

Supporting Information

PPy-constructed core-shell structure from MOFs for confining lithium polysulfides

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Experimental Section

Synthesis of MIL-96

MIL-96 crystal was prepared using a solvothermal method. In detail, 5 mmol 1,3,5-benzenetricarboxylic acid (BTC) and 5 mmol aluminum nitrate nonahydrate were dissolved in 60 mL mixture solution of 30 mL N,N-Dimethylformamide (DMF)/30 mL deionized water. The obtained solution was transferred to a 100 mL Teflon high-pressure autoclave. After sealing, the autoclave was kept at 160 °C for 24 h and then naturally cooled down to room temperature. The precipitation was collected by centrifugation and washed several times with deionized water and methanol. Then the product was heated at 80 °C in vacuum drying oven for 24 h to remove the DMF and deionized water in MIL-96.

Synthesis of MIL-96-S

Sublimed sulfur was introduced into MIL-96 through a melt-diffusion method at 155 °C. 100 mg of MIL-96 powder was firstly grinded together with 150 mg of sublimed sulfur into a fine mixture that was transferred into a 25 mL Teflon-line sealed autoclave and heated at 155 °C for 12 h to generate the MIL-96-S sample.

Synthesis of MIL-96-S-PPy

To prepare MIL-96-S-PPy, we choose FeCl_3 as oxidizing agent to motivate the polymerization of pyrrole monomer. 200 mg of MIL-96-S particles were dispersed in 15 mL 0.4 M PVP aqueous solution via ultrasonic for 1 min. The resulting turbid suspension was stirred for 30 mins. In the same time, Fe^{3+} solution was prepared (0.9 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ + 10 mL deionized water). After centrifuging the above turbid

suspension using deionized water for three times, stirred with pyrrole monomers in 15 ml deionized water for 10 mins, the prepared Fe^{3+} solution (pyrrole: Fe^{3+} = 1:3 by molar ratio) was added and stirred in dark for 12 h at 0 °C. After reaction, the black precipitate was collected by centrifuging and washed repeatedly with deionized water and ethanol to remove pyrrole monomers and salt residue in the product. Finally, the precipitate was dried at 60 °C in vacuum for 12 h to provide the final dry MIL-96-S-PPy.

Characterization

SEM images were obtained using Zeiss-Supra 55 microscopes at an acceleration voltage of 5 kV. The PXRD patterns was performed by Bruker AXS D8 advance with Cu K α radiation of 40 kV (λ = 1.5418 Å). FT-IR measurement was investigated on a TENSOR27. The N₂ adsorption-desorption isotherms and pore size distributions were obtained by Autosorb-iQ via the BET method. EDS elemental mapping scans were recorded using Tecnai G2 F30 S-TWIN at an acceleration voltage of 300 kV. XPS analysis was carried out using a Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectrometer with Al K α radiation of 1486.6 eV as the excitation source. The survey thickness is 2-3 nm. Elemental analysis data (mass fraction) of samples were obtained from Vario EL cube Co.

Adsorption and soaking tests

For the adsorption test, 20 mg MIL-96-S and MIL-96-S-PPy were soaked in 3 mL Li₂S₄ solution (10 mmol/L). The Li₂S₄ solution were prepared in a solvent mixture of 1,3-dioxolane (DOL) and dimethoxyethane (DME) (1:1 in volume) according to the

reaction equation S(1):



UV-vis spectra of the above solutions (diluted 5 times before testing) were recorded by using a UV2550 instrument (Shimadzu, Japan). The concentration variation of polysulfides in these solutions was detected from the UV-vis spectra.

Li-S cell preparation and testing

Electrode preparation of MIL-96-S: The slurry was mixed with MIL-96-S, Super P, and Polyvinylidene Fluoride (PVDF) in a weight ratio of 7:2:1 in N-methyl-2-pyrrolidone (NMP) as dispersant. Then the slurry was cast on the Al foil and dried overnight at 60 °C under vacuum condition. The preparation of the sulfur electrode was different from the above. To improve the electrical conductivity of sublimed sulfur, Super P was firstly grinded together with sublimed sulfur (weight ratio of Super P and sublimed sulfur = 80:20) and transferred into a 25-mL Teflon-line sealed autoclave and heated at 155 °C for 12 h to generate the S-Super P, then mixed with Super P and PVDF like above. The obtained working electrodes were cut to obtain circular electrodes with a diameter of 12 mm. The accurate sulfur mass on each electrode was calculated according to thermogravimetric analysis (TGA) curves under N₂ flow and the elemental analysis data from Elementar, VarioELcube Co. The loading of active sulfur was 0.8-1.2 mg cm⁻². The CR 2032-type coin cells were fabricated using the working electrode, lithium foil as the counter and anode electrode, Celgard 2400 as the separator. The electrolyte was used 1.0 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI Sigma-Aldrich (USA), 99.95%) in 1, 3-

dioxolane (DOL, Sigma-Aldrich (USA), 99.0%) and 1,2-dimethoxyethane (DME, Sigma-Aldrich (USA), 99.0% (volume ratio, 1:1) with 1 $\omega\%$ LiNO₃. 35 μL of electrolyte was used in the fabrication of each Li-S cell in an argon-filled glove box (where both water and oxygen levels are below 0.1 ppm. The GCD tests were estimated in the voltage window of 1.7-2.7 V. The rate capability was also tested by varying the current density from 0.1 C to 1 C (1 C = 1675 mA g⁻¹) on a battery measurement system (CT2001A, Wuhan Land, China) at room temperature. CV and EIS curves were measured on an electrochemical workstation (CHI660E, Chenhua, Shanghai, China).

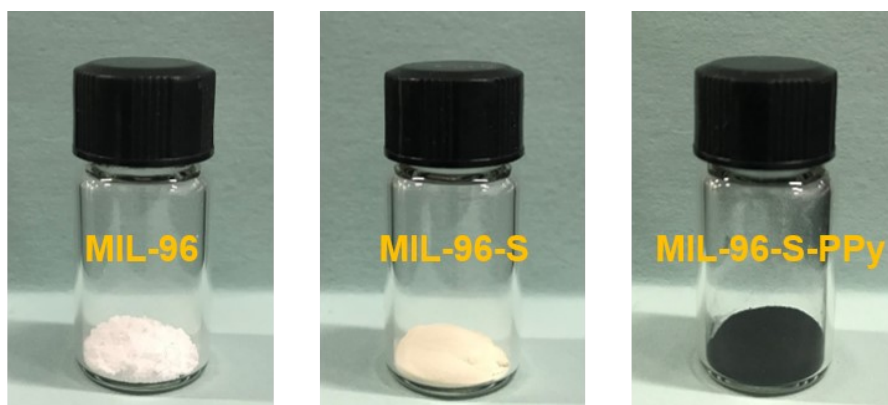


Fig. S1. Optical images of MIL-96, MIL-96-S, and MIL-96-S-PPy.

Table S1. Elemental analysis data (mass fraction) of the samples.

Samples	N %	C %	S %
MIL-96	2.73	35.24	0
MIL-96-S	1.08	13.61	59.45
MIL-96-S-PPy	7.64	38.42	41.50

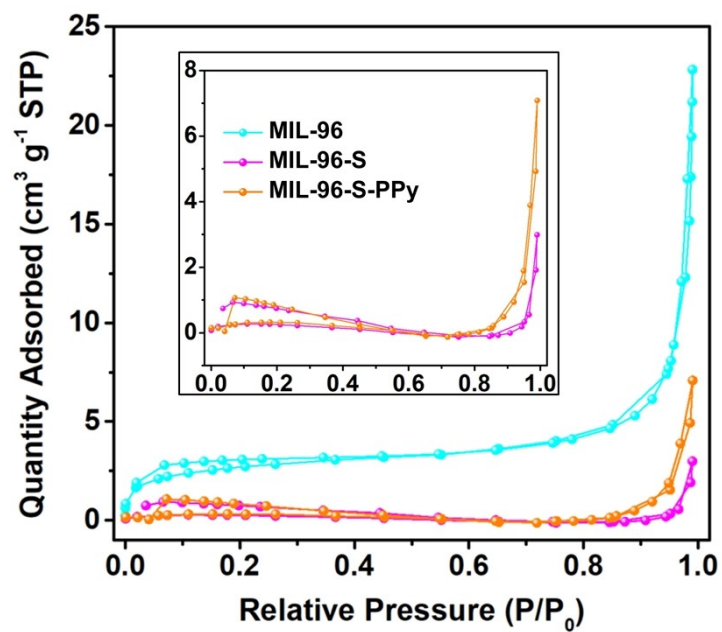


Fig. S2. N₂ adsorption-desorption isotherm of MIL-96, MIL-96-S, and MIL-96-S-PPy.

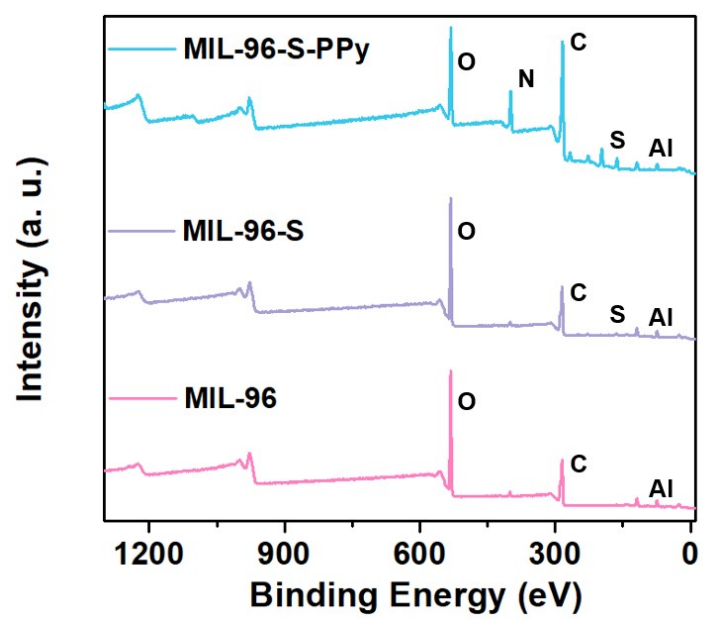


Fig. S3. Full XPS survey of MIL-96, MIL-96-S, and MIL-96-S-PPy.

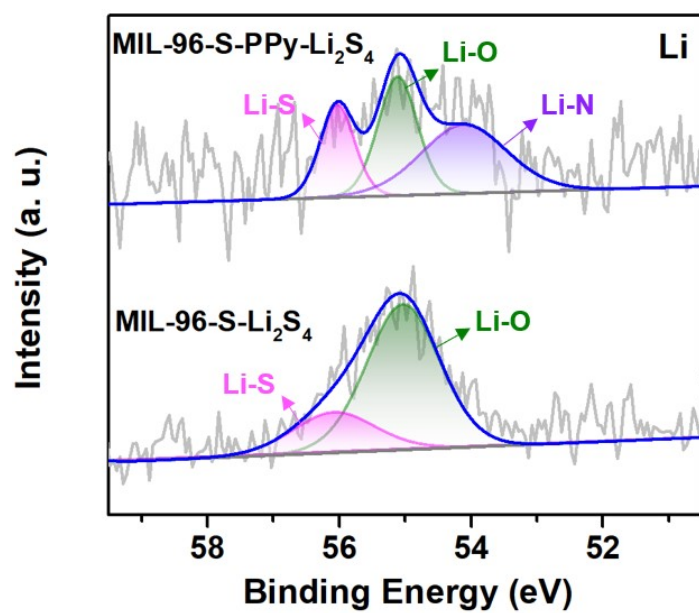


Fig. S4. Li 1s XPS spectra of MIL-96-S-Li₂S₄ and MIL-96-S-PPy-Li₂S₄.

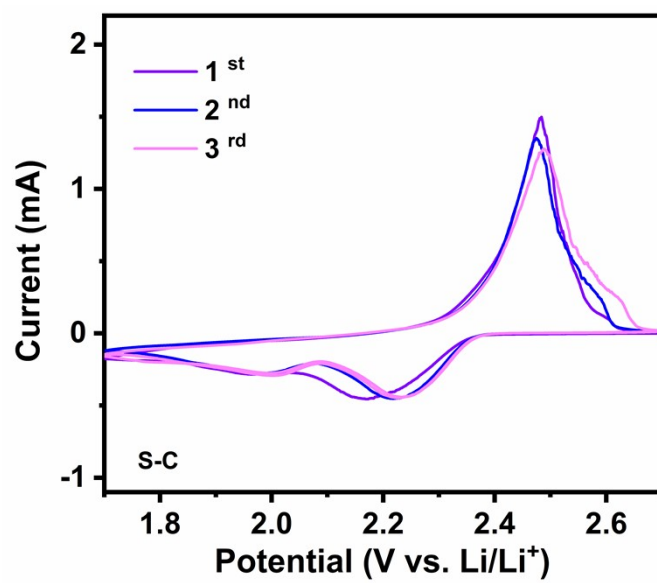


Fig. S5. CV curves of initial three cycles of S-C.

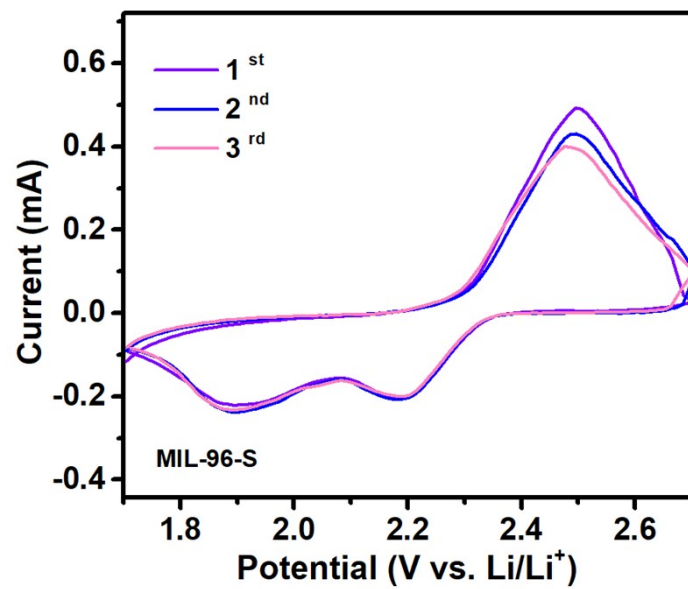


Fig. S6. CV curves of initial three cycles of MIL-96-S.

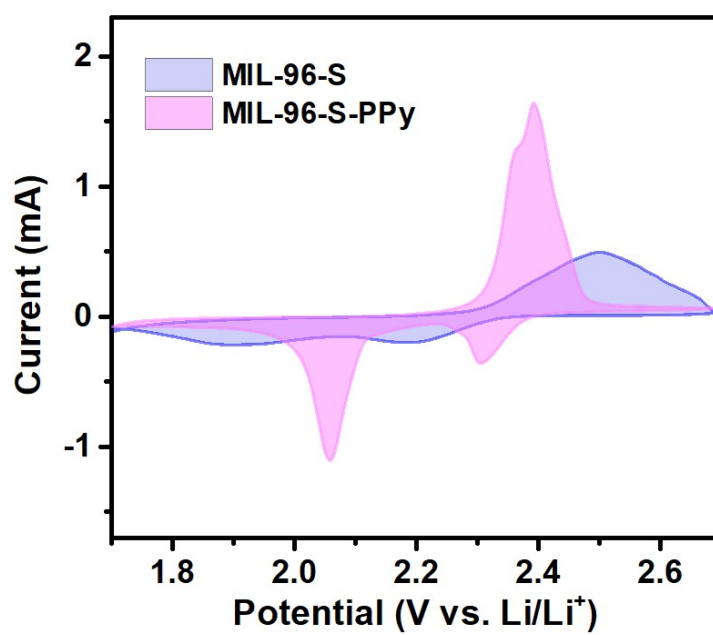


Fig. S7. Comparison of the first-circle CV curve of the MIL-96-S and MIL-96-S-PPy.

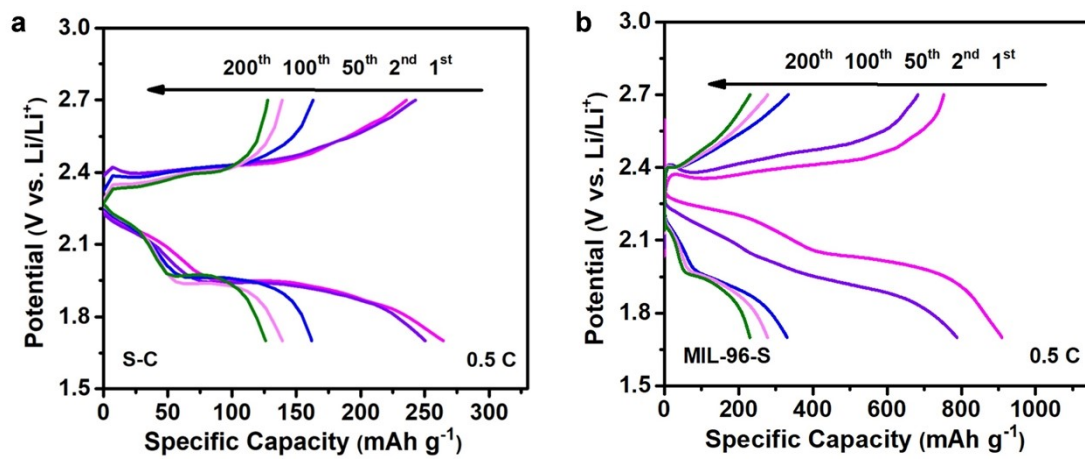


Fig. S8. GCD profiles of S-C and MIL-96-S at 0.5 C.

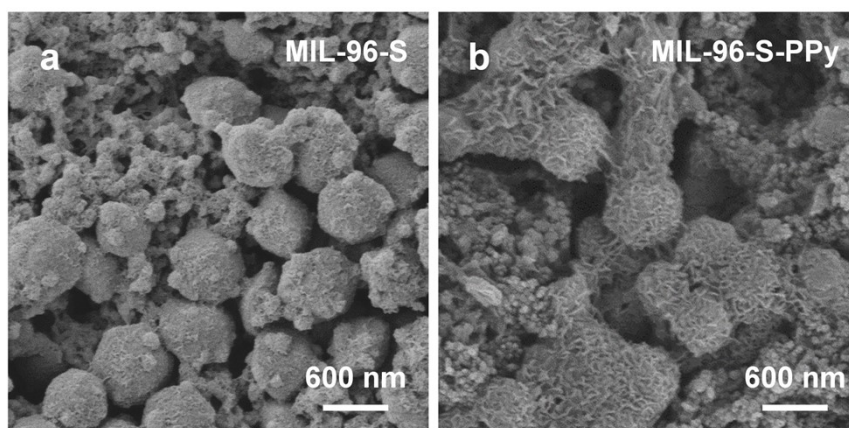


Fig. S9. SEM images of MIL-96-S and MIL-96-S-PPy on Al foil after 200 GCD cycles at 0.5 C.

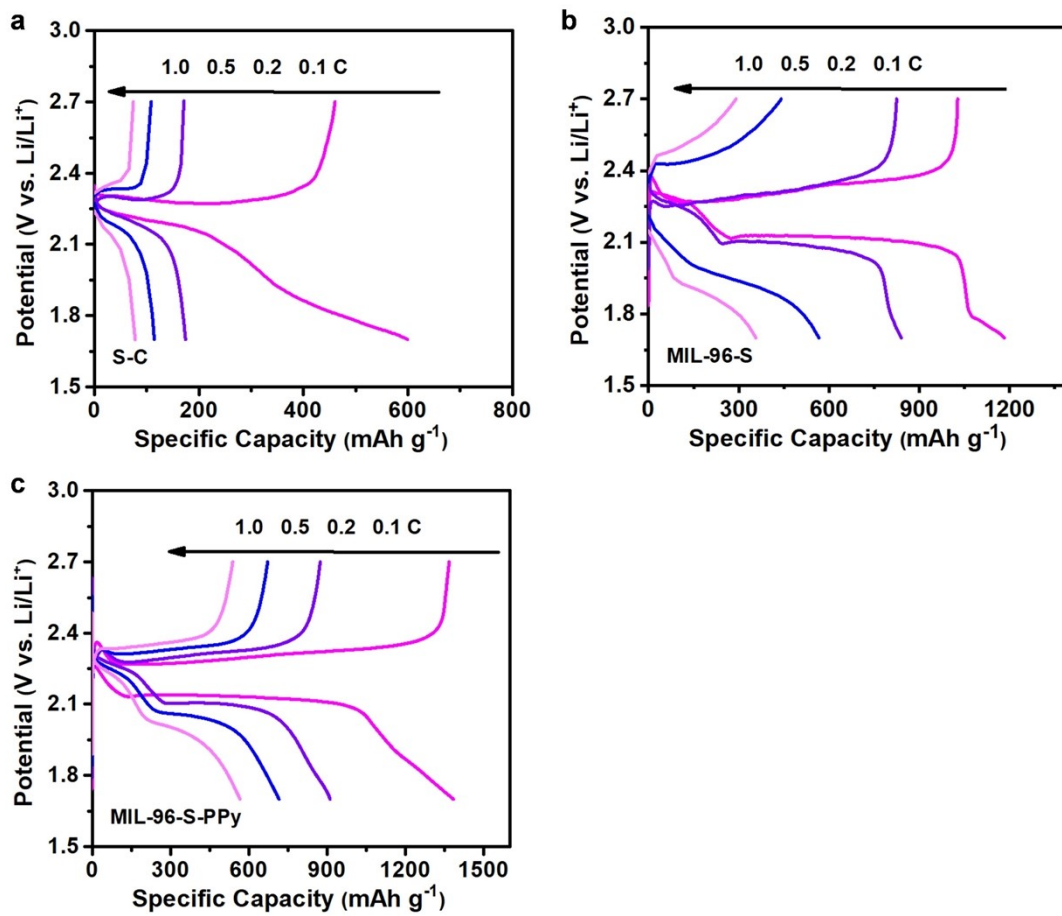


Fig. S10. GCD profiles of S-C, MIL-96-S, and MIL-96-S-PPy at different discharge rate.

Table S2. Comparison of the specific capacity for reported sulfur host.

Host Materials	Initial Capacity (mAh g ⁻¹)	Capacity after 100 cycles (mAh g ⁻¹)	Cycles Number	Final Capacity (mAh g ⁻¹)	Discharge Rate (C)	Ref.
S-in-MIL-101	~795	/	80	~310	0.3	1
S/NH ₂ -MIL-53	1125	/	70	436	0.1	2
MIL-100(Cr)/S	1580	/	60	~450	0.1	3
Ni-MOF/S	689	/	100	611	0.1	4
S/MOF-808 MeOH-TEA	~590	~440	300	~225	1.0	5
S@HKUST-1	657	/	50	~573	0.2	6
MIL-96-S-PPy	1233.8	423.3	200	308.7	0.5	This

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