Supplementary Information

Multifunctional separator modified with catalytic multishelled structural CoS_2 enables stable lithium-sulfur battery

Experimental

Synthesis of Co_3O_4 hollow multishelled structures (Co_3O_4 HoMS): All reagents (purchase from Beijing Chemical Co., Ltd.) were analytical grade and used without further purification. Cobalt acetate tetrahydrate ($Co(Ac)_2·4H_2O$) was used as the metal precursor. Using the synthesis of the triple-shelled Co_3O_4 hollow microspheres as an example[1], a typical synthesis process was described as follows. The diameter of 2-3 μm carbonaceous microspheres (CMSs) were synthesized through the emulsion polymerization reaction under hydrothermal conditions. CMSs (0.6 g) were dispersed in 1 M cobalt acetate solution (water/ethanol = 1:3, v/v, 30 mL) with the aid of ultrasonication. After that, the resulting suspension was transferred to 30 °C water bath and stirred for 12 h, then filtered, washed with deionized water for three times, and dried at 80 °C for 12 h. The microspheres after absorbed cobalt ions were heated to 400 °C in air at the rate of 1 °C min^{-1}, and kept at 400 °C for 2 h. Finally, the triple-shelled Co_3O_4 hollow microspheres was prepared. The synthesis processes of single-, and double-shelled Co_3O_4 hollow microspheres are similar to which of the triple-shelled Co_3O_4 hollow microspheres. Single-, and double-shelled Co_3O_4 hollow microspheres were synthesized by changing the solvent ratio (water/ethanol =1:0 and 1:1, respectively) and using the same thermal procedure described above.

Synthesis of CoS_2 hollow multishelled structures (CoS_2 HoMS): CoS_2 HoMS were prepared via an atom-exchange process. The as-prepared Co_3O_4 HoMS were sulfurated by thermal vaporization of sulfur powder under argon atmosphere. The detail procedures are as follows: 40 mg of Co_3O_4 HoMS and 600 mg of sulfur powder were put two separate positions in a porcelain boat with sulfur power at the upstream side of the tube furnace. After that, another porcelain boat was put on it and wrapped it by aluminum foil. Then, the samples were annealed at 400 °C for 2 h with a heating rate of 5 °C min^{-1} under argon atmosphere. Finally, CoS_2 HoMS were obtained after cooling to room temperature naturally and kept it in drying conditions.

Synthesis of CoS_2 nanoparticles (CoS_2 NP): For comparison, we also prepared CoS_2 NP by sulfurizing Co_3O_4 nanoparticles. First, we synthetized Co_3O_4 NP according previous articles[2]. Briefly, 2 g of $Co(CH_3COO)_2·4H_2O$ was dissolved in a solution containing 25 ml of water and 10 ml of ammonia. Then the suspension was transferred into 50 ml autoclave and hydrothermal reaction at 150 ℃ for 3 h. After that, the autoclave was cooled to room temperature naturally. The resulting black solid products were washed with water via centrifugation, dried at 70 ℃ for 12 h, and collected for characterization. Finally, the CoS_2 NP was prepared by sulfurate according to the method of CoS_2 HoMS.

Fabrication of different modified separators: The CoS_2 HoMS modified separators were fabricated by vacuum filtration. Typically, 6 mg CoS_2 HoMS and 1 mg carbon nanotubes were dispersed into N-methyl-2-pyrrolidone (NMP) at a concentration of 0.4 mg mL^{-1} by sonication for 2 h. Then, the obtained suspension was mixed with 1 mg polyvinylidene fluoride (PVDF) and vacuum filtered onto one side of a commercial PP membrane (Celgard 2400). The obtained CoS_2 HoMS modified separator was dried in a vacuum oven at 70 °C overnight and punched into disks with a diameter of 16 mm. The areal loading of CoS_2 HoMS was 0.3-0.4 mg cm^{-2}. For comparison, the CoS_2 NP modified separators was also prepared by the similar process with a similar loading.

Materials characterization:

Powder X-ray diffraction (XRD) patterns were recorded on a Panaltical X'Pert-pro MPD X-ray power diffractometer using Cu Kα radiation (λ=1.54056 Å). Scanning electron microscope (SEM) was performed on a JEOL JSM-7800F scanning electron microscope. Transmission electron microscope (TEM) was performed on JEOL

JEM-2100F electron microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) was performed under a normal mode by using a K-Alpha (Thermo Scientific Inc. UK) XPS system with monochromatic Al Kα X-ray. All XPS spectra are corrected using the C 1s line at 284.8 eV, followed by curve fitting and background subtraction.

Li_2S_6 diffusion test: The Li_2S_6 solution was prepared by adding Li_2S and S with a molar ratio of 1:5 into a solution containing 1,3-dioxolane (DOL) and dimethoxyethane (DME) (1:1, v/v). A brownish-red Li_2S_6 solution was obtained after vigorous stirring overnight at 70 °C. For the diffusion test, we used H-type visualized glass vessel. CoS_2 HoMS modified separators or common PP separators was put middle of this glass cell. One side of this vessel added pure DOL/DME solvent and the other side added containing Li_2S_6 DOL/DME solvent. All of the above steps were operated in an argon-filled glove box.

Symmetrical battery assembly and measurements: Symmetric cells were assembled with two identical electrodes that consisted of a mixture of 80 wt% of CoS_2 HoMS or carbon nanotubes (CNT), 10 wt% CNT, and 10 wt % of poly(vinylidene fluoride) (PVDF). The active material mass loading was about 1.0 mg cm^{-2}. The electrolyte used DOL/dimethoxyethane (1:1, v/v) as solvent and added 1M LiTFSI and 0.5 M Li_2S_6 as solute. Cyclic voltammetry (CV) was performed between -1.5 V and 1.5 V at a scan rate of 5 mV s^{-1}.

Electrochemical measurements:

To prepare the sulfur electrodes, 60 wt% sublimed sulfur, 30 wt% CNT, and 10 wt% PVDF were mixed in an agate mortar using N-methyl-2-pyrrolidone (NMP) as solvent to form homogeneous slurry, which was then uniformly coated onto an Al foil and dried in a vacuum oven at 70 °C for 12 h. CR2032-type coin cells were assembled in an Ar-filled glove box with the S/CNT cathode, modified separator or PP separator, and lithium anode for the electrochemical evaluations. The electrolyte was 1.0 M LiTFSI in DOL: DME=1:1 Vol% with 2.0% $LiNO_3$. The ratio of electrolyte to sulfur (E/S) was 10 mL g^{-1}. The galvanostatic charge−discharge measurements were tested on a Neware battery testing system. The cyclic voltammetry and electrochemical impedance spectroscopy were measured by electrochemical workstation (CHI 604C).

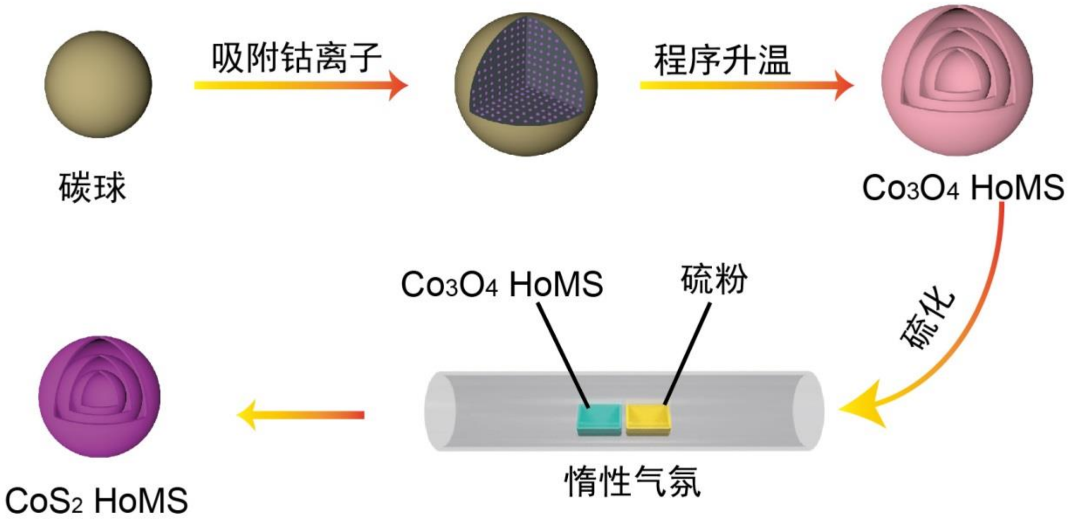

Figure S1. Schematic illustration of the preparation procedures of CoS_2 HoMS.

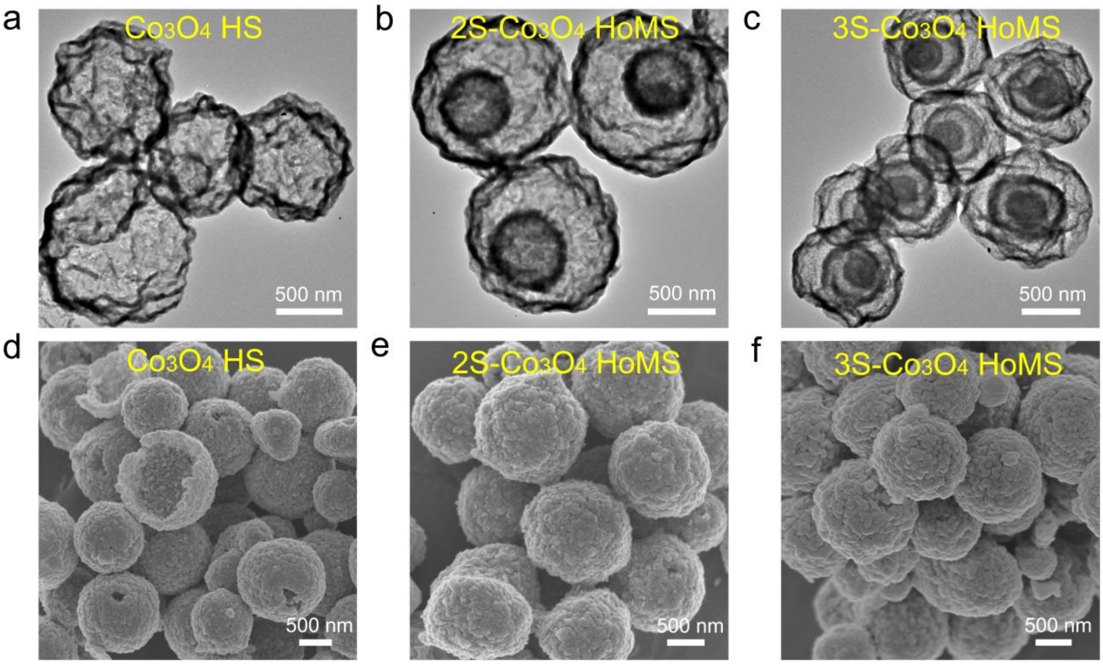

Figure S2. (a,b,c) TEM and (d,e,f) SEM images of single (1S-), double (2S-), and triple (3S-) shelled Co_3O_4 HoMS.

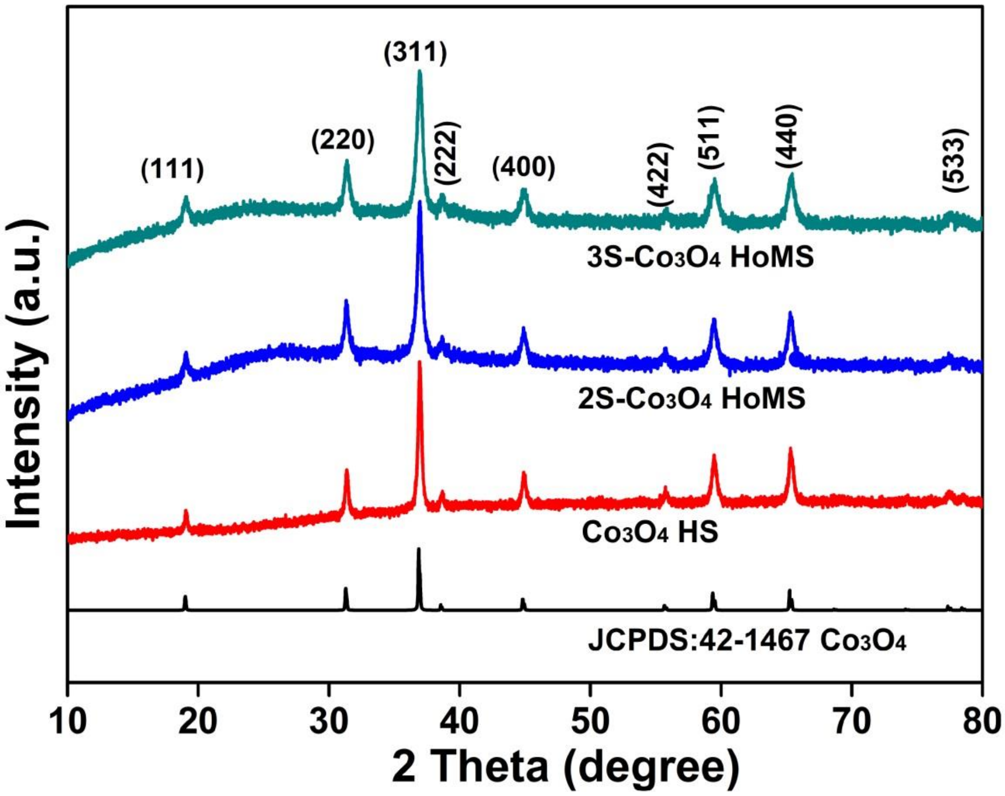

Figure S3. The XRD patterns of the as-prepared i) 1S-, ii) 2S-, and iii) 3S-shelled Co_3O_4 HoMS.

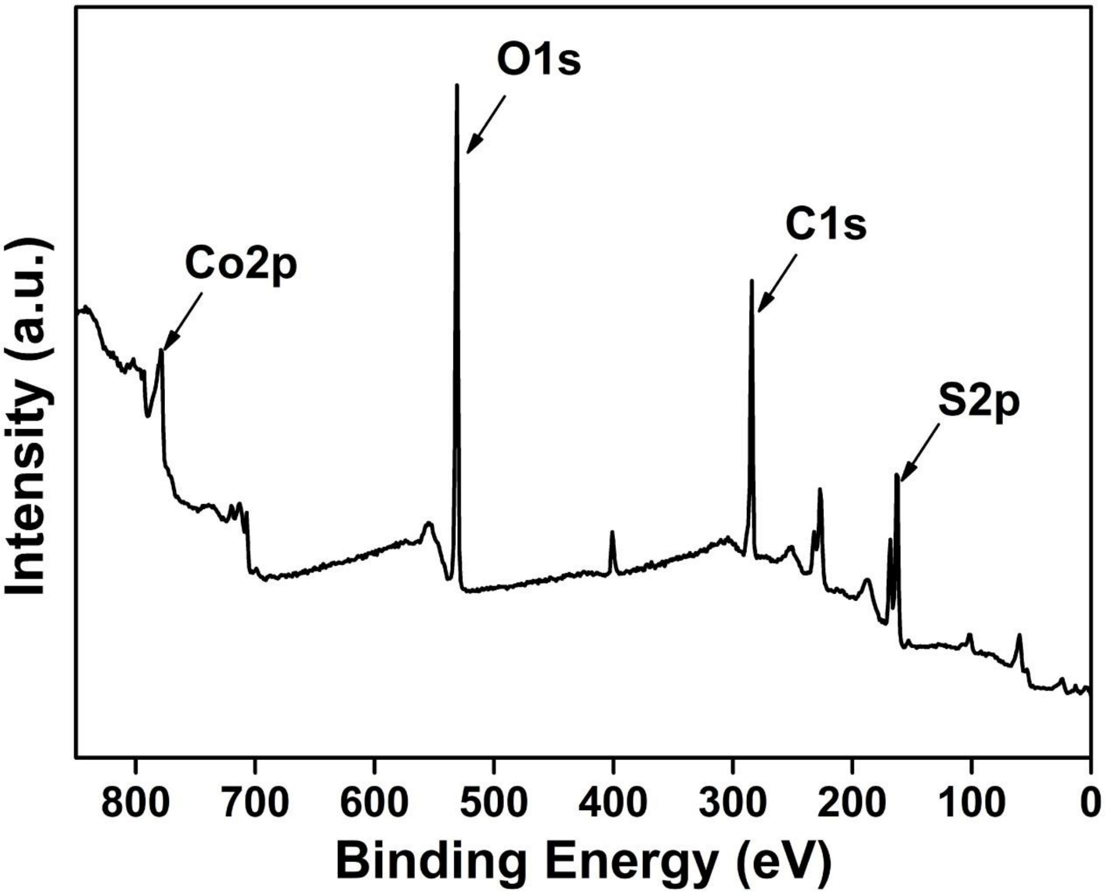

Figure S4. XPS patterns of the 3S-CoS_2 HoMS.

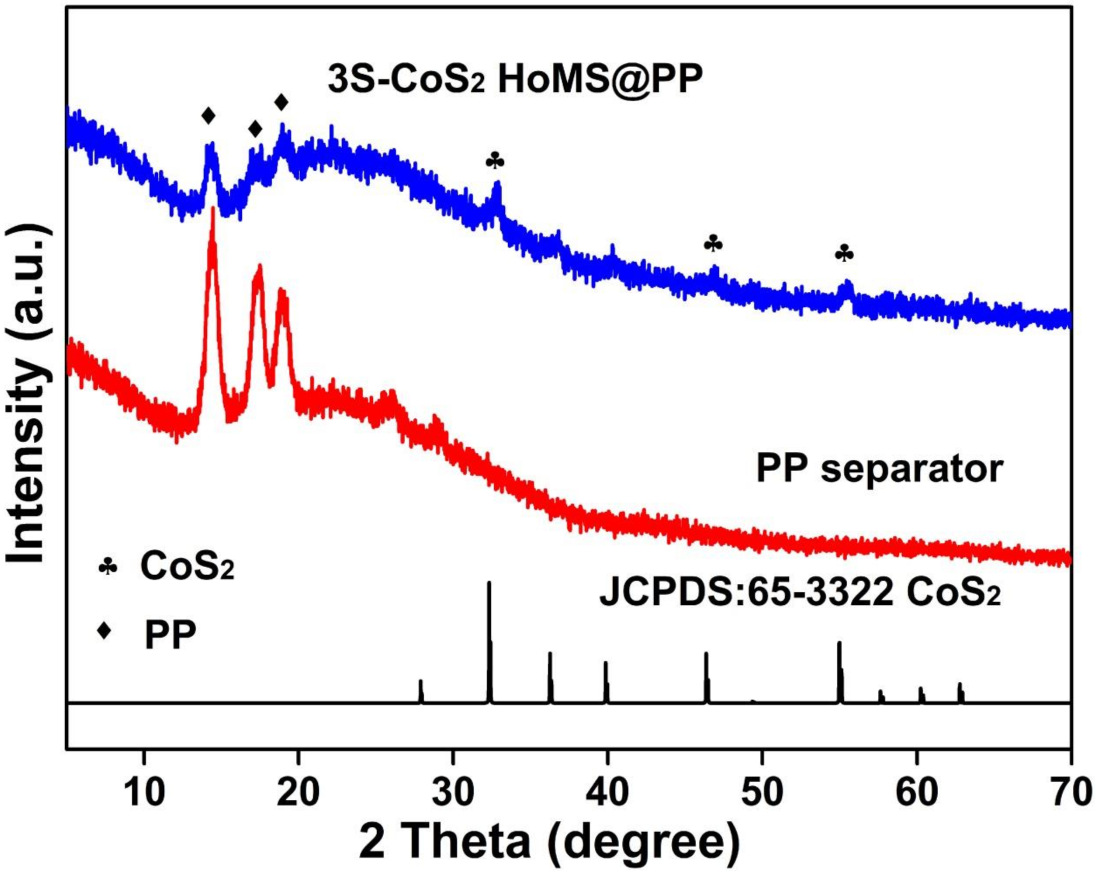

Figure S5. The XRD patterns of PP separator and 3S-CoS_2 HoMS modified separator.

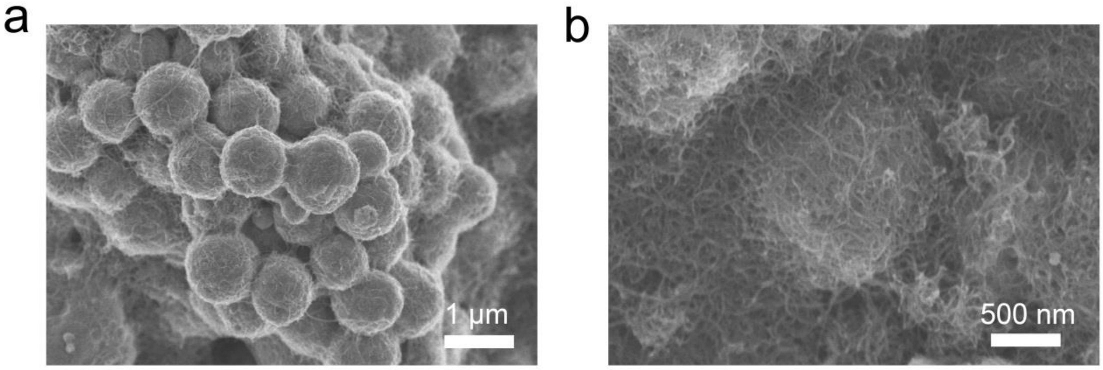

Figure S6. Magnified SEM images of the top surface of 3S-CoS_2 HoMS modified separator at different region.

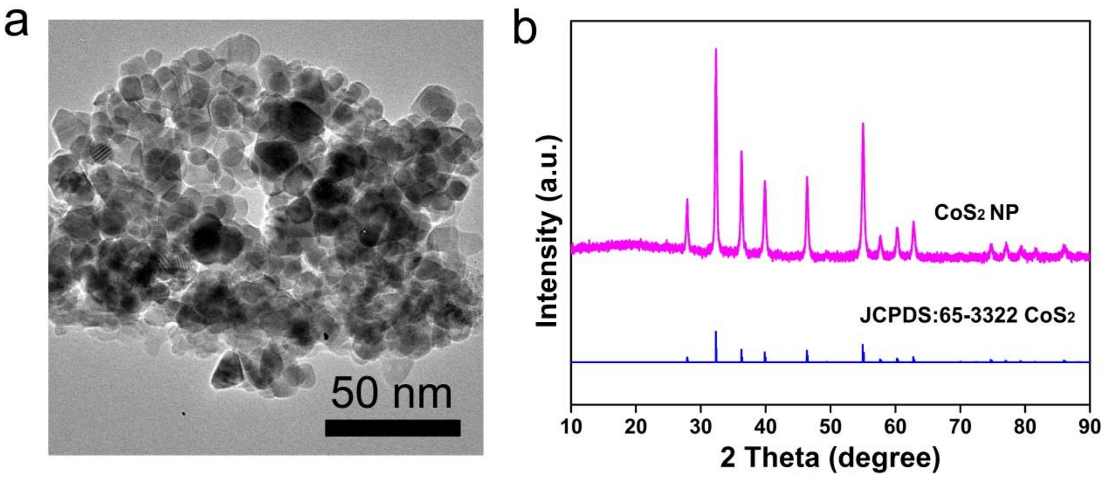

Figure S7. TEM images (a) and XRD patterns (b) of CoS_2 NP.

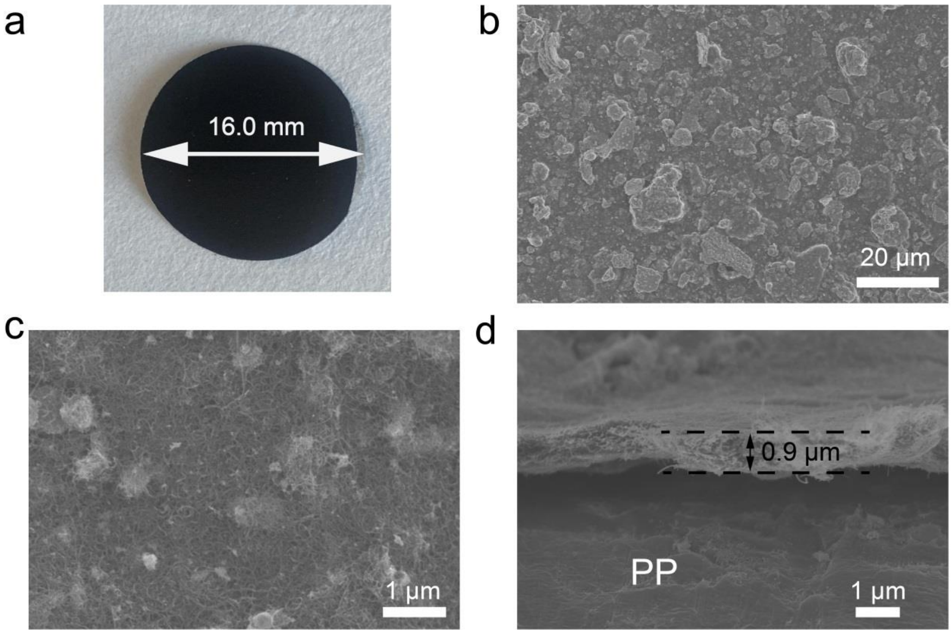

Figure S8. (a) Photograph, and (b-d) SEM images of CoS_2 NP modified PP separator (b-c, top surface and d, cross section).

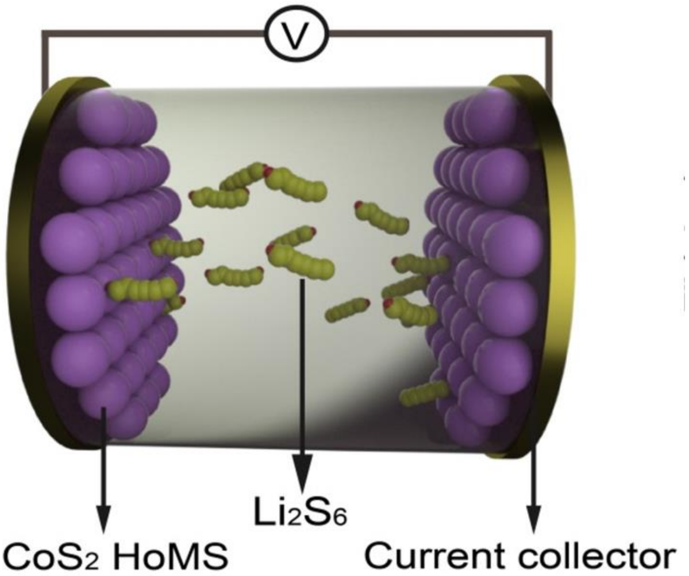

Figure S9. Schematic of symmetric battery using two identical electrodes loaded with 3S-CoS_2 HoMS or CNT.

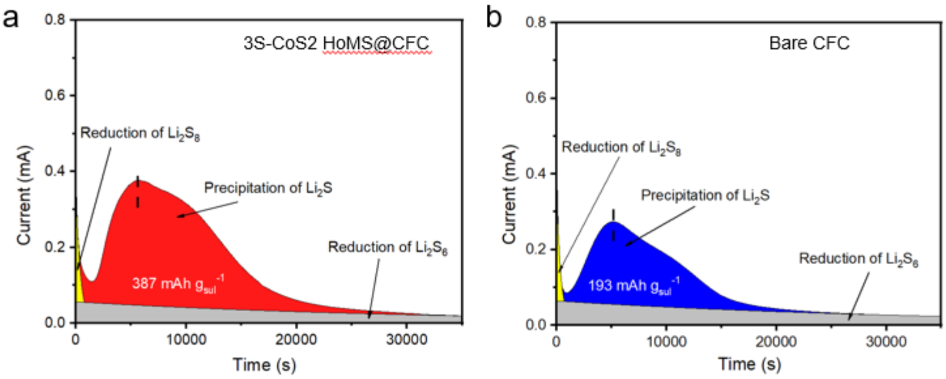

Figure S10. Fitting of current vs. time curves for a potentiostatic discharge at 2.02 V. Cells were fabricated with (a) 3S-CoS$_2$ HoMS modified separator or (b) unmodified separator.

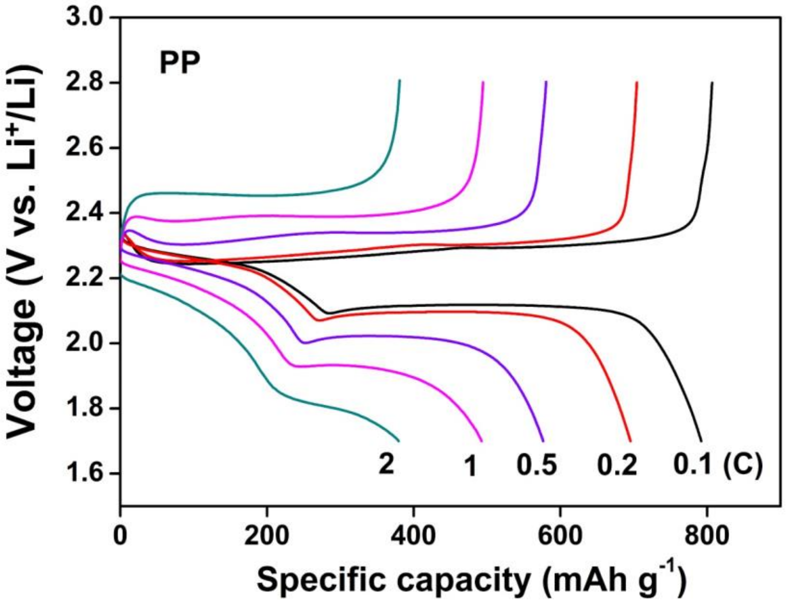

Figure S11. Galvanostatic charge–discharge profiles of battery with PP separator at different current densities.

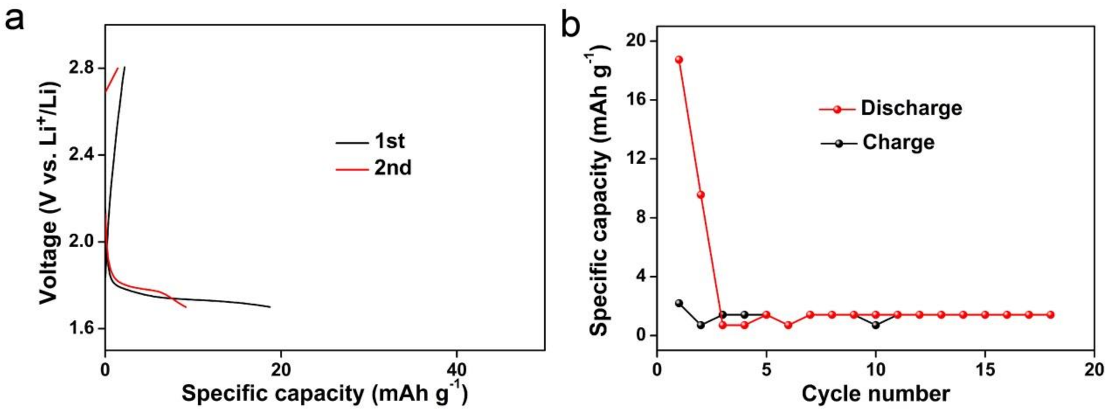

Figure S12. (a) Galvanostatic charge–discharge curves and (b) cycling performance curves of the 2S-CoS_2 HoMS at a current density of 200 mA g^{-1} in the voltage of 1.7-2.8 V.

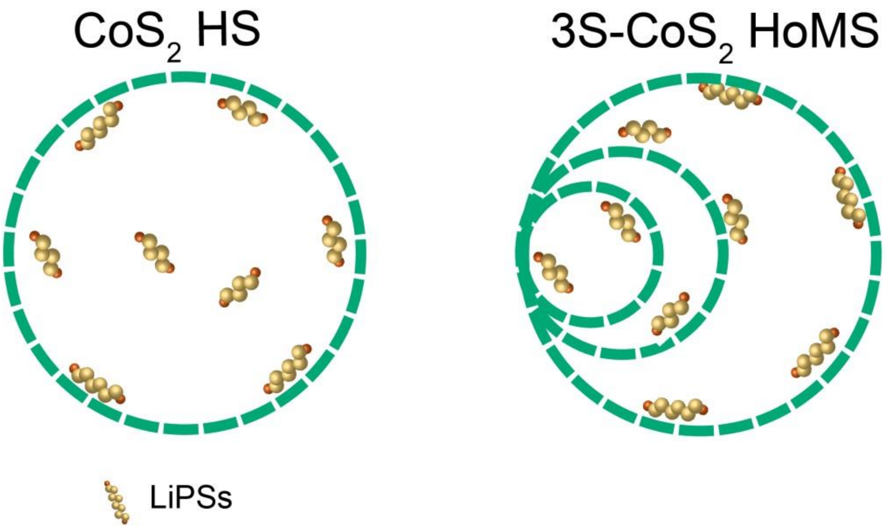

Figure S13. Schematic illustration of CoS$_2$ HS and 3S-CoS$_2$ HoMS adsorbed LiPSs.

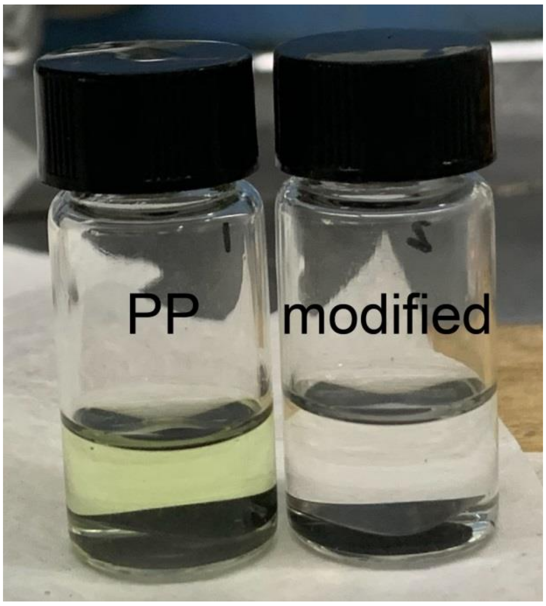

Figure S14. Photographs of cycled S electrodes (at the state of charge) with PP separator and 3S-CoS_2 HoMS modified separator in DME/DOL solvent.

Table S1. Different resistances of symmetric battery were obtained from the equivalent circuit in Figure 3b.

Parameters	CNT	3S-CoS_2 HoMS
R1	4.3	3.5
R2	110.6	68.0
W1	56	51.7

Table S2. Values of lithium ion diffusion coefficients for the Li-S batteries with PP and 3S-CoS_2 HoMS coated separators.

Parameters	PP	3S-CoS_2 HoMS modified
D_{Li^+} at peak C1 [cm^2 s^{-1}]	2.1×10^{-8}	4.5×10^{-8}
D_{Li^+} at peak C2 [cm^2 s^{-1}]	6.4×10^{-9}	3.7×10^{-8}
D_{Li^+} at peak A2 [cm^2 s^{-1}]	5.1×10^{-8}	2.5×10^{-7}

Table S3. Different resistances of Li-S battery were obtained from the equivalent circuit in Figure 4c.

Parameters	PP	CoS_2 NP@PP	CoS_2 HS@PP	2S-CoS_2 HoMS@PP	3S-CoS_2 HoMS@PP
R1	3.2	2.9	5.1	7.6	2.0
R2	134.8	75.5	72.7	56.6	40.5
W1	55.8	46.4	88.4	69.2	11.0

References

[1] Wang J., Yang N., Tang H., Dong Z., Jin Q., Yang M., Kisailus D., Zhao H., Tang Z., Wang D., *Angew Chem Int Ed* **2013,** *52*, 6417.

[2] Dong Y., He K., Yin L., Zhang A., *Nanotechnology* **2007,** *18,* 435602.