscopy (TEM, JEOL JEM-2100 F). Samples for transmission electron microscopy (TEM) were prepared by dispersing the materials in alcohol by ultrasonic treatment for several minutes before observation. The surface area and pore structure were characterized by nitrogen sorption using a Micrometrics ASAP 2020 physisorption analyzer. The surface area was calculated by the Brunauer–Emmett–Teller (BET) method. The pore size distributions (Dp) were derived from the adsorption branches of isotherms using the Barrett–Joyner–Halenda (BJH) model. X-ray photoelectron spectroscopy (XPS) was carried out on Physical Electronics 5400 ESCA. All spectra were fitted with Gaussian–Lorentzian functions and a Shirley-type background using CasaXPS software. The binding energy values were all calibrated using the C 1s peak at 284.8 eV. It is worth noting that only the peaks located at a lower binding energy of the Cu 2p<sub>3/2</sub>/2p<sub>1/2</sub> and S 2p<sub>3/2</sub>/2p<sub>1/2</sub> spin-orbit

doublet were discussed here. S 2p peaks were fit using two equal full-width half maximum S 2p doublets with 2:1 area ratios and splittings of 1.2 eV.

Visualized adsorption test and XPS sample preparation:  $\text{Li}_2\text{S}_4$  solution was prepared by adding  $\text{Li}_2\text{S}$  and sulfur at a molar ratio of 1:3 in the DME/DOL (1:1, by volume) followed by vigorous magnetic stirring. Solutions with  $\text{Li}_2\text{S}_4$  concentration of  $10 \text{ mmol L}^{-1}$  were used for adsorption test. HCOS and commercial graphene with same surface area ( $0.3 \text{ m}^2$ ) were added to 3.0 mL of  $\text{Li}_2\text{S}_4$  solutions separately, and the mixtures were vigorously stirred to realize thorough adsorption. 3.0 mL untreated  $\text{Li}_2\text{S}_4$  solution was used as a comparison. Afterwards, the suspensions were centrifuged and the solids for XPS analysis were obtained after drying in a vacuum for 5 h. All procedures were completed in an Ar-filled glovebox.

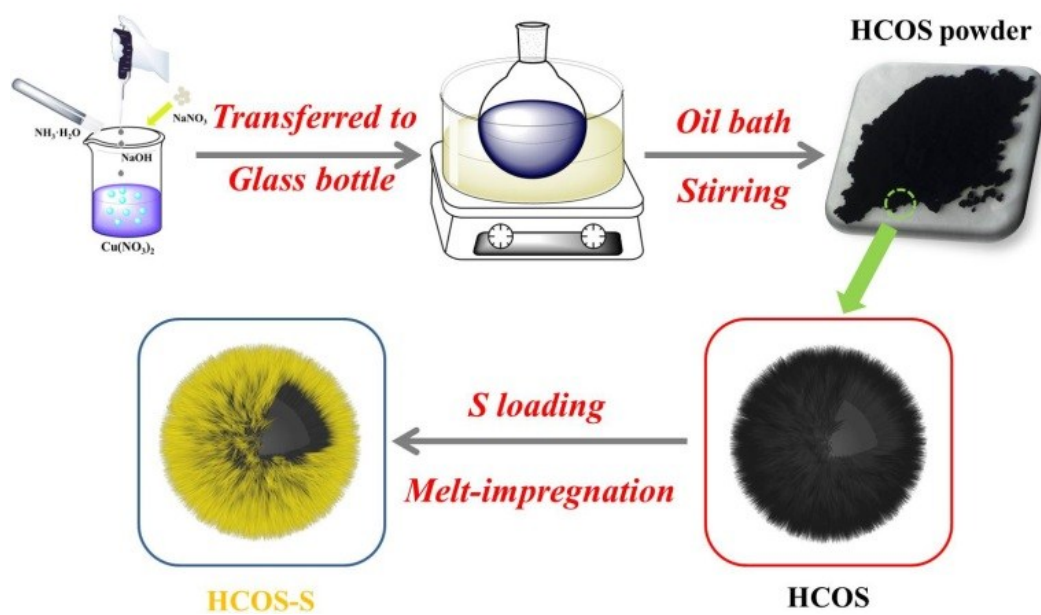
Preparation of cycled electrode samples for SEM imaging: Cycled electrodes were retrieved at a discharged status by disassembling the cells in the glovebox. Dried electrodes were then transferred to the SEM chamber under an Ar atmosphere for imaging.

### *1.3 Electrochemical measurements*

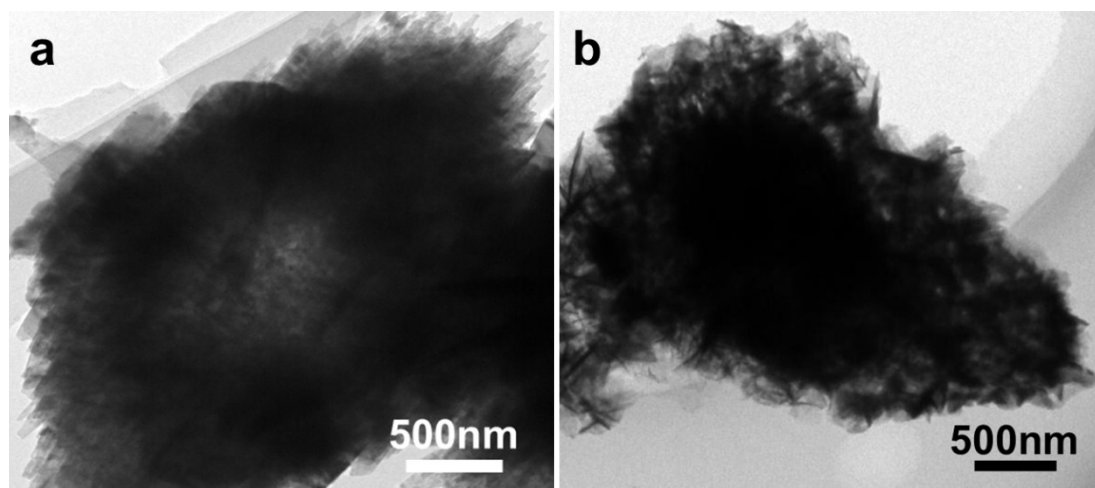
The as-prepared samples were mixed with Super P and PVDF binder in a ratio of 7:2:1. The mixture was slurried onto aluminum foil. The electrode was dried for 12 h in a vacuum at  $60 \text{ }^\circ\text{C}$ . The average sulfur loading in the 12 mm circular disks is  $\sim 3.5 \text{ mg cm}^{-2}$ . CR-2025 type coin cells were assembled in a glove box filled with argon. The lithium metal

was employed as anode and the electrolyte was 1.0 mol L<sup>-1</sup> LiTFSI/DOL + DME (1:1 by volume) with 1 wt% LiNO<sub>3</sub> additives. 60 μL electrolyte was added to each coin cell. Galvanostatically curves and cycle performance data for the cells were collected by a battery test system (LAND CT2001A) between 1.8 and 2.8 V vs. Li<sup>+</sup>/Li. Electrochemical impedance spectroscopy (EIS) was measured by a PARSTAT 2273 at a frequency range from 100 kHz to 100 mHz with an AC voltage amplitude of 5 mV. Cyclic voltammetry (CV) experiments were conducted at a scan rate of 0.1 mV s<sup>-1</sup> between 1.8 and 2.8 V vs. Li<sup>+</sup>/Li on a CHI660D (Shanghai Chenhua Instrument).

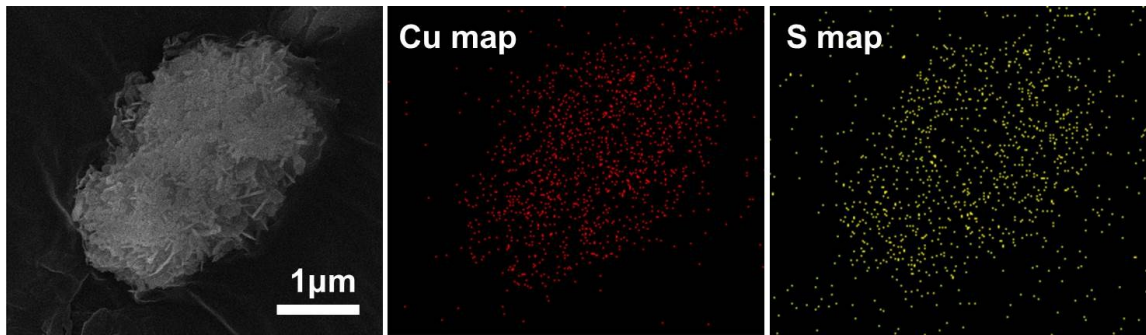
## 2. Supporting Figures



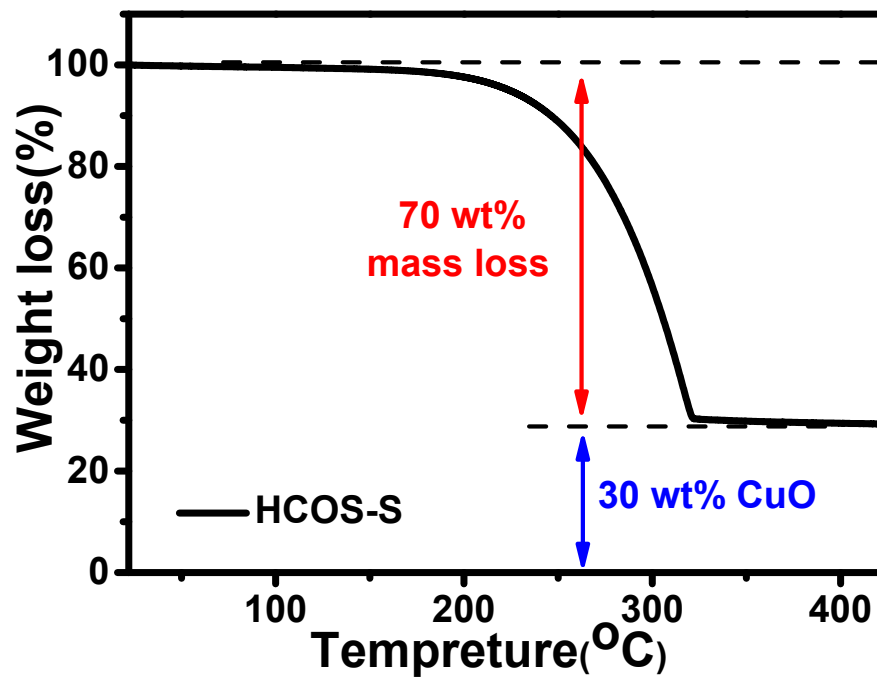
**Fig. S1** Schematic illustration of the fabrication of HCOS and HCOS-S composite.



**Fig. S2** TEM images of (a) the HCOS host and (b) the HCOS-S composite.



**Fig. S3** The elemental mapping of HOCS-S composite before cycling.



**Fig. S4** TGA curves of HCOS-S composite.

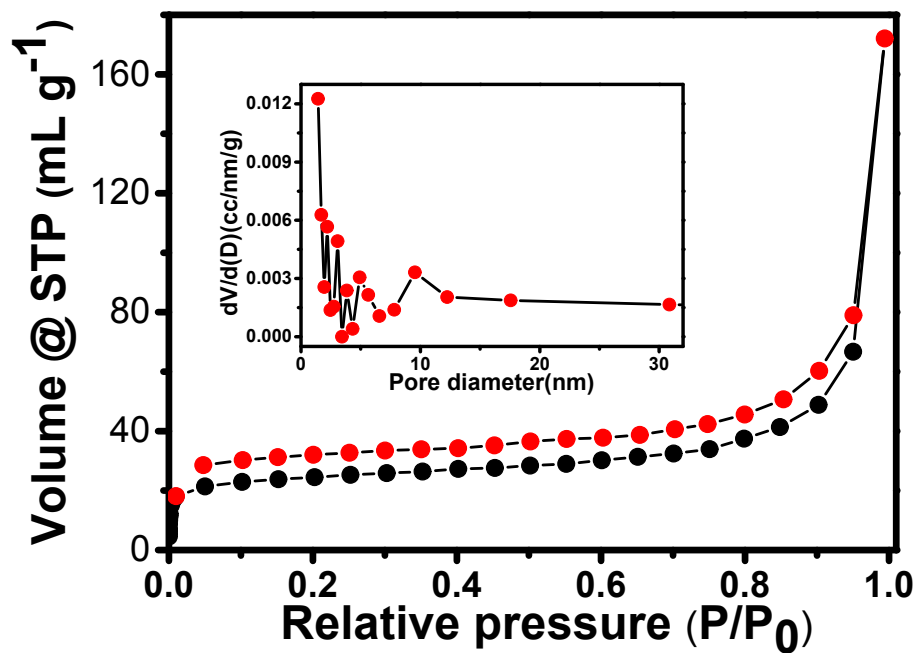
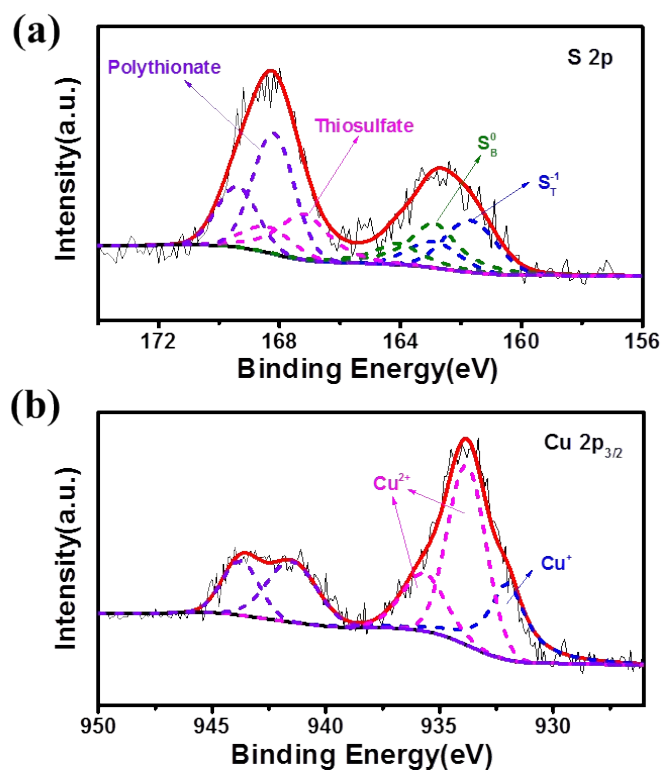


Fig. S5  $N_2$ -sorption isotherms and pore-size distribution of the HCOS.

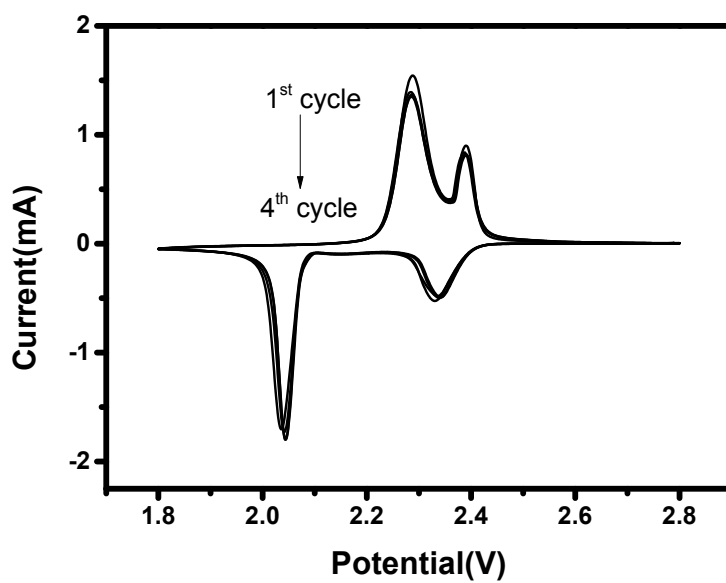


Fig. S6 Photograph of the polysulfide solutions after adsorption.

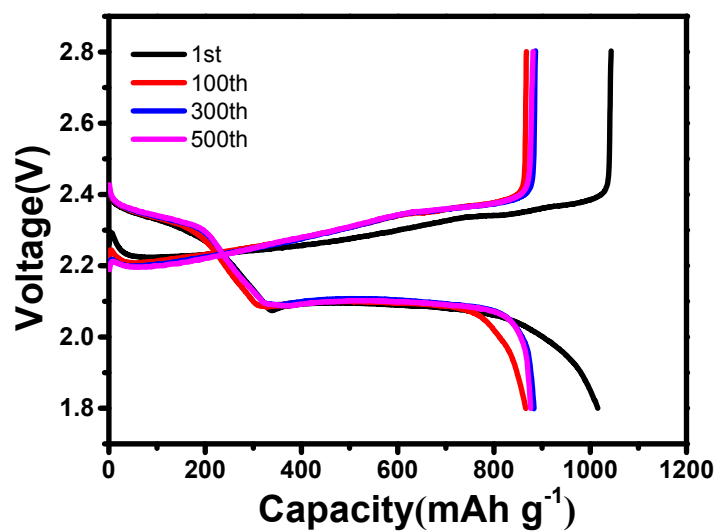




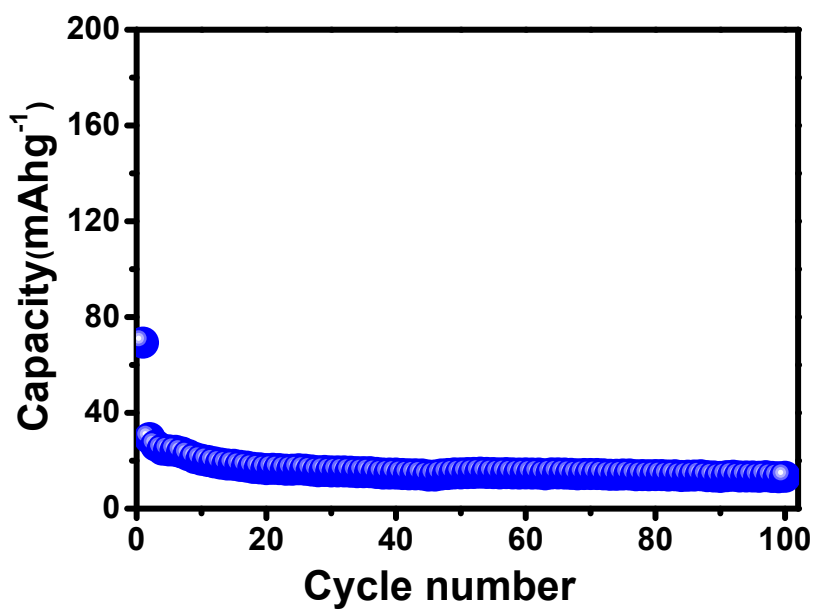
**Fig. S7** High-resolution XPS (a) S 2p and (b) Cu 2p of  $Li_2S_4/CuO$ .



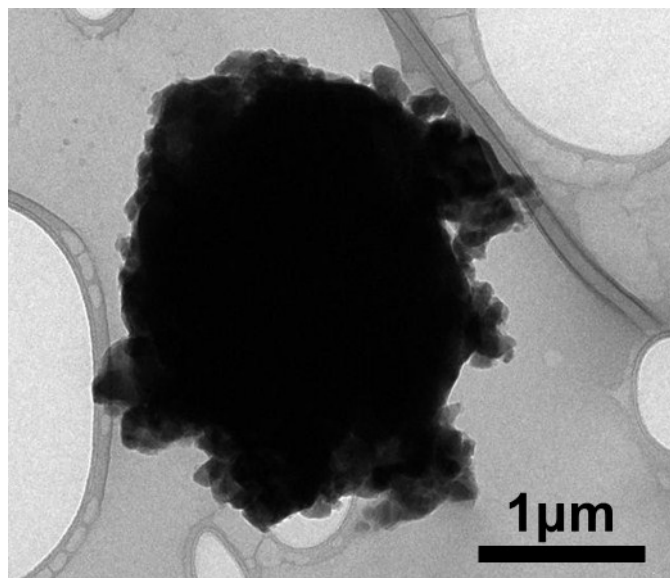
**Fig. S8** The cyclic voltammetry (CV) curves of HCOS-S cathode.



**Fig. S9** Discharge/charge profiles of HCOS-S cathode at 1C during 500 cycles.



**Fig. S10** Cycling performance at the current rate of 1 C for the HCOS-S electrode without sulfur.



**Fig. S11** TEM image of the cycled HCOS-S electrode.

**Table S1** The performance comparison of this work with some similar composite cathodes.

Host material	S content	Areal mass loading of S (mg cm <sup>-2</sup> )	Initial Cap. (mAh g <sup>-1</sup> )	Areal cap. (mAh cm <sup>-2</sup> )	Capacity loss per cycle		Ref.
					Cycles	Loss (%)	
HCOS	70%	3.5	1015 at 1C	3.6	500	0.02	This work
TiO@C-HS	70%	4	886 at 0.05C	3.5	50	0.15	[1]
MnO <sub>2</sub>	75.5%	1.7-2.1	1240 at 0.2C	1.9-2.3	200	0.05	[2]
Co <sub>9</sub> S <sub>8</sub>	75%	4.5	890 at 0.5C	4.0	1500	0.045	[3]
CoS <sub>2</sub> /G	75%	2.9	1003 at 2C	2.9	2000	0.034	[4]
TiC@G	61%	3.5	1032 at 0.2C	3.6	100	0.35	[5]
Ti <sub>4</sub> O <sub>7</sub>	70%	0.9	850 at 2C	0.77	500	0.06	[6]
MnO <sub>2</sub> @HCF	71%	3.5	890 at 0.5C	3.1	300	0.08	[7]

## References:

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