Supporting Information

Facile Synthesis of Elemental Sulfur-Mediated Fluorine-Containing Covalent Triazine Frameworks and Their Performance in Lithium-Sulfur Batteries

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Materials and methods

Tetrafluoroterephthalonitrile (TFTN), 1,4-Dicyanobenzene (DCB) was purchased from the energy chemical; Anhydrous zinc chloride (ZnCl$_2$), Tetrahydrofuran (THF), and hydrochloride (HCl) were purchased from the Sinopharm Chemical Reagent Ltd. Co. (Shanghai, China); Crystalline Sulfur, Super P and poly(1,1-difluoroethylene) (PVDF) was purchased from the Aladdin; N-methyl-2-pyrrolidone (NMP) and carbon tetrachloride (CCl$_4$) was purchased from the Alfa Aesar. Unless stated otherwise, all the solvents and chemicals were of analytical grade and obtained from local suppliers and used without further purification.

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Perkin-Elmer model FT-IR-frontier infrared spectrometer. For all FT-IR tests, a small amount of samples can be directly mixed with potassium bromide and ground into a powder, and then compressed, and the pressed product can be directly tested. The solid UV-visible analyzer was used for Shimadzu UV-3600. For the UV test, the blank sample test is first carried out with the solid barium sulfate powder as the background, and then the holder with solid samples of composites was mounted onto the window of the integration sphere. X-ray photoelectron spectra (XPS) were recorded on an ESCALAB250Xi electron spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, USA). Field-emission scanning electron microscopy (FE-SEM) images were performed on a JEOL model JSM-6700 operating at an accelerating voltage of 5.0 kV. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku model RINT Ultima III diffractometer by depositing powder on glass substrate, from 20 = 2.5° up to 80° with 0.02° increment. Nitrogen sorption isotherms were measured at 77 K with ASIQ (iQ-2) volumetric adsorption analyzer. Before measurement, the samples were degassed in vacuum at 120 °C for more than 12 h. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface areas and pore volume. The non-local density functional theory (NLDFT) method was applied for the estimation of pore size and pore size distribution. The electrochemical properties of the samples were tested on a CHI660 electrochemical station. The method of preparing the measurement samples is the pulp cloth coating method. After assembling the CR2025
type coin cell, the electrochemical performance of the electrodes was tested at room temperature. The discharge charge performance of the battery was measured at the LAND electrochemical workstation. Cyclic voltammetry (CV) performance in the fixed potential range of 1.6-2.8 V (vs. Li⁺/Li) was tested on the CHI660 electrochemical station. The method for preparing the electrode is the pulp cloth coating method.
Synthetic procedures

Synthesis of FN-CTFs

Synthesis of FN-CTF(1:3): Tetrafluoroterephthalonitrile (TFTN, 30.1 mg, 0.15 mmol), 1,4-dicyanobenzene (DCB, 57.7 mg, 0.45 mmol) and anhydrous zinc chloride (ZnCl₂, 0.44 g) were mixed and ground, and then transferred to a quartz ampoule under an inert atmosphere. The ampoule was then circulated 3 times under vacuum/nitrogen. After evacuating 3 times, it was sealed, and then the reaction was heated to 400 °C for 40 h. After the reaction was complete, the ampoule was cooled to room temperature and opened. The reacted mixture was washed thoroughly with water to remove most of the ZnCl₂. The solid product was collected by filtration and washed sequentially with tetrahydrofuran and water, respectively. The product was then vacuum dried at 120 °C for 12 h. The isolated yield was about 72.6%. (Found: C 66.67%; H 2.05%; N 19.44%)

Synthesis of FN-CTF(1:x) (x=0.2, 0.5, 1, 5): Synthesis method refer to FN-CTF(1:3).

Synthesis of SFN-CTFs

Synthesis of SFN-CTF(1:2): The polymer FN-CTF(1:3) and crystalline sulfur S₈ were mixed and ground at a mass ratio of 1:2, and then transferred to a quartz ampoule under an inert atmosphere. The ampoule was then circulated 3 times under vacuum nitrogen. After evacuating 3 times, it was sealed, and then the reaction was heated to 160 °C for 20 h. After the reaction was complete, the ampoule was cooled to room temperature and opened. The reacted mixture was washed thoroughly with water and THF until floating black oil was no longer present. The product was then vacuum dried at 60 °C for 12 h. The isolated yield was about 93.5%. (Found: C 19.64%; H 0.11%; N 4.68%; S 71.91%)

Synthesis of SFN-CTF(1:x) (x=0.5, 1, 3, 4): Synthesis method refer to SFN-CTF(1:2).
Synthesis of SFN-CTF(1:2)-1 prepared by one-pot method

By studying the electrochemical properties of FN-CTFs and SFN-CTFs material, the best ratio of monomer TFTN, DCB and $S_8$ was found. According to this ratio, tetrafluoroterephthalonitrile (TFTN, 20.1 mg, 0.1 mmol), 1,4-dicyanobenzene (DCB, 38.4 mg, 0.3 mmol) and crystalline sulfur $S_8$ (0.117 g) were transferred into a quartz ampoule under inert atmosphere. After evacuating 3 times, it was sealed, and then the reaction was heated to 160 °C for 20 h, then heated to 400 °C for 20 h. All heating processes should be controlled at 5 °C min$^{-1}$. After the reaction was complete, the ampoule was cooled to room temperature and opened. The obtained black solid powder was washed thoroughly with water, THF and CCl$_4$, respectively. Then the product was vacuum dried at 60 °C for 24 h. Finally, SFN-CTF(1:2)-1 prepared by one-pot method was obtained with an isolated yield of about 69.8%. (Found: C 19.55%; H 0; N 4.42%; S 71.92%)
**Assembly of Li-S batteries**

Electrodes were fabricated using a slurry coating method. SFN-CTF(1:2) or SFN-CTF(1:2)-1, conductive additive (Super P), and binder polyvinylidene fluoride (PVDF) were mixed in N-methyl-2-pyrrolidone (NMP) at a weight ratio of 6:2:2, respectively, and converted into a slurry by thorough grinding in mortar. The slurry was coated on carbon-coated aluminum foil and dried at 60°C for 8 h. The prepared electrodes were cut into discs with a diameter of 12 mm and further dried in a vacuum oven at 60°C for 12 h before use.

**Assembly of a CR2025 coin cell battery**

SFN-CTF(1:2) electrodes and SFN-CTF(1:2)-1 electrodes were used as working electrodes, respectively. Li foils were used as counter and reference electrodes. The electrolyte is a mixture containing 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in, 1,3-dioxolane (DOL) and 1,2-dimethoxyethane (DME) (volume ratio is 1:1) and additives (0.5 wt% LiNO₃ solution) in 30 μL of each solution. Celgard 2500 membranes were used as separators, and cells were assembled in a glove box under an argon atmosphere. The sulfur loading of each electrode is 0.45~0.55 mg cm⁻².
Figure S1. UV absorption spectra of (a) the monomers TFTN, DCB and the polymers FN-CTFs, (b) FN-CTF(1:3), SFN-CTFs and crystalline sulfur, (c) FN-CTF(1:3), SFN-CTF(1:2) and SFN-CTF(1:2)-1.
**Figure S2.** PXRD patterns of the monomers TFTN, DCB and the polymers FN-CTFs.

**Figure S3.** X-ray photoelectron spectra of (a) FN-CTF (1:2) N 1s, (b) SFN-CTF (1:2) N 1s, (c) FN-CTF (1:2) F 1s, (d) SFN-CTF (1:2) F 1s.
Figure S4. SEM images of the FN-CTFs polymers (a) FN-CTF (1:5), (b) FN-CTF (1:3), (c) FN-CTF (1:1), (d) FN-CTF (1:0.5), and (e) FN-CTF (1:0.2), respectively (scale bar: 2 µm).

Figure S5. SEM images of the samples loaded with crystalline sulfur (a) SFN-CTF (1:2), and (b) SFN-CTF (1:2)-1 (scale bar: 3 µm).
Figure S6. The cyclic voltammetry curves with different scan rates of (a) FN-CTF (1:0.2), (b) FN-CTF (1:0.5), (c) FN-CTF (1:1), (d) FN-CTF (1:3) and (e) FN-CTF (1:5).
Figure S7. The cyclic voltammetry curves with a different scan rate of (a) SFN-CTF (1:0.5), (b) SFN-CTF (1:1), (c) SFN-CTF (1:2), (d) SFN-CTF (1:3), and (e) SFN-CTF (1:4).
Figure S8. PXRD of SFN-CTF(1:2)-1 and recovered SFN-CTF(1:2)-1.

Table 1 Comparison of electrochemical properties of SCTF in the literature.\textsuperscript{1-12}

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<thead>
<tr>
<th>Electrode material</th>
<th>Capacity (mAh g\textsuperscript{-1})</th>
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<tbody>
<tr>
<td>S@CTF-Mono</td>
<td>725</td>
</tr>
<tr>
<td>SF-CTF-1(1:3)</td>
<td>1138.2</td>
</tr>
<tr>
<td>S@CTF/TNS</td>
<td>1141</td>
</tr>
<tr>
<td>CTF@PDDA</td>
<td>970</td>
</tr>
<tr>
<td>CTF/CNT/Celgard</td>
<td>1314</td>
</tr>
<tr>
<td>CTF/MWCNT</td>
<td>982</td>
</tr>
<tr>
<td>cPpy-S-CTF</td>
<td>1203.4</td>
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<tr>
<td>NO-CTF-1</td>
<td>1250</td>
</tr>
<tr>
<td>CTF-PO71</td>
<td>869.9</td>
</tr>
<tr>
<td>S/P-CTFs@rGO</td>
<td>1130</td>
</tr>
<tr>
<td>FCTF-S</td>
<td>862</td>
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<tr>
<td>S@CTFO</td>
<td>791</td>
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References