Supplementary Information

From Industrial By-Products to High-Value Materials: Synthesizing Sulfur-Rich Polymers for Lithium-Sulfur Battery Cathodes from C5 Fraction and Sulfur

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1. Experimental Section

1.1 Materials

Sulfur (S_8; ≥99.5%; Shanghai Chemical Reagent Co., Ltd., China). Zn(DTC)$_2$ (Zinc diethyldithiocarbamate; ≥99%; Shanghai Bide Pharmaceuticals Science & Technology Co., Ltd., China). C5 fraction (PetroChina Lanzhou Petrol-Chemical Industry Company, the detailed composition is shown in Table S1). *N*-methyl-2-pyrrolidone (NMP), 1,2-dimethoxyethane (DME), 1,3-dioxolane (DOL), Lithium metal (Li), Poly(vinylidene fluoride) (PVDF 900), Ketjen Black (ECP-600 JD), Diaphragm (Celgard 2400), Cell shell (CR2032, 316 stainless steel), and carbon-coated aluminum foil (Al) were all of battery grade, Guangdong Zhuguang New Energy Technology Co., Ltd, China. The electrolyte was prepared and utilized within a glovebox, composed of a 1 M LiTFSI/0.1 M $LiNO_3$, dissolved in a mixed solvent of 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (v/v 1:1).

Table S1. Composition of C5 fraction

Compound type	Compound name	Content (wt%)
Diene	1,4-Pentadiene, 1,3-Butadiene, 1,3-Pentadiene, Cyclopentadiene, Isoprene, Dicyclopentadiene	58.05
Monoene	2-Butene, 1-Butene + Isobutene, 3-Methyl-1-Butene, 1-Pentene, Cyclopentene, 2-Pentene, 2-Methyl-1-Butene, 2-Methyl-2-Butene	18.98
Alkane	n-Butane, Neopentane, Isobutane, n-Pentane, Isopentane	18.75
Alkyne	Vinylacetylene, Butyne	1.36
Others	Unknown C4, Benzene, Sum of all light components up to C4	5.61

1.2 Synthesis of Poly(S-C5)

A typical procedure for the catalytic inverse vulcanization reaction involved the following steps: within the reactor, 10 grams of sulfur, 10 grams of C5 fraction (calculated based on unsaturated hydrocarbons), and 0.2 grams of Zn(DTC)$_2$ (1 wt%) were introduced, after which 10 mL of toluene was added as a solvent. Subsequently, the temperature was raised to 135 °C, and the reaction was carried out under cold reflux conditions. The heating was terminated as soon as the reaction system initiated gelation.

1.3 Materials Characterization Methods

1.3.1 Structural Characterization

The functional groups of the polymers were characterized using Fourier transform infrared spectroscopy (FT-IR, Digilab ft-3000) within the spectral range of 400-4000 cm^{-1}. Nuclear magnetic resonance spectroscopy (NMR, Varian Mercury -400 Plus) was employed to determine the elemental composition and structure of the polymers, using deuterated chloroform ($CDCl_3$) as the deuterated solvent. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal standard, and the solvent peak was recorded at 7.26 ppm for ^{1}H-NMR. The crystalline structure of the polymers was investigated using X-ray diffraction (XRD, Bruker D8 Advance) with Cu-targeted Kα-rays (λ = 1.5418 Å), scanning within a range of 5-80º at operating voltages of 40 kV and 100 mA. X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha) was utilized to analyze the elemental species, valence states, and content on the surfaces of the polymers.

1.3.2 Thermal Characterization

The thermal stability of the polymers was investigated via thermogravimetric analysis (TGA, HITACHI STA200) in a nitrogen atmosphere. The assessment was performed at a heating rate of 10 °C min^{-1}, ranging from room temperature to 800 °C. Differential scanning calorimetry (DSC, TA DSC25) was employed to examine the thermal transition behavior of the polymers under a nitrogen atmosphere. The temperature scope was between -50 °C and 150 °C, with a heating and cooling rate of 5 °C min^{-1}.

1.3.3 Microstructural Characterization

The microscopic morphology of the polymers and the composition of their microregions were examined using scanning electron microscopy (SEM, ZEISS GeminiSEM 300), complemented by energy-dispersive X-ray diffraction spectrometry (EDS). To enhance conductivity, the sample surfaces were coated with a layer of gold. The internal fine structure of the material was investigated using spherical aberration-corrected transmission electron microscopy (AC-TEM, FEI Theims Z).

1.4 Electrochemical Testing of Materials

1.4.1 Cell Preparation and Assembly

To eliminate any residual sulfur, the polymer was immersed in CS_2 before the preparation of the electrode paste. The polymer, Ketjen Black (ECP-600 JD), and poly(vinylidene fluoride) (PVDF 900) were manually grounded together in a mortar and pestle for 30 minutes in a ratio of 8:1:1. Subsequently, an appropriate amount of anhydrous *N*-methyl-2-pyrrolidone (NMP) was added to the mixture, and further grinding was conducted for 30 minutes to ensure the complete dissolution of PVDF 900. The resulting slurry was coated onto a smooth, flat, single-sided carbon-coated aluminum foil and then vacuum-dried at 60 °C for 24 hours. The resulting electrode was stamped into a 12 mm disc, and the active sulfur loading on all cathodes was controlled by approximately 2 mg cm^{-2}. The electrode was then placed in a glovebox for 12 hours to remove any residual oxygen and water from its surface. The CR 2032 coin cell was assembled in an argon-filled glovebox, using lithium as the negative electrode, Celgard 2400 polymer film as the separator, and 30 μL mg^{-1} of electrolyte. After allowing the cell to rest for 12 hours, it was subjected to testing.

1.4.2 Electrochemical Testing

Cyclic voltammetry (CV) experiments were performed using a Shanghai Chenhua electrochemical workstation. The CV scan rate was configured between 0.1 and 0.5 mV s^{-1}, with a voltage sweep extending from 1.7 to 2.8 V (vs. Li/Li^+). Constant-current charging/discharging tests were conducted on a Neware test system. within the voltage range of 1.8 to 2.7 V (vs. Li/Li^+) at different C rates (1 C = 1675 mAh g^{-1}, based on the mass of active sulfur). All tests were conducted at ambient temperature.

2. Results and Discussion

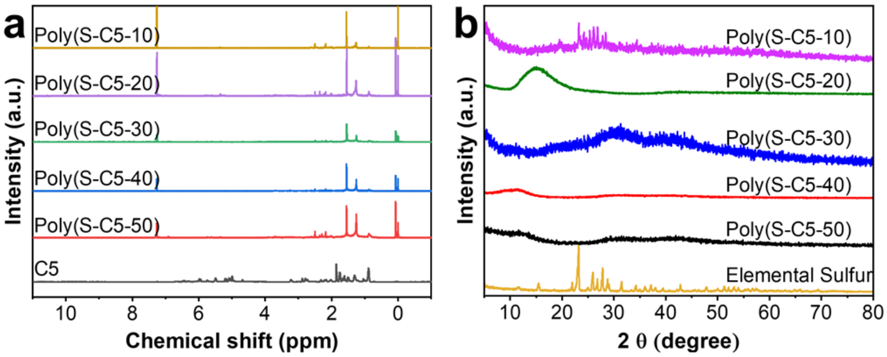

Figure S1. a) ^{1}H-NMR spectrum of Poly(S-C5-x). b) X-ray diffraction characterization of Poly(S-C5-x).

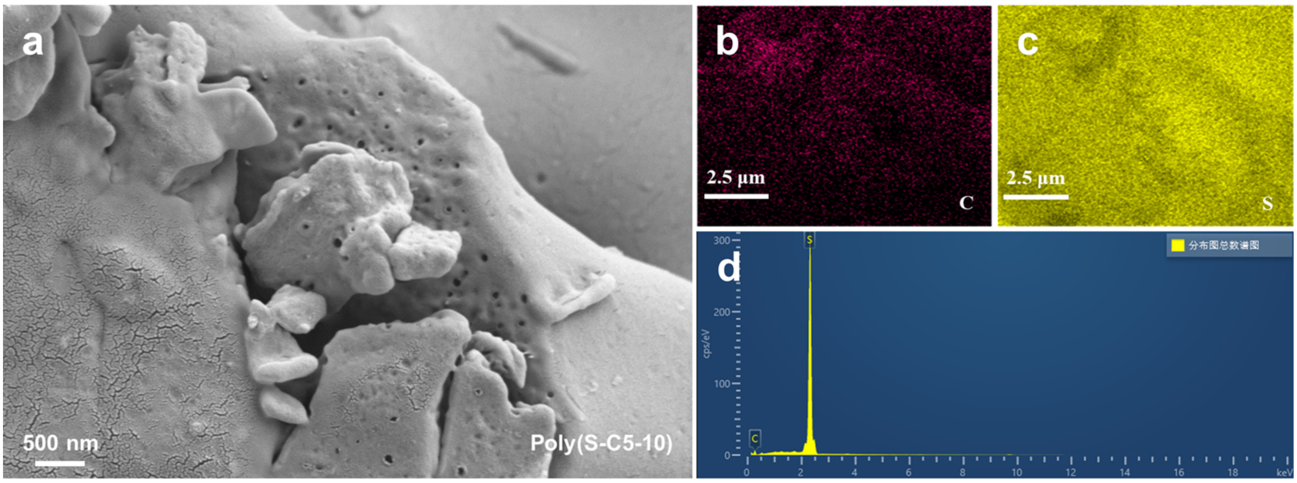

Figure S2. Microstructural characterization of Poly(S-C5-10). a) Scanning electron microscopy (SEM). b), c), and d) X-ray diffraction spectrometry (EDS).

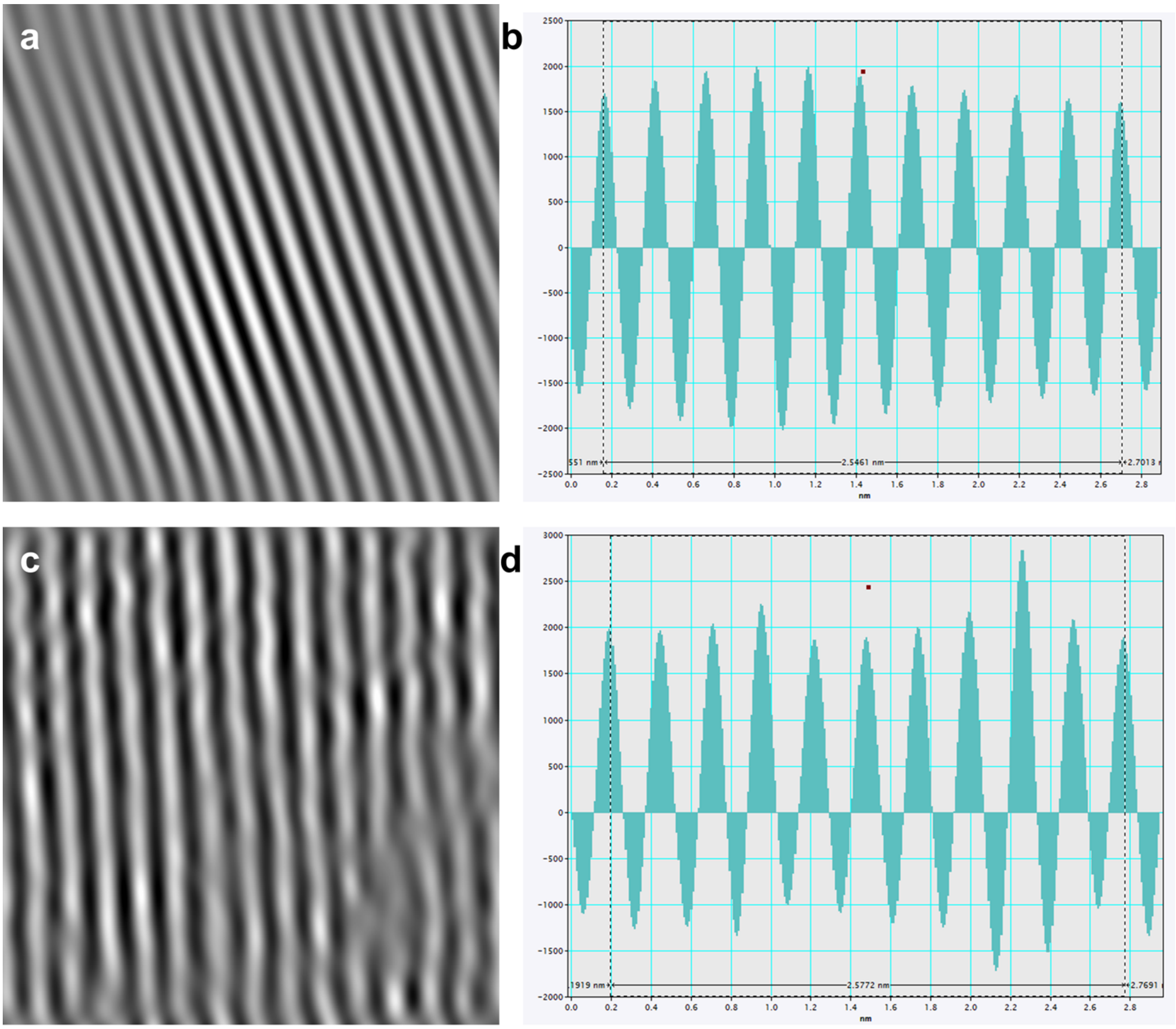

Figure S3. Spherical aberration-corrected transmission electron microscopy (AC-TEM) of Poly(S-C5-10). a) and c) Inverse fast Fourier transform. b) and d) Lattice spacing.