Supporting Information

Design of sulfur host with $CuCo_2O_4$ supported on carbon cloth for lithium sulfur batteries

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Experimental Section

Synthesis of Co_3O_4/CC and $CuCo_2O_4$/CC: The carbon cloth (CC, Hesen) was first cut into a 2.8 cm square and dealt with an aqueous solution of nitric acid to remove the surface impurities. The obtained CC was washed three times with ethanol and deionized water for 20 minutes, followed by drying in an oven at 60 °C for 12 h. Then the ZIF-67 cubes were synthesized by a simple process. 0.004 g cetyltrimethylammonium bromide (CTAB, 99%, Aladdin) and 0.291 g cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 99%, Aladdin) were dissolved in 10 mL deionized water to form a uniform ZIF-67 precursor solution. And the precursor was poured into 70 mL aqueous solution containing 4.54 g 2-methylimidazole (2-MeIm, 98%, Aladdin) under magnetic stirring. After the solution turned purple, the pre-treated CC was added into the solution and aged for 48 h. The final ZIF-67 cubes supported on CC (ZIF-67/CC) was synthesized by washing with ethanol and deionized water for several times followed by drying at 60 °C for 12 h. In contrast, Cu-based ZIF-67 cubes supported on CC (Cu-ZIF-67/CC) was obtained with 0.121 g copper nitrate trihydrate ($Cu(NO_3)_2 \cdot 3H_2O$, 99%, Aladdin) under the same conditions. To fabricate Co_3O_4/CC and $CuCo_2O_4$/CC, ZIF-67/CC and Cu-ZIF-67/CC were placed in a tube furnace and calcined at 450 °C for 2 h followed by cooling down to room temperature, respectively.

Characterizations: The morphology of the samples was investigated by scanning electron microscopy (SEM, Verios 460L). The X-ray diffraction (XRD) patterns with the SmartLab 9 KW diffractometer were used to study the crystallographic information. The chemical composition was evaluated by X-ray photoelectron spectroscopy (XPS, ESCALAB250Xi).

Visualized lithium polysulfides adsorption measurement: The 8 mM Li_2S_6 electrolyte was made up of the mixture containing sulfur and Li_2S with a molar ratio of 5:1. The same diameter

of discs of the Co_3O_4/CC and $CuCo_2O_4$/CC fabrics were added into glass bottles containing 5 mL Li_2S_6 electrolyte. The supernatant was analyzed by a UV-vis spectrophotometer to determine the adsorption capability of lithium polysulfides.

Symmetric batteries measurement: The symmetric batteries were assembled with the same working electrode and counter electrode with 0.5 M Li_2S_6 electrolyte. The CV curves were tested in the range of -1.5 to 1.5 V with a scan rate of 1 mV s^{-1}.

Linear Sweep Voltammetry (LSV) measurement: The three-electrode setup was consisted of working electrode (Co_3O_4/CC or $CuCo_2O_4$/CC), Ag/AgCl as reference electrode, carbon rod as counter electrode and 0.1 M Li_2S/methanol as electrolyte. The LSV curves were measured on electrochemical workstation in the range of -0.8 to -0.2 V with a scan rate of 10 mV s^{-1}.

Li_2S nucleation measurement: The 0.25 M Li_2S_8 electrolyte was prepared with sulfur and Li_2S (a molar ratio of 7:1) in tetraglyme. Co_3O_4/CC or $CuCo_2O_4$/CC was used as the working electrode with Li_2S_8 electrolyte, while Li foil was employed as the counter electrode without Li_2S_8 electrolyte. The cell was performed a galvanostatically discharge at a current of 0.112 mA until the voltage dropped to 2.06 V, and then maintained a constant potential discharge at 2.05 V.

Electrochemical Measurement: The sulfur loading of S@Co_3O_4/CC or S@$CuCo_2O_4$/CC cathode was calculated by adding the 0.7 M Li_2S_6 catholyte on the cathode. 0.7 M Li_2S_6 catholyte was dissolved into 10 mL electrolyte with 1.12 g sulfur powder and 0.322 g Li_2S. The electrolyte was prepared consisting 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) (v/v=1:1) with the addition of 1.0 wt% $LiNO_3$. Then 30, 40, 50, 60 μL of 0.7 M Li_2S_6 catholyte were added to the cathode, corresponding to the sulfur loading of 3.5, 4.7, 5.9, 7.1 mg cm^{-2}, respectively. Galvanostatically

charge-discharge measurements were measured on the LAND-CT2001A system from 1.7 to 2.8 V. Both CV and EIS were tested on the LK2010 workstation.

Density Functional Theory (DFT) calculations: First-principles density functional theory (DFT) calculations were conducted on the Vienna Ab initio simulation package program (VASP). The Perdew-Burke-Ernzerhof (PBE) functional under the generalized gradient approximation (GGA) were used to described the exchange-correction energies. A energy cut-off was set to be 400 eV and the geometry optimization was convergent until the force less than 0.03 eV $Å^{-1}$. The Li_2S_6 adsorption on Co_3O_4 (311) surface and $CuCo_2O_4$ (311) surface were adopted.

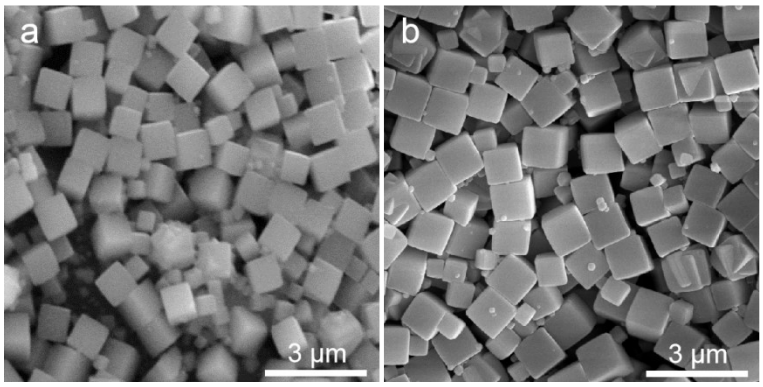

Fig. S1 SEM images of (a) ZIF-67 cubes and (b) Cu-based ZIF-67 cubes.

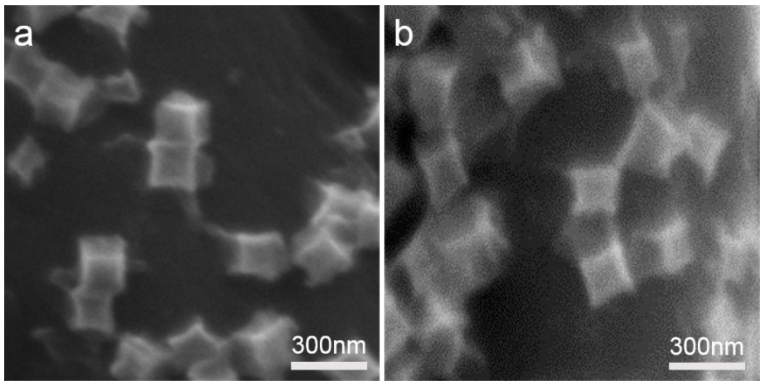

Fig. S2 High-magnification SEM images of (a) Co_3O_4/CC and (b) $CuCo_2O_4$/CC.

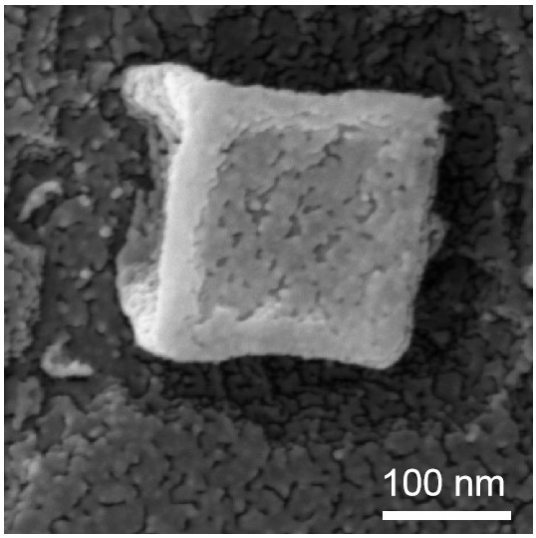

Fig. S3 High-magnification SEM image of $CuCo_2O_4$/CC.

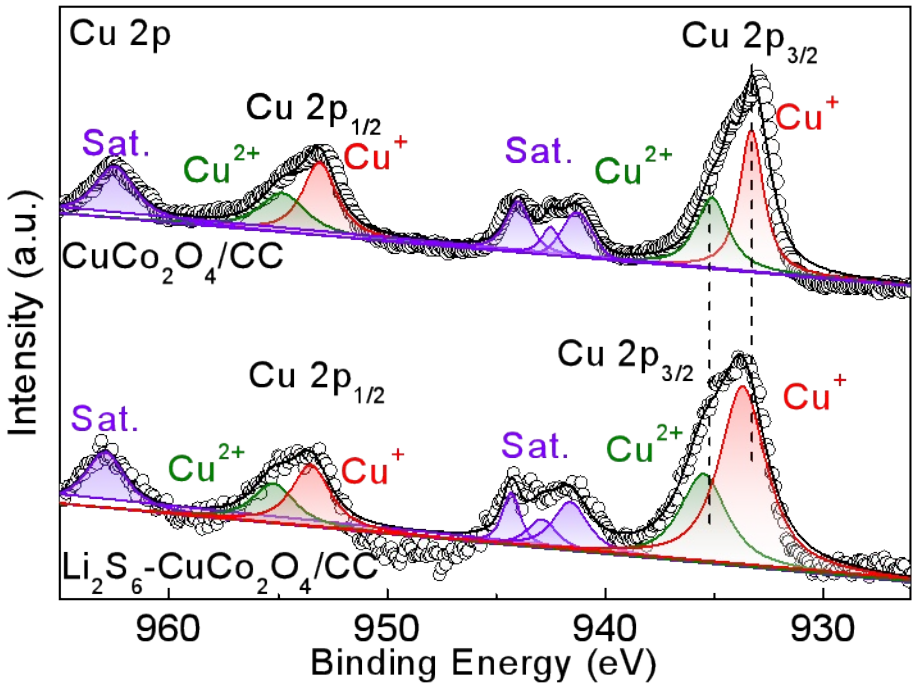

Fig. S4 Cu 2p high-resolution XPS spectra before and after Li_2S_6 adsorption of $CuCo_2O_4$/CC.

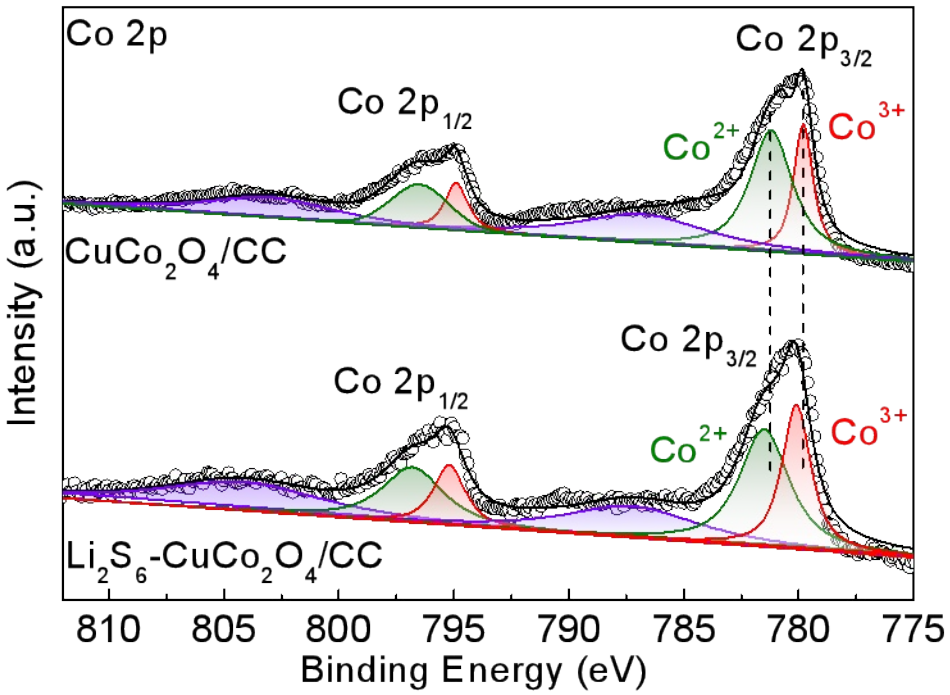

Fig. S5 Co 2p high-resolution XPS spectra before and after Li_2S_6 adsorption of $CuCo_2O_4$/CC.

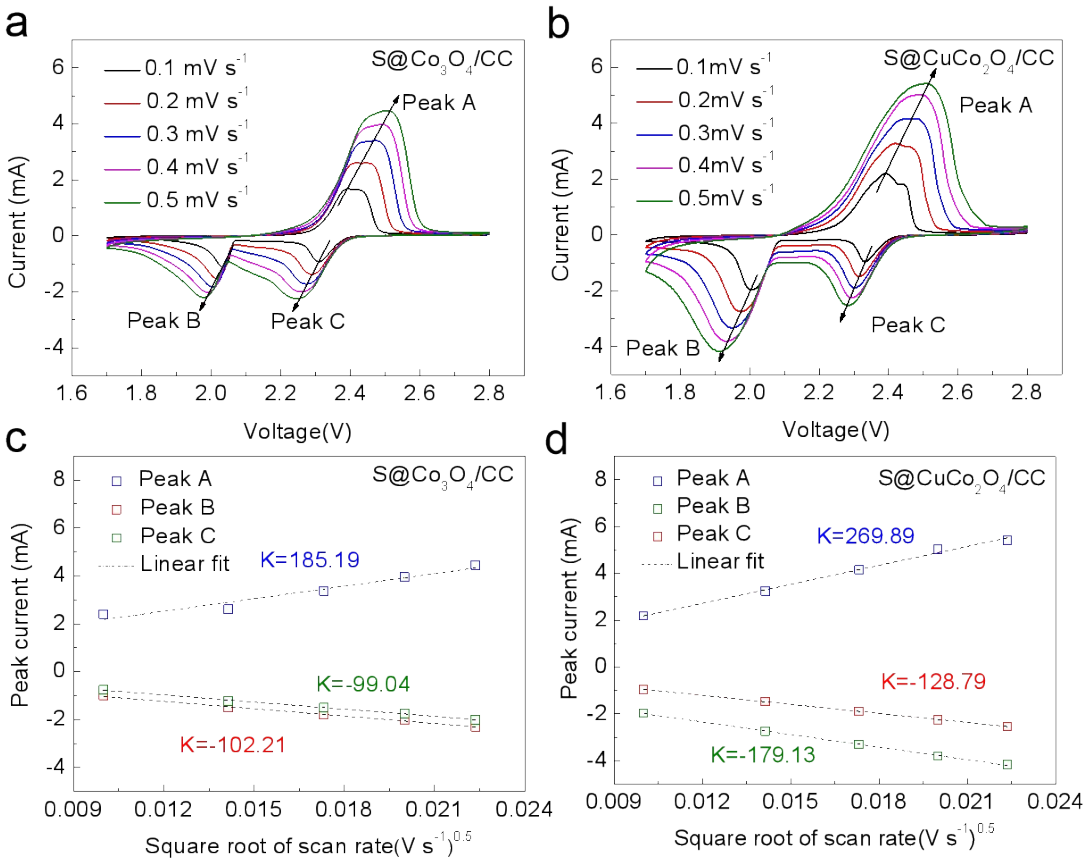

Fig. S6 Lithium-ion diffusion characteristics. CV curves of (a) $S@Co_3O_4/CC$ and (b) $S@CuCo_2O_4/CC$ at different scan rates; (c, d) corresponding plots of the CV peak currents with the square root of scan rates.

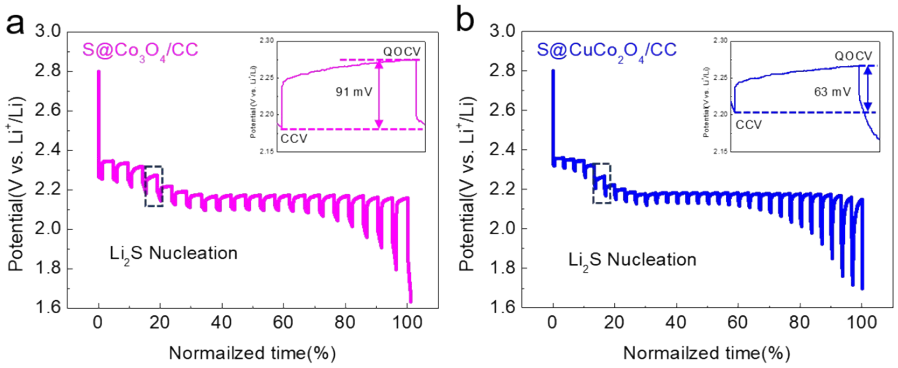

Fig.S7 Galvanostatic intermittent titration technique (GITT) voltage profiles and the corresponding potential difference points of quasi open-circuit voltage (QOCV) and closed-circuit voltage (CCV) at Li_2S nucleation point for the (a) S@Co_3O_4/CC cathode and (b) S@$CuCo_2O_4$/CC cathode.

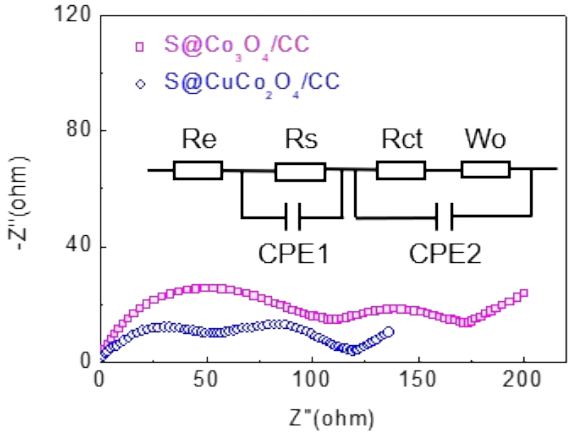

Fig. S8 EIS plots after 50 cycles and the corresponding equivalent circuit model for the lithium sulfur batteries with $S@Co_3O_4/CC$ cathode and $S@CuCo_2O_4/CC$ cathode.

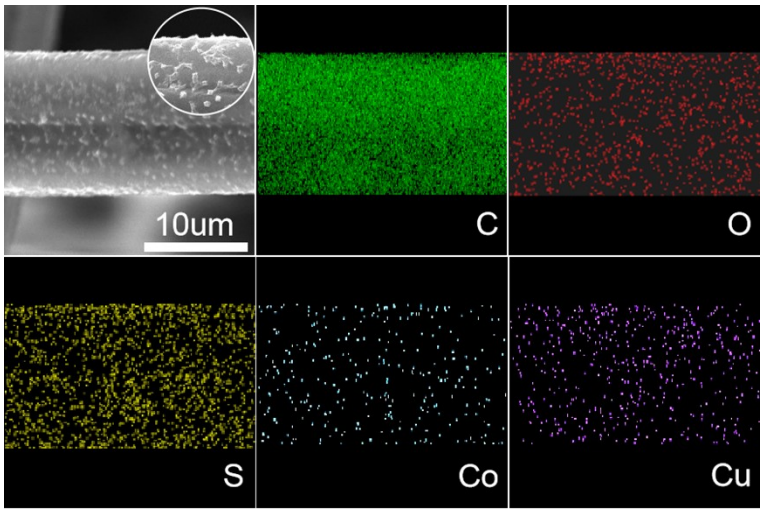

Fig. S9 SEM image and the corresponding element mappings of S@$CuCo_2O_4$/CC cathode after 50 cycles.

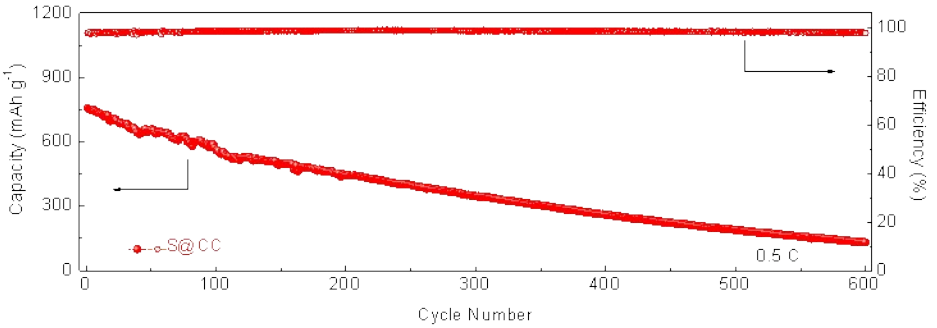

Fig. S10 Long cycling performance at 0.5 C of the lithium sulfur battery with S@CC cathode.

Table S1 The lithium ions diffusion coefficient of different electrodes.

samples	$S@Co_3O_4/CC$	$S@CuCo_2O_4/CC$
Peak A	$3.91*10^{-6}$ cm^2 s^{-1}	$5.71*10^{-6}$ cm^2 s^{-1}
Peak B	$2.16*10^{-6}$ cm^2 s^{-1}	$3.79*10^{-6}$ cm^2 s^{-1}
Peak C	$2.09*10^{-6}$ cm^2 s^{-1}	$2.72*10^{-6}$ cm^2 s^{-1}

Table S2 Electrochemical performance comparison of this work with that of other relevant report in lithium sulfur batteries.

material	S loading (mg cm^{-2})	Cycles & capacity (mAh g^{-1})	Rate (mAh g^{-1})	Ref.
$CuCo_2O_4$/CC	**3.5 mg cm^{-2}**	**0.5 C, 600th, 776**	**3.0 C, 767**	**This**
	7.1 mg cm^{-2}	**0.1 C, 100th, 585**	**0.5 C, 362**	**work**
$Co_xFe_{3-x}O_4$@S	3.5 mg cm^{-2}	0.2 A g^{-1}, 100th, 678	/	[30]
CF/NC@Li_2S_6	5.75 mg	0.2 C, 300th, 609	1.0 C, 658	[31]
S/$NiCo_2O_4$/CC	1.1-1.3 mg cm^{-2}	0.5 C, 400th, 828	2.0 C, 624	[32]