Supporting Information

Bifunctional Electrocatalytic Hybrid Heterostructures for Polysulfide

Anchoring/Conversion for a Stable Lithium-Sulfur Battery

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Reagents used for the synthesis.

All the reagents used in the synthesis were of commercial grade. Ammonium molybdate ($(NH_4)_6Mo7O_{24}\cdot4H_2O$, Merck, extra pure), thiourea ($CS(NH_2)_2$, ACS reagent, ≥99.0% Sigma Aldrich), Hydrogen peroxide (H_2O_2, Merck, 30%), oleic acid (potassium salt, Merck), Pluronic (P123, Sigma Aldrich, average M_n ~2,000), D-Xylose (≥99% GC), 1M LiTFSI in DME/DOL 1:1 (v/v) with 2wt% $LiNO_3$ Electrolyte (MSE PRO), Sulfur (99.998% trace metals basis), Polyvinylidene fluoride or polyvinylidene difluoride (PVDF, Sigma Aldrich), 1-Methyl-2-pyrrolidinone (NMP, Merck).

Methods

SI-1.1 Synthesis of hollow carbon Nanopots Synthesis: Porous hollow Carbon nanostructures resembling nano pots were synthesized in a typical procedure using 0.2 mmol oleic acid (potassium salt) and 0.01 mmol P123. The above two reagents were dissolved in 20 mL of deionized water and stirred slowly to form a clear solution. Then, 60 mL of an aqueous solution containing a biomass-based derivative, xylose (4g), was added. The mixture formed an almost transparent solution after stirring for 30 min at room temperature. The resultant solution was transferred into a 100 mL autoclave and hydrothermally treated at 180 °C for 10 h. After the autoclave cooled to room temperature, the solid products were collected by centrifugation (8000 rpm, 10 min), washed three times with deionized water, and dried at 80 °C overnight in vacuum oven. The sample is further pyrolyzed at 800 °C for 2 hrs in inert atmosphere to obtain hollow nanopots.

SI-1.2 Cell Assembly: The coin cells, CR 2032 were fabricated by mixing the active materials (80 wt%) with polyvinylidene fluoride binder (PVDF, 10 wt%) and Super-P® conductive carbon black (10 wt%) in N-methyl-2-pyrrolidone (NMP) as solvent. The resultant slurry was evenly

pasted onto Al foil current collectors, dried at 120°C for 2 h and then roll-pressed. The test half-cells were assembled in a glove box into a two-electrode configuration. Celgard 2500 (polypropylene) membrane was used as the separator and Lithium metal was used as the anode. The cathode active materials were prepared by loading sulfur into the hosts materials (CMS or C-nanopots). Sulfur deposition was obtained by wetting CMS or C-nanopots with sulfur solution (prepared by dissolving sulfur in CS_2/NMP). The electrolyte was composed of 1 M lithium bis(trifluoromethyl sulfonyl) imide (LiTFSI) and 2.0 wt% lithium nitrate ($LiNO_3$) mixed in a 1 : 1 volume ratio of 1,3-dioxolane (DOL) / 1,2-dimethoxyethane (DME). The cathode material consisted of either C-nanopots or CMS samples (with a sulfur mass loading of approximately 3-4 mg cm^{-2}). The typical voltage window for the charge-discharge tests was 1.6-2.8 V. A Princeton electrochemical workstation (Versastat-3) and battery cycler - BTS-4000 Cell tester were employed for electrochemical measurements.

SI-1.3 Polysulfide (Li_2S_6) electrolyte preparation: Li_2S and sublimed sulfur precursors were incorporated into the electrolyte in a 1:5 mass ratio. Subsequently, the mixture was added to a 1.0 M LiTFSI solution in DOL and DME (1:1 v/v) containing 2.0 wt% $LiNO_3$. To ensure thorough mixing, the solution underwent vigorous magnetic stirring at 70 °C for an extended period, resulting in the formation of a brownish-red Li_2S_6 electrolyte.

SI-1.4 Material Characterizations

X-ray diffraction (XRD) was conducted within the 2θ range of 5-80° at a scan speed of 4 min^{-1} (Bruker D8, with Cu Ka irradiation with a wavelength of 0.1542 nm). The sample's nanostructure and surface morphologies were characterized utilizing a field-emission scanning electron microscope (JEOL JSM-7600F FEG-SEM) equipped with EDS for elemental mapping. A high-resolution transmission electron microscope (FEI, Technai G2) equipped with

EELS (Model 965, GIF Quantum) is used for imaging, atom identification and chemical bonding of the interfaces. A multipurpose JEOL, JEM-2100 F was also employed for obtaining high resolution images and internal structures. In order to determine the functional groups, FTIR spectroscopy was performed using a spectrometer (Agilent Carry 630), Surface area and pore size measurements were carried out using Brunauer-Emmett-Teller (BET) surface area analysis using N_2 adsorption and Desorption isotherm (2390 Gemini VII (Micromeritics)). Micro-Raman spectroscopic investigations (HR800-UV confocal, Horiba Jobin Yvon, France) have been carried out to understand the vibration modes and phase purity of the samples
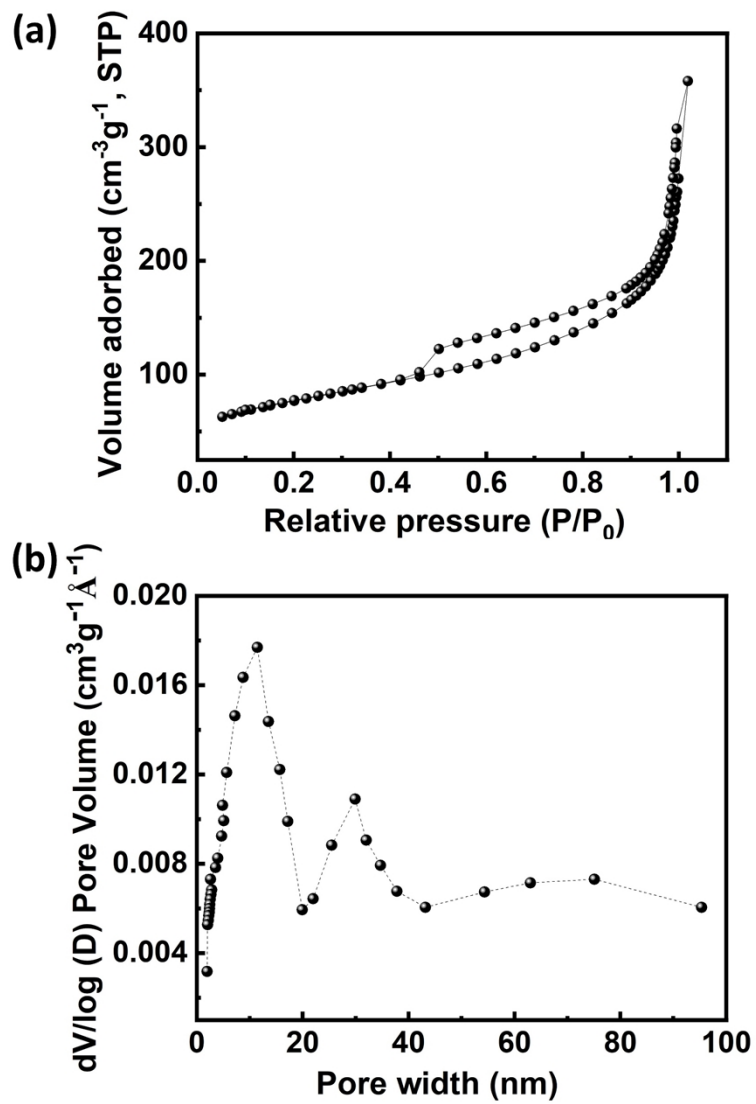
Figure S1. Brunauer-Emmett-Teller (BET) surface area analysis of C-nanopots (BET surface area of 261.2 m^2g^{-1}): (a) Adsorption and desorption isotherms, (b) pore size distribution.
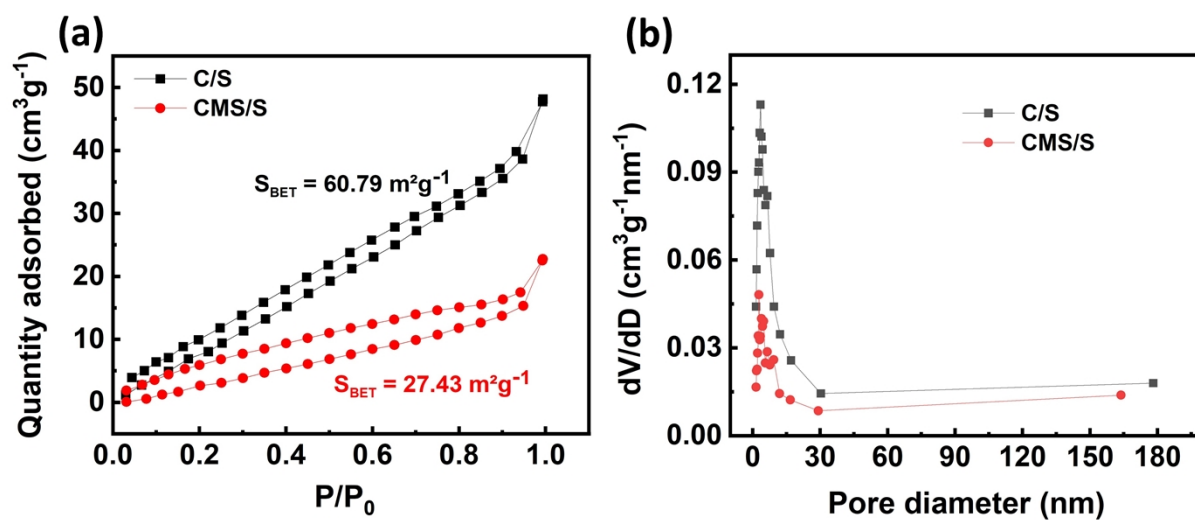
Figure S2. (a) N2 adsorption–desorption isotherms with surface areas of C/S and CMS/S; (b) Pore size distribution profiles of C/S and CMS/S.
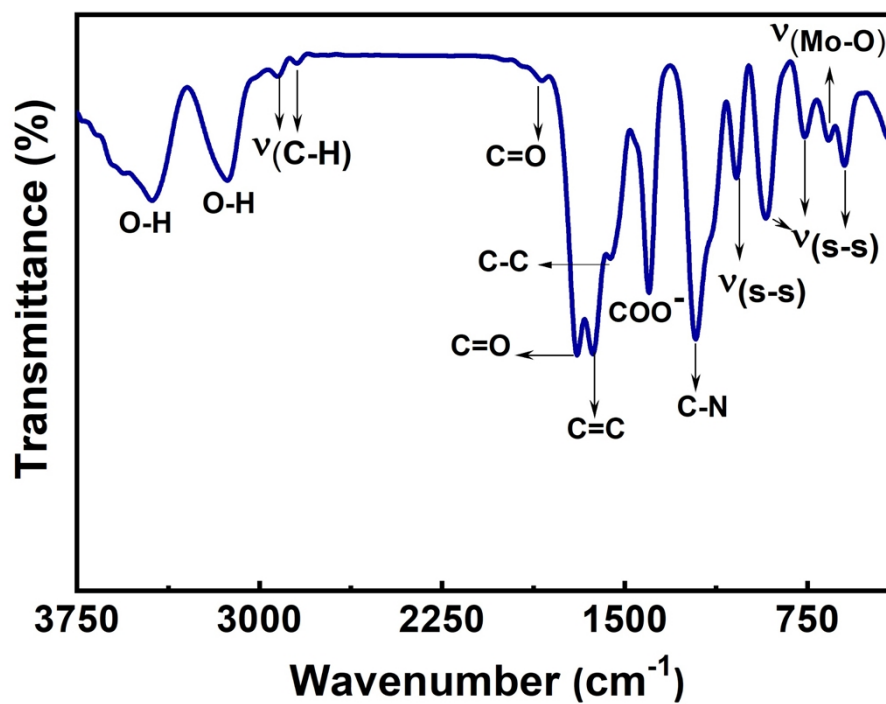
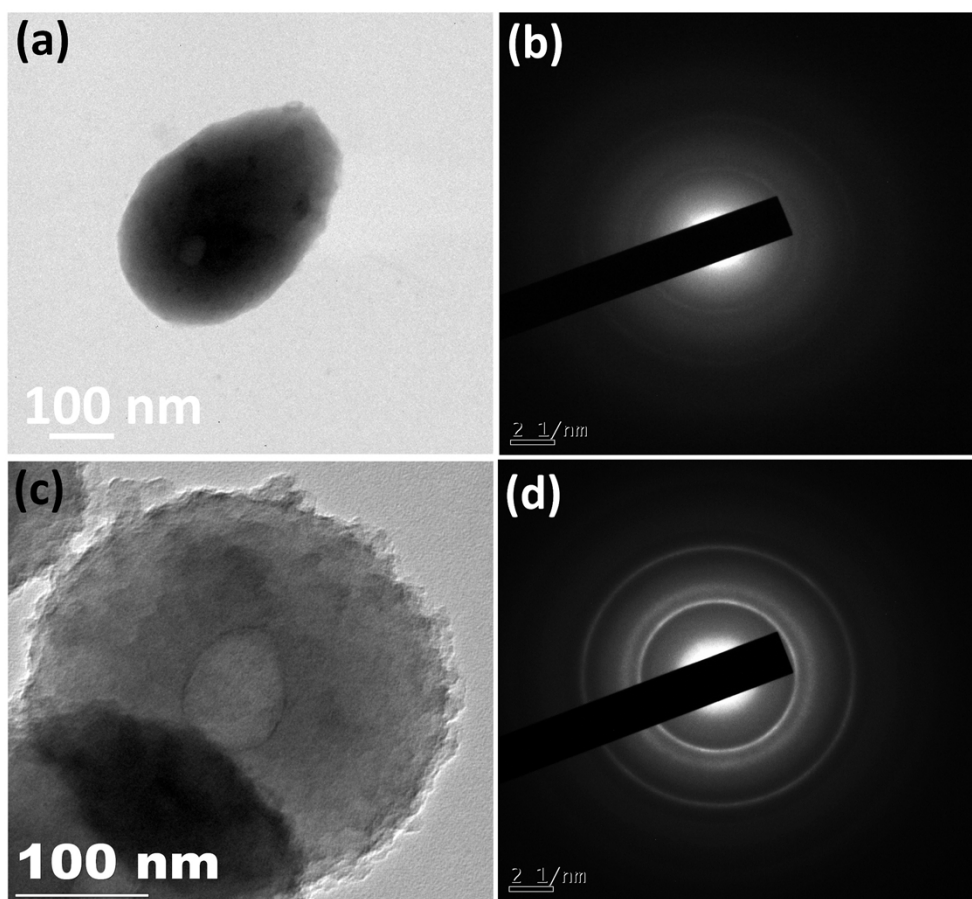**Figure S3.** Fourier Transform Infrared Spectrum of CMS.

Figure S4. (a) TEM image of C-nanopot, (b) SAED pattern of C-nanopot, (c) TEM micrograph of CMS, and (d) SAED pattern of CMS.
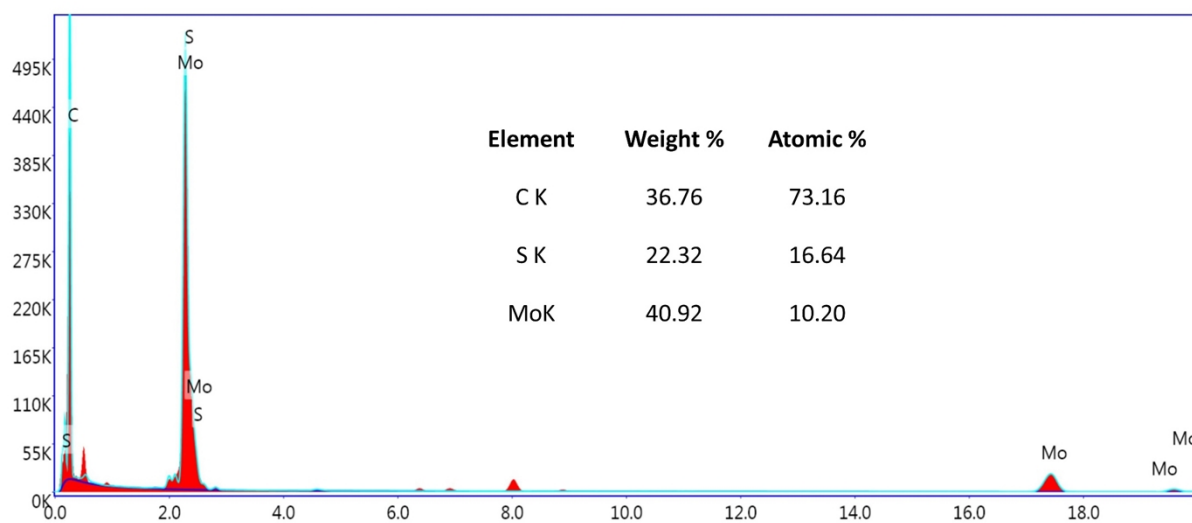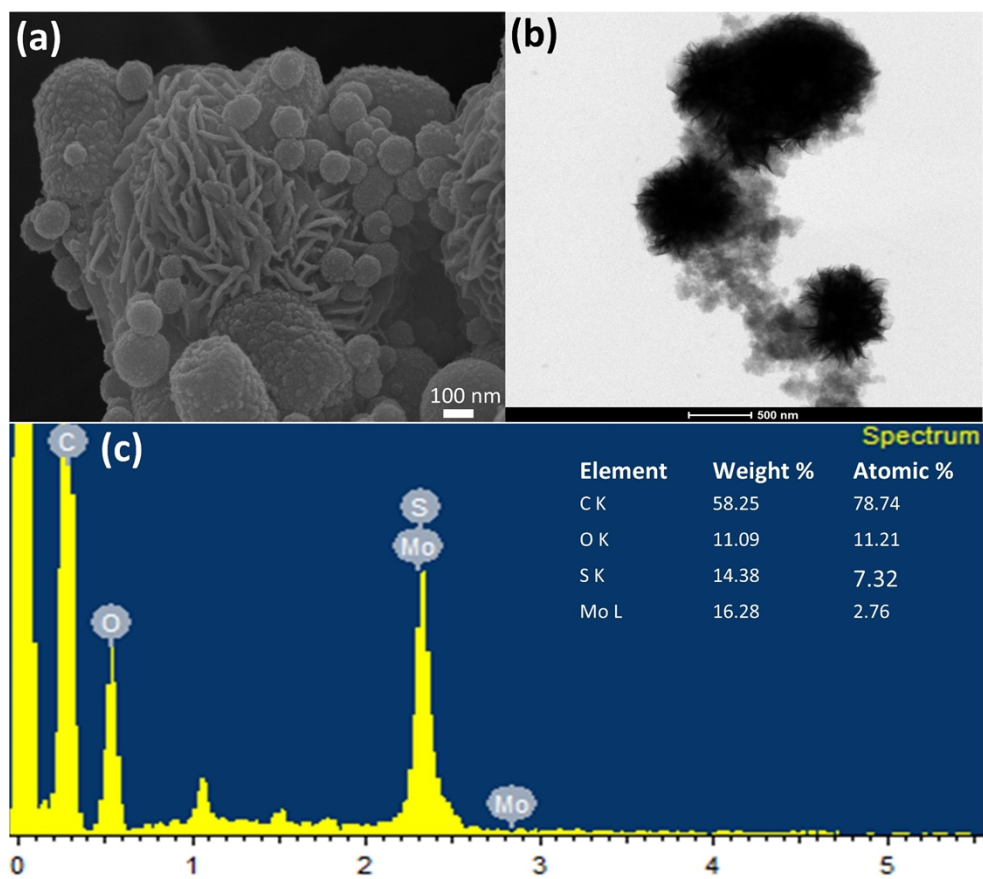
Element	Weight %	Atomic %
C K	36.76	73.16
S K	22.32	16.64
MoK	40.92	10.20

Figure S5. EDS profile of 1T MoS2/C.

Element	Weight %	Atomic %
C K	58.25	78.74
O K	11.09	11.21
S K	14.38	7.32
Mo L	16.28	2.76

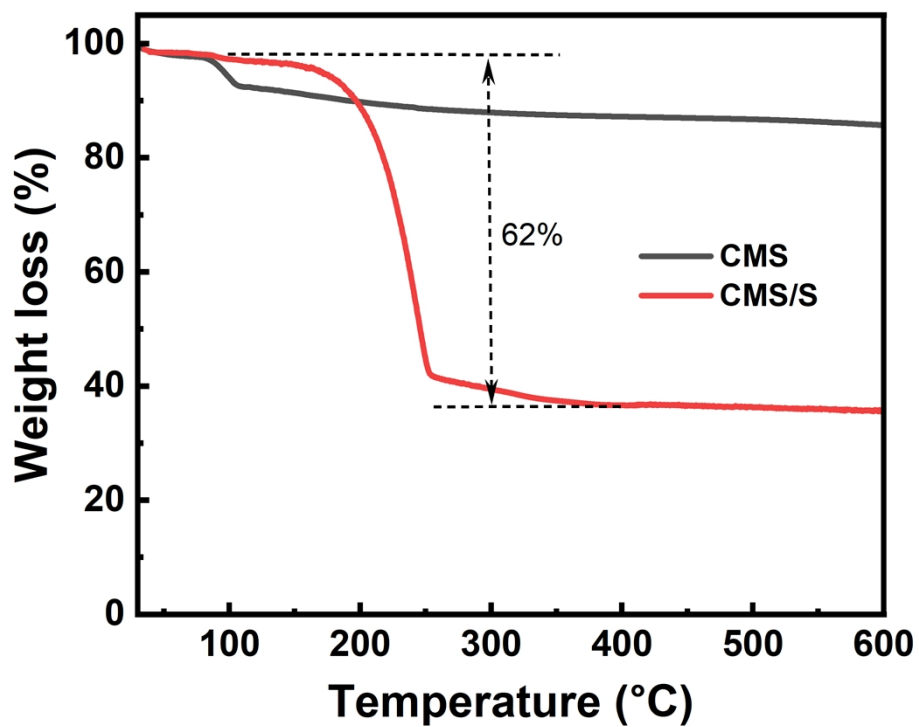**Figure S6.** (a), (b) SEM and TEM of CMS/S, and (c) EDS spectrum of CMS/S cathode obtained on carbon tape support.

Figure S7. TGA profiles of CMS and CMS/S. A sulfur loading of 62% is incorporated in CMS/S cathode.
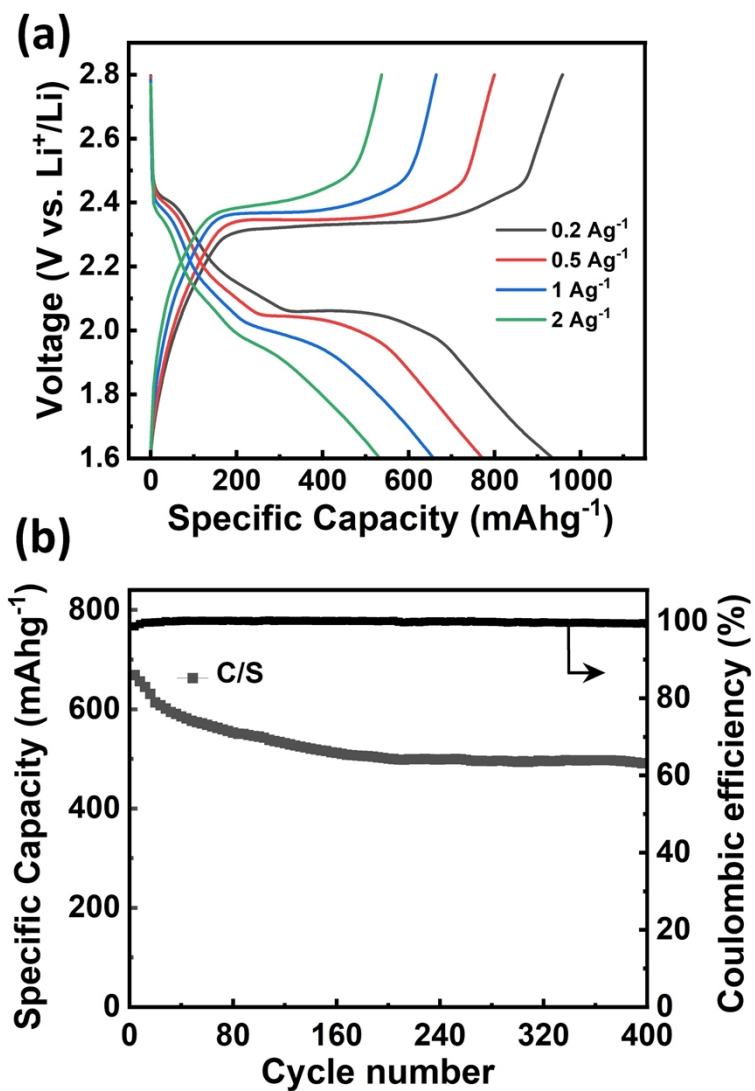
Figure S8. Initial specific capacities of sulfur loaded C-nanopots electrode (C/S) at various current densities and (b) Cycle life stability and coulombic efficiency profile of C/S electrode at 1 Ag^{-1}.
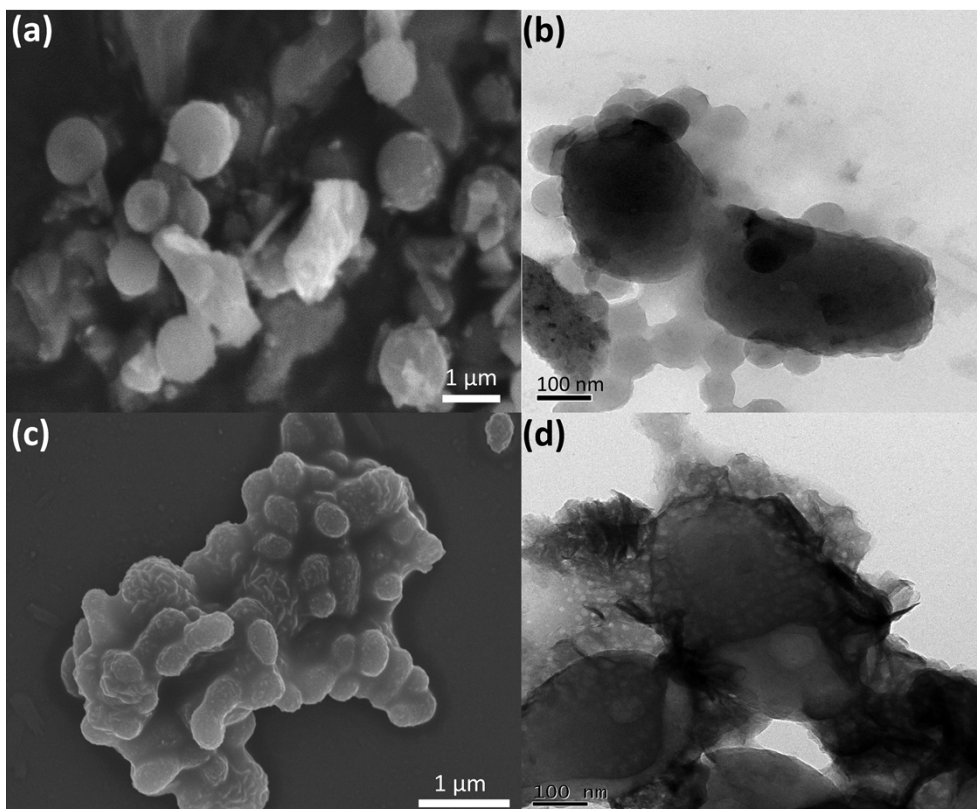
Figure S9. Morphological characterizations: (a) and (c) SEM micrographs of C/S and CMS/S respectively after cycling for 100 cycles; (b) and (d) TEM micrographs of C/S and CMS/S respectively, showing Li2S surrounding the samples after cycling.
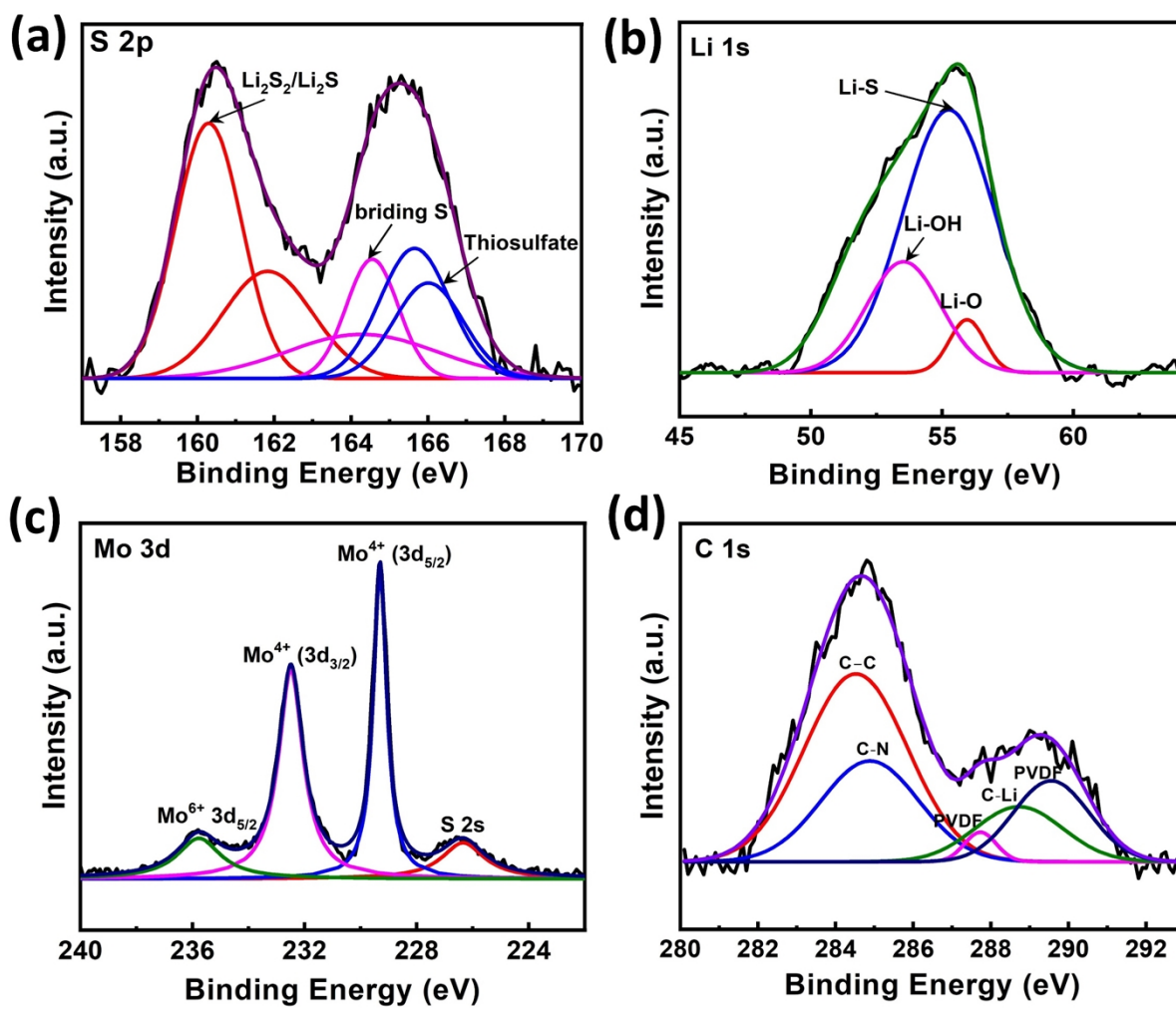
Figure S10. XPS spectra of cycled CMS/S cathode (a) S 2p; (b) Li 1s; (c) Mo 3d and; (d) C 1s