Synthesis of triazine-based covalent organic framework nanoparticles as cathode materials for lithium-sulfur batteries

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Materials

1,3,5-triformylphloroglucinol (Tp), 1,3,5-tris (4-aminophenyl)triazine (Tapt) were purchased from Jilin Chinese Academy of Sciences-Yanshen Technology Co., Ltd. Other reagents including 1,4-dioxane, mesitylene, N, N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), N-methylpyrrolidone (NMP), acetic acid, hexadecyl trimethyl ammonium bromide (CTAB) and sodium dodecyl sulfate (SDS) were purchased from Sigma-Aldrich Inc. The electrolyte (1 M LiTFSI in DOL/DMW, v:v = 1:1, including 1% $LiNO_3$) used in the electrochemical measurements was purchased from DoDoChem. None of the reagents mentioned above underwent further purification.

Experimental

Preparation of S@COF composites

The preparation process for S@COF composites was as follows, using 70S@TpTapt as an example. Took 39 mg of TpTapt and 91 mg of sublimed sulfur separately, grinding the mixture in a mortar for 20 min, then transferred it to a reactor and sealed it under an Ar atmosphere. The mixture was heated at 155°C for 12 h to melt the sulfur and embed it within the COF's pore structure. The resulting product contained

70% sulfur by mass and was designated as 70S@TpTapt. Similarly, TpTapt-NP and TpTapt-Mill were synthesized via the same procedure, yielding 70S@TpTapt-NP and 70S@TpTapt-Mill, respectively.

Preparation of S@COF electrode

Took 90 mg of the S@COF material to be tested and 45 mg of acetylene black. Ground the mixture in an agate mortar for 10 minutes, then transfered the mixture to a 10 mL glass vial and add 300 μL of PVDF solution (5%, w/v) dropwise to achieve a mass ratio of S@COF:PVDF = 6:3:1. Next, mixture was diluted with 0.7 mL NMP and stir at 800 rpm for 6 hours to obtain the electrode slurry. Applied the slurry uniformly onto aluminum foil and vacuum-dry at 60°C for 12 h. The aluminum sheet coated with electrode material was then cut into 12 mm diameter discs. The active material loading on each electrode was precisely determined by weighing, with the loading calculated solely based on the mass of sulfur. The active mass per electrode disc ranged from 0.8 to 1.1 mg.

Assembly of lithium-sulfur batteries

The entire battery assembly process was conducted in a glove box under an argon atmosphere with low moisture and oxygen content. The coin cell battery used was of the CR 2032 specification. First, the testing electrode was placed on the battery's cathode cap. 40 μL of the electrolyte (LiTFSI in 1 M DOL/DME (v:v=1:1), containing 1 % $LiNO_3$)was dispensed, followed by the placement of a 19 mm diameter separator. After that, a 15.8 mm diameter metallic lithium foil was placed next, followed by a stainless steel spacer and anode cap. The battery was then sealed and transferred outside the glove box, left to rest for 10 hours before testing.

Electrochemical performance tests

Electrochemical performance tests of lithium-sulfur batteries were conducted on an AutoLab electrochemical workstation. Cyclic voltammetry (CV) testing was

performed within a potential range of 1.7-2.8 V at scan rates of 0.2-1.0 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) testing was conducted within a frequency range of 0.01-100,000 Hz with an applied perturbation voltage of 5 mV.

Battery performance tests

The performance tests of lithium-sulfur batteries were conducted on the Neware CT-4008T battery workstation. Rate performance tests were performed at current densities of 0.1 C, 0.5 C, 1 C, 2 C, and 5 C (1 C = 1672 mA g^{-1}). After five cycles at each rate, the current density was reset to 0.1 C. The charge and discharge specific capacities were recorded for each cycle. Long-term stability testing was conducted at a current density of 2 C for 300 cycles.

Distribution of relaxation time (DRT) analysis

The DRT analysis of lithium-sulfur batteries was performed using the same cells as in electrochemical and battery performance testing. Test cells underwent 10 charge-discharge cycles at 2 C, followed by a discharge procedure. EIS spectra were recorded at 2.8 V, the discharge plateau, and 1.7 V respectively. The DRT analysis of the EIS spectra was performed using the DRTools software package, developed by Professor Francesco Ciucci's group which based on the radial basis functions (RBF) algorithm[1-4].

Supporting Figures

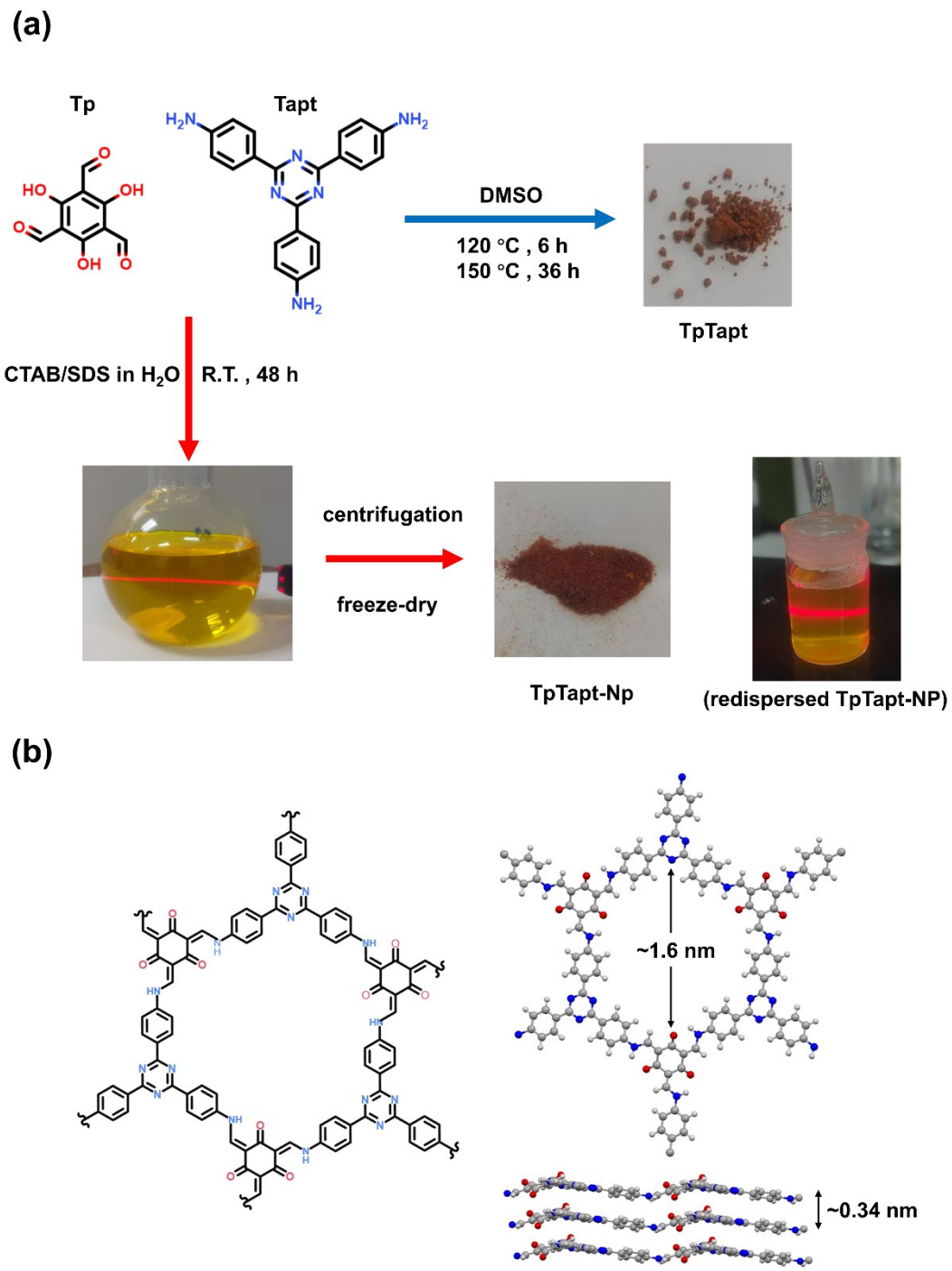

Fig. S1 (a)Synthesis process of TpTapt and TpTapt-NP, (b) the model of TpTapt after optimization

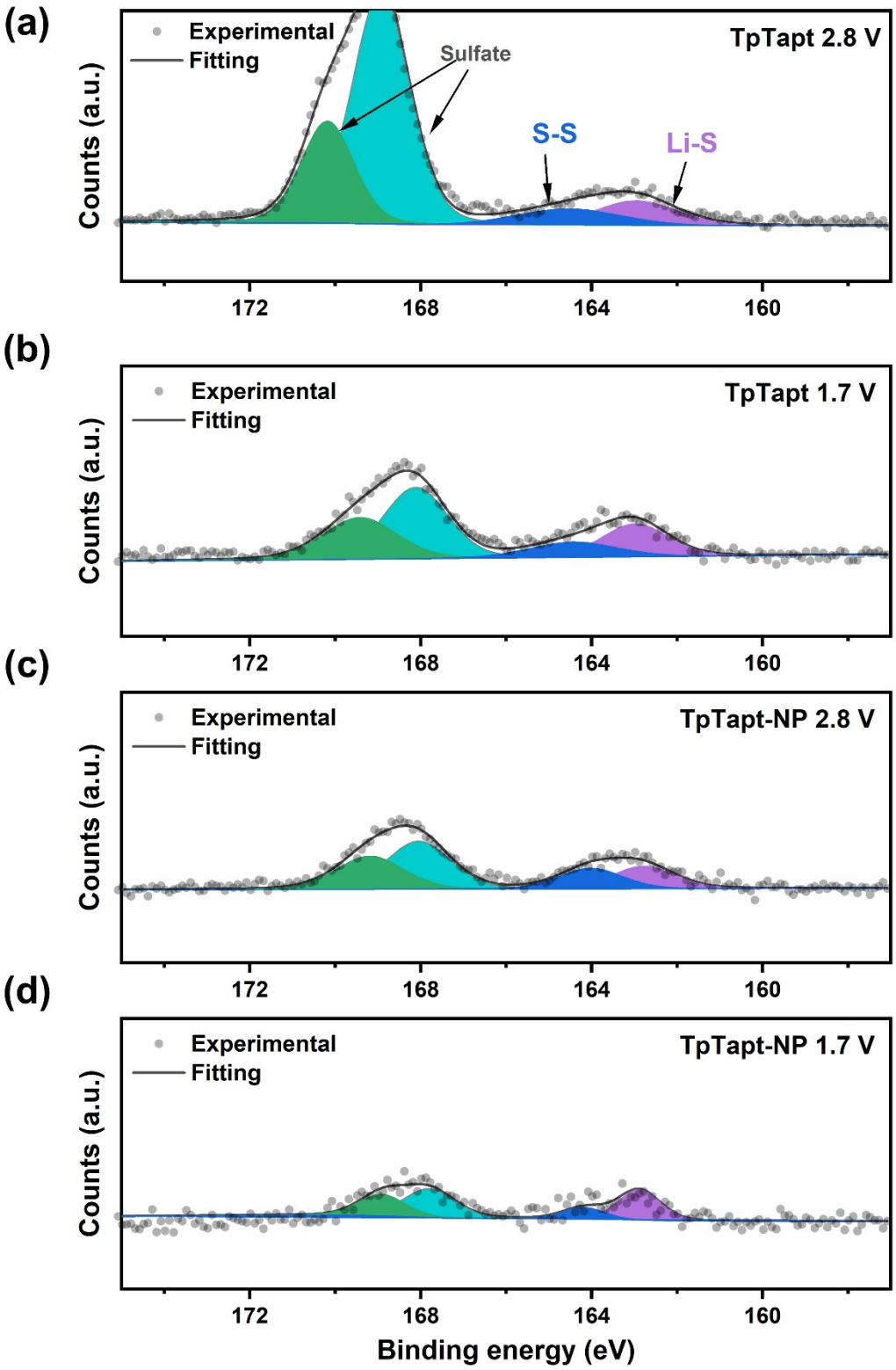

Fig. S2 XPS S2p spectra of (a-b) TpTapt and (c-d) TpTapt-NP electrode at 2.8 V and 1.7 V

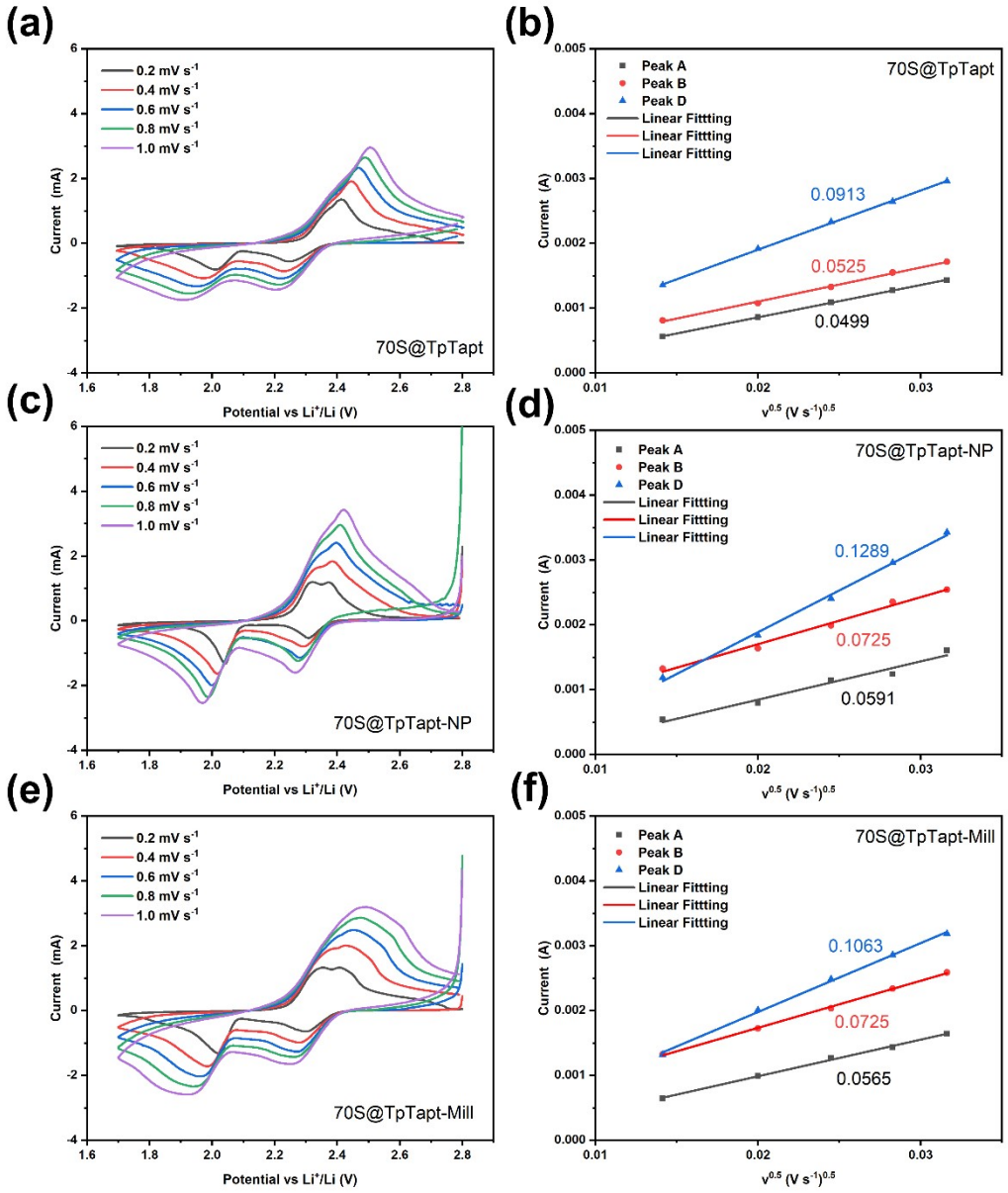

Fig. S3 CV curves of (a) (b)70S@TpTapt, (c) (d) 70S@TpTapt-NP, and (e) (f) 70S@TpTapt-Mill at different scan rates and results of fitting the Randles-Sevcik equation

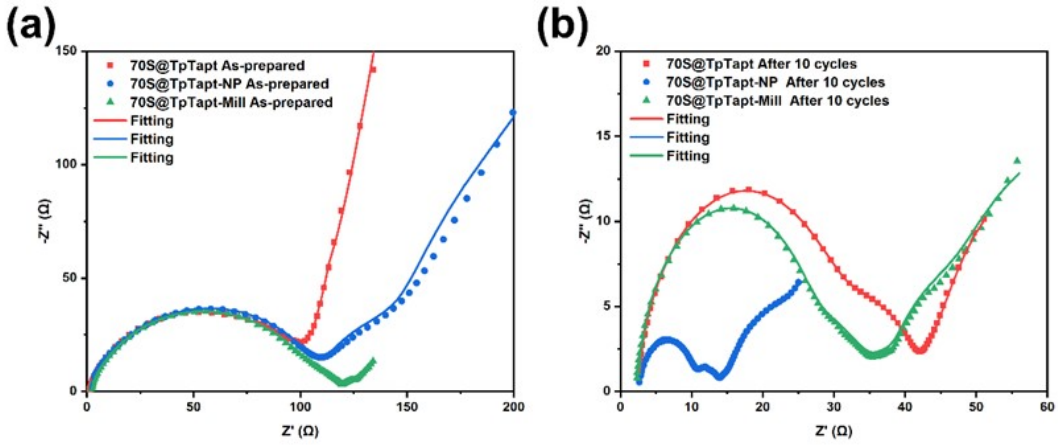

Fig. S4 Nyquist plots of 70S@TpTapt, 70S@TpTapt-NP, and 70S@TpTapt-Mill before (a) cycling and after (b) 10 cycles

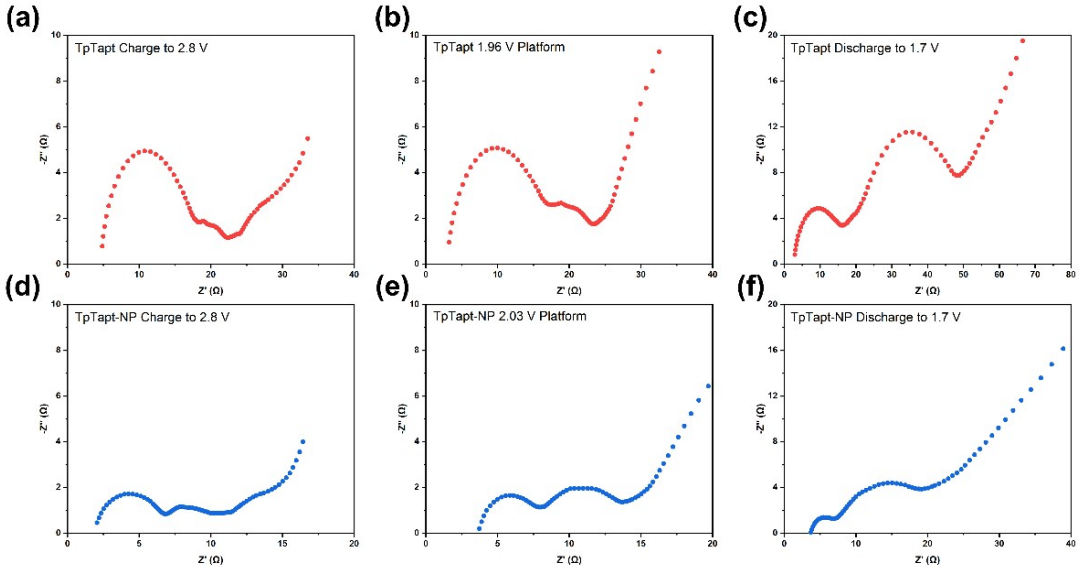

Fig. S5 Nyquist plots of (a-c) 70S@TpTapt and (d-f) 70S@TpTapt-NP at different potentials at a current density of 2 C

References

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3 J. Liu, T. H. Wan and F. Ciucci, *Electrochimica Acta*, 2020, **357**, 136864.
4 T. H. Wan, M. Saccoccio, C. Chen and F. Ciucci, *Electrochimica Acta*, 2015, **184**, 483-499.