

Supplementary Information for

Rational design of zwitterionic porous organic framework loading Co(II) ions to host sulfur and synergistically boost polysulfides redox kinetics for lithium sulfur batteries

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Section S1: DFT calculations

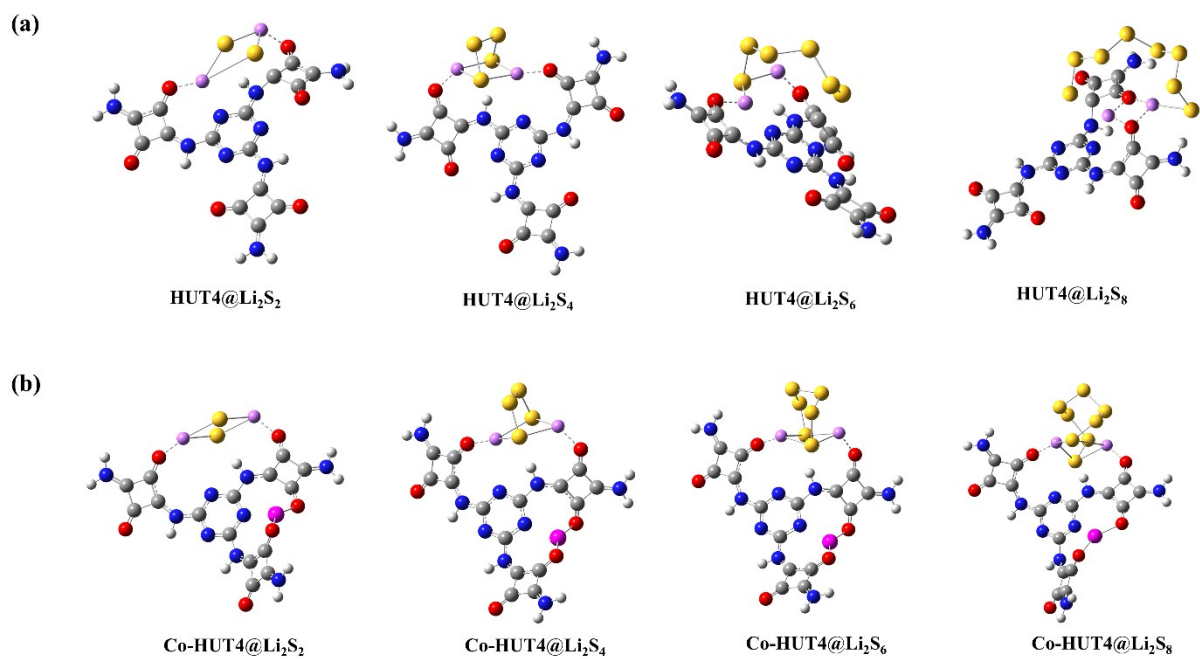


Fig S1 Optimized structures of (a) HUT4@LiPSs and (b) Co-HUT4@LiPSs.

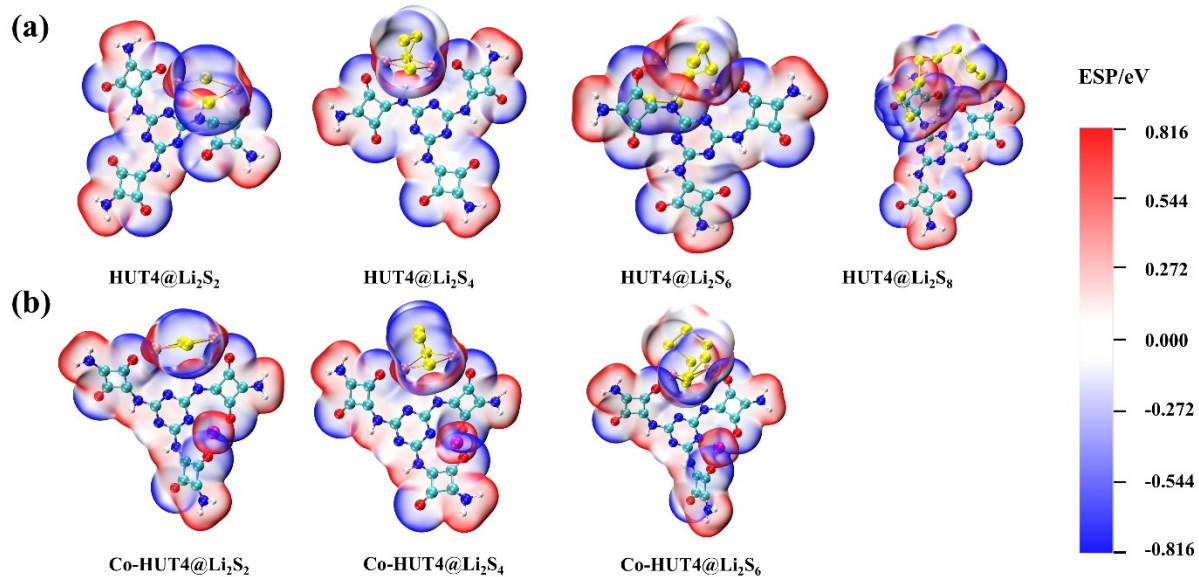


Fig. S2 Electrostatic potential of (a) HUT4@LiPSs and (b) Co-HUT4@LiPSs except Co-HUT4@Li₂S₈

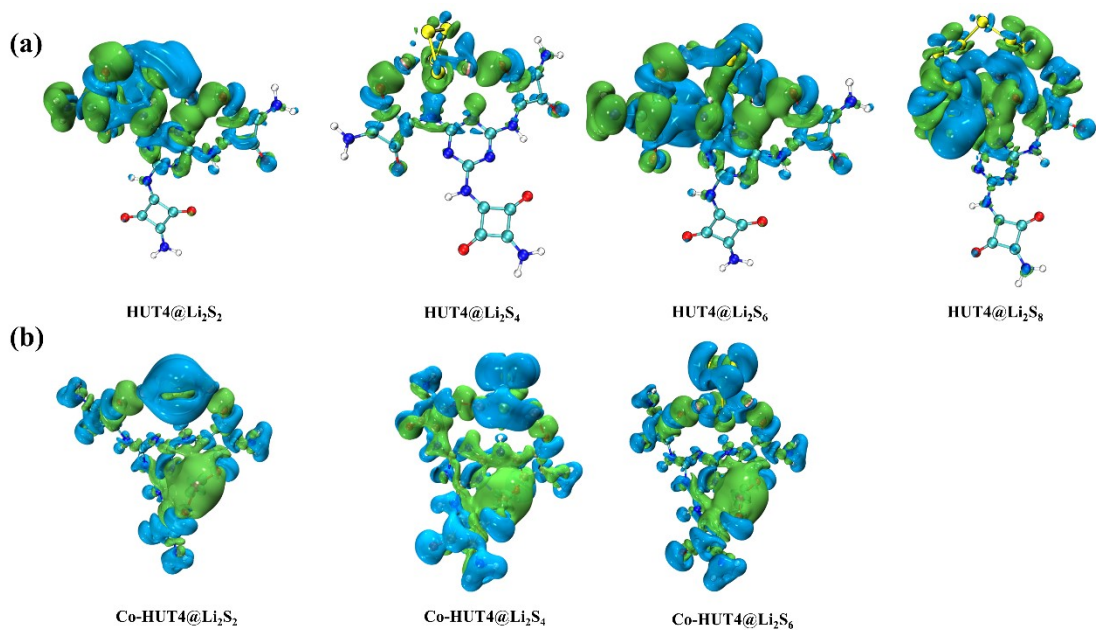


Fig. S3 Charge density differences of (a) HUT4@LiPSs and (b) Co-HUT4@LiPSs except Co-HUT4@Li₂S₈

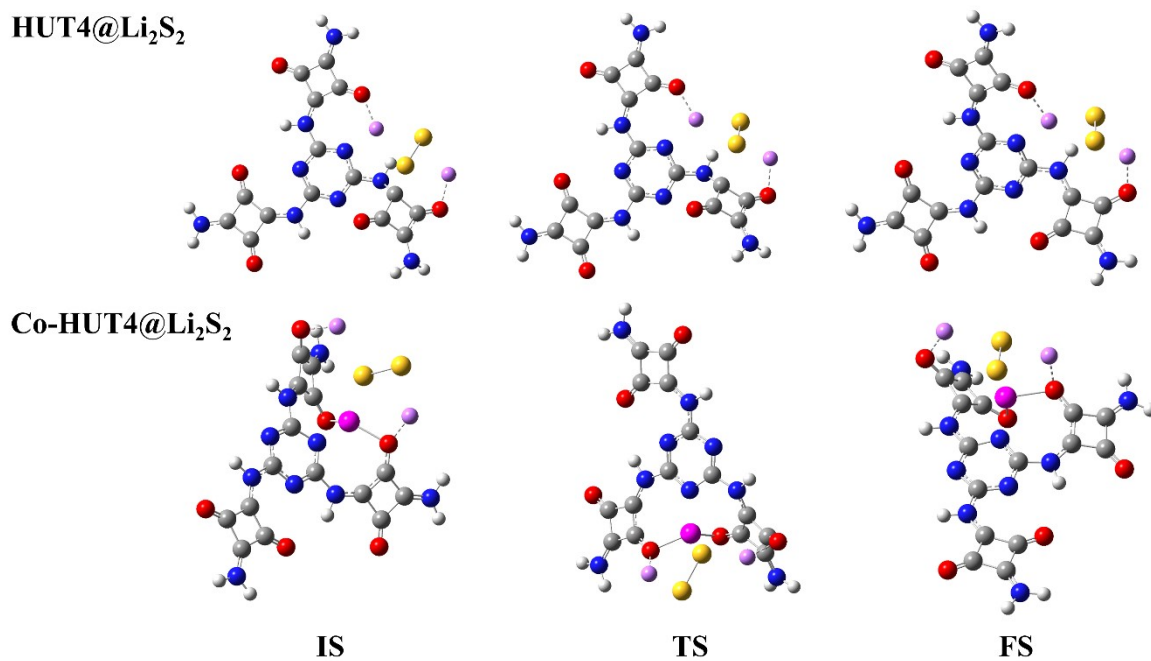


Fig. S4 Initial states(IS), transitional states(TS) and final states(FS) of HUT4@Li₂S₂ and Co-HUT4@Li₂S₂

Section S2: Chemicals and Instruments

All the chemical reagents used are at least in analytical grade. Melamine, squaric acid and Cobalt (II) acetate tetrahydrate [Co(OAc)₂·4H₂O] were all purchased from Macklin Co. Ltd (Shanghai, China). Mesitylene, n-butanol, acetone and tetrahydrofuran (THF) were purchased from Hengshan Chemical Technology Co., Ltd (TianJin, China). All reagents purchased above were used without further purification. The water used was doubly deionized water provided by ultrapure water machine.

The morphology of the synthesized samples was observed by scanning electron microscope (SEM, Nova Nano 450, FEI) and transmission electron microscope (TEM, Talos F200S, FEI). The Fourier Transform infrared (FT-IR) spectra were conducted with a TENSOR 27 spectroscopy system in the 400-4000 cm⁻¹ region (Bruker, Germany). The structures of materials were tested by X-ray diffraction (XRD, D8 Discover, Bruker) equipped with Cu-Kα radiation within 2θ angular range from 5°~65°. The N₂ adsorption-desorption measurement (Auto-sorb IQ, Quantachrome) was used to explore the specific surface areas and pore size distribution based on Brunner-Emmet-Teller (BET) theory. The chemical states of samples were analyzed by X-ray photoelectron spectra (XPS, ESCALAB 250Xi, Thermo Fisher Scientific). The UV-Vis spectra were obtained by a Lambda-25 UV-Vis spectrophotometer (Perkin Elmer, USA)

in the range of 200-800 nm. The Thermo gravimetric analysis (TGA, TG/DTA6300, Hitachi) were tested with a temperature ramp rate of $10^{\circ}\cdot\text{min}^{-1}$ from room temperature to 450 °C.

Section S3. Material Characterization

3.1 Synthesis reaction

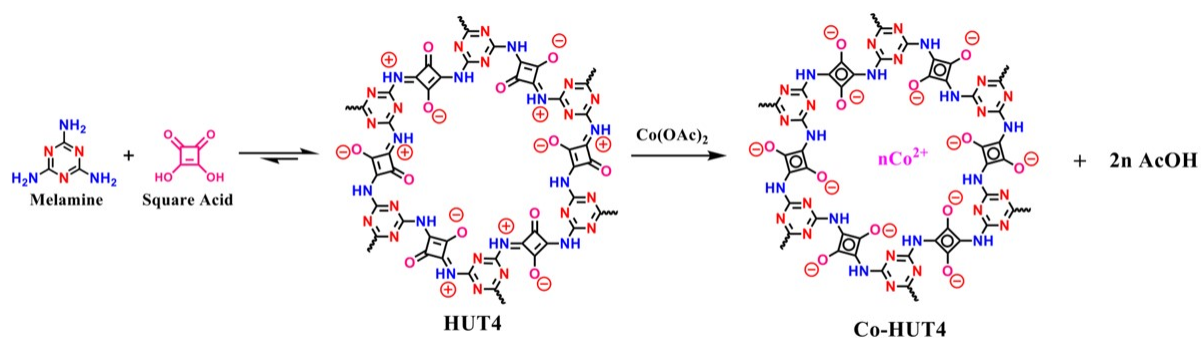


Fig. S5 Synthesis process of Co-HUT4.

3.2 FTIR study

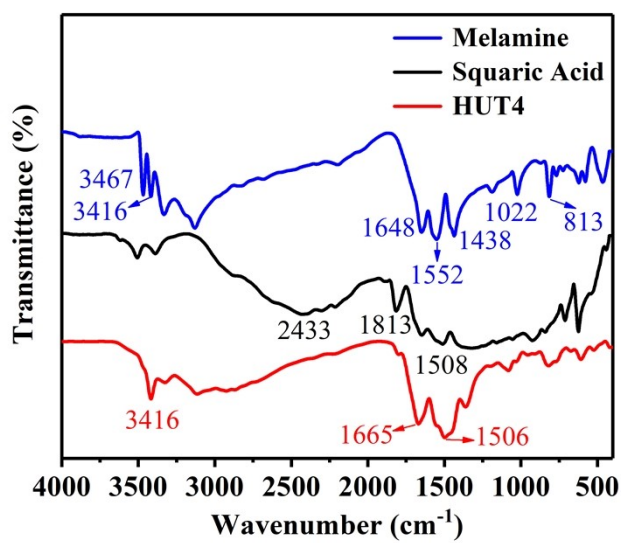


Fig. S6 FTIR spectra of HUT4.

3.3 ^{13}C NMR spectral study

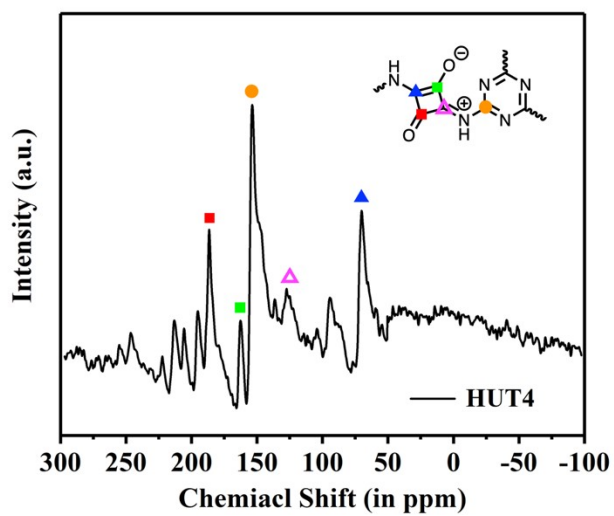


Fig. S7 ^{13}C NMR spectra of HUT4.

3.4 SEM images study

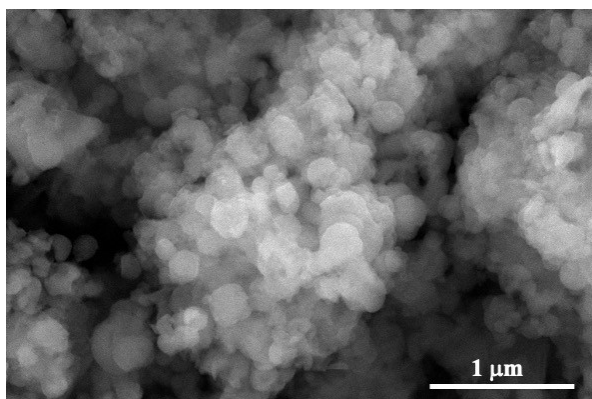


Fig. S8 SEM image of Co-HUT4.

3.5 XRD spectral study

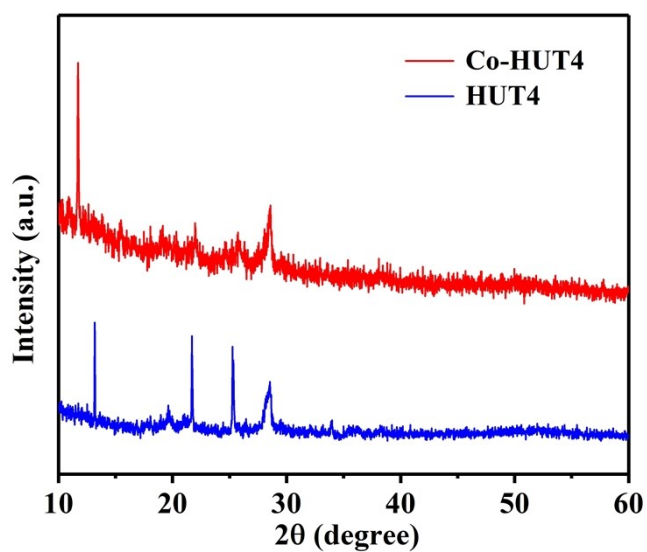


Fig. S9 XRD spectra of HUT4 and Co-HUT4.

3.6 Thermo Gravimetric Analysis (TGA)

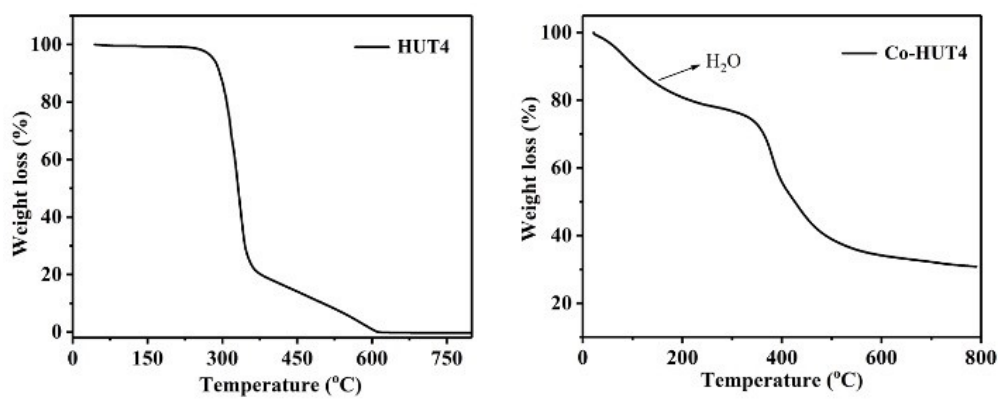


Fig. S10 TGA profile of HUT4 and Co-HUT4 in N₂ atm.

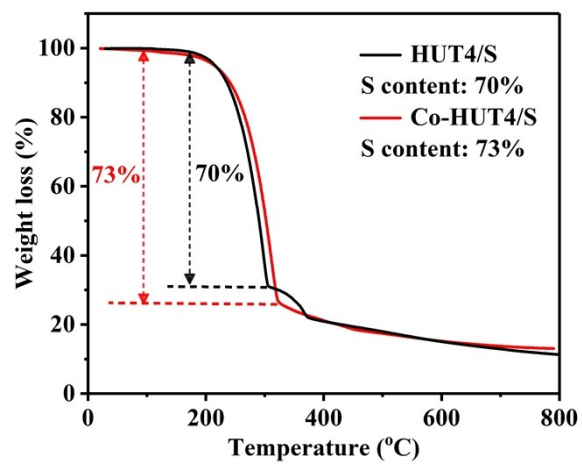


Fig. S11 TGA profiles of HUT4/S and Co-HUT4/S composites in N₂ atm.

Section 4. Electrochemical Study

4.1 Electrochemical measurements

The galvanostatic cycling test was performed on a BTS-5V5mA multichannel battery tester (Neware) between 1.7 and 2.8 V (vs Li/Li+). The CV and EIS curves were measured by a CHI660 electrochemical workstation. All the electrochemical tests were performed at 25 °C.

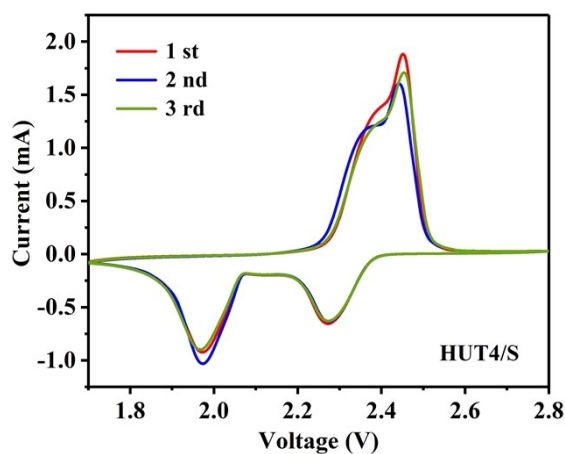


Fig. S12 CV curves of HUT4/S electrode in initial three cycles at 0.1 mV/s.

4.2 Symmetric Battery Test

The symmetrical cells were assembled with Co-HUT4 (or HUT4) as the identical working and counter electrodes and 0.1 M Li_2S_6 solution as electrolyte in order to test the LiPSs conversion kinetics before and after cobalt modification. The CV measurement was carried out in a potential range from -1.5 to 1.5 V with a scanning rate from 5 to 25 $\text{mV}\cdot\text{s}^{-1}$.

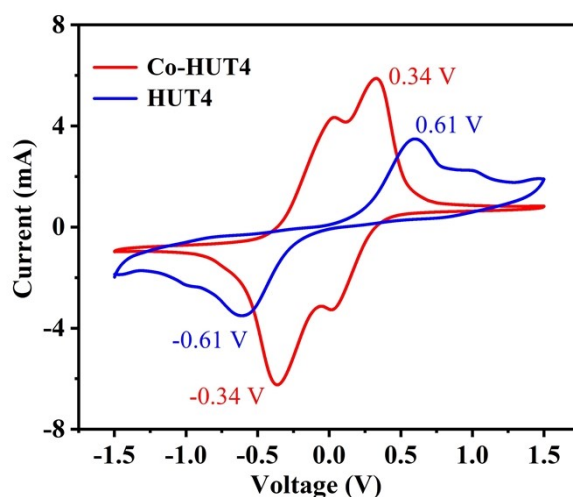


Fig. S13 CV curves of symmetric cells with HUT4/S and Co-HUT/S electrodes.

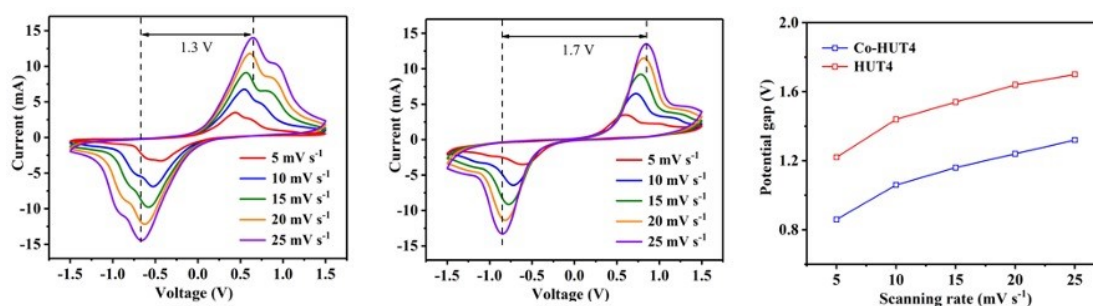


Fig. S14 CV curves of symmetric cells with a) Co-HUT/S, b) HUT4/S and c) the corresponding peak widening rate.

4.3 LSV Test

The Co-HUT4 (or HUT4), Super P and PVDF binder were dispersed in NMP solvent with a weight ratio of 8:1:1 to form a uniform slurry. Then, the slurry was dropped onto the glassy carbon electrode. The LSV tests were performed at a scanning rate of 10 mV s^{-1} with $0.1 \text{ M Li}_2\text{S}$ /methanol solution as electrolyte, Pt sheet as the counter electrode and Ag/AgCl as reference electrode.

4.4 Li_2S_6 Adsorption experiment test

Firstly, the Li_2S_6 solution was prepared by mixing the Li_2S and sulfur

with a molar ratio of 1:5 in DME/DOL solvent (1:1 in volume). Then, the Co-HUT4 and HUT4 powders with a certain amount were immersed in 5×10^{-3} M Li_2S_6 solution and stand for 3 hours for comparison.