Supporting information

# Chemically Anchoring of SeS<sub>2</sub> on Fluoro-Substituted Covalent Organic Framework as a High-Performance Cathode Material

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## 1. Materials and methods

All commercially available reagents and solvents were used as received without further purification, unless otherwise noted. 4,4',4"-(1,3,5-triazine-2,4,6-triyl)trianiline was synthesized following the published procedures. <sup>1</sup>H NMR spectra were taken on Inova 400 and Inova 500 spectrometers. Solid-state cross polarization magic angle spinning (CP/MAS) <sup>13</sup>C NMR spectra were recorded on an AVANCE III 400 MHz spectrometer produced by Bruker. The FT-IR spectra were obtained from Agilent Technologies Cary 630 FT-IR. Thermogravimetric analyses (TGA) were performed on a thermogravimetric/ differential thermal analyzer by heating the samples at 10 °C min<sup>-1</sup> to 700 °C under nitrogen atmosphere. The morphologies of COF-F and COF-F-SeS<sub>2</sub> were recorded by scanning electron microscopy (SEM, FEI SIRION200) and transmission electron microscopy (TEM, JEOL JEM-2100F). Before SEM tests, all the samples were coated with gold. The powder wide angle X-ray diffraction pattern (PXRD) were recorded on an X Pert-Pro MPD diffractometer (Netherlands PANalytical) with a Cu K $\alpha$  X-ray source ( $\lambda = 1.540598$  Å). X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCALab MKII X-ray photoelectron spectrometer using Mg-Ka radiation. According to the absorptiondesorption isotherms, BET (Brunauer-Emmett-Teller) specific surface area, pore size distribution and pore volume could be evaluated. Before each measurement, the samples were degassed at 100 °C for 6 h.

## 2. Electrochemical characterization

The cathode slurry was prepared by blending 70 wt.%  $SeS_2$  powder or the COF-F-SeS<sub>2</sub> composite (the content of  $SeS_2$  is 40 wt.%), 20 wt.% carbon black, and 10 wt.% PVDF in NMP solvent. Then, the obtained homogeneous slurry was pasted on an aluminum foil and dried at 60° for 12 h. Subsequently, the dried cathode was cut into discs with 12 mm diameter and used for cell assembly. Electrochemical measurements were performed by assembling CR2016 coin-type cells with lithium metal as the counter and Celgard 2400 membranes as the separator. The electrolyte contains 1 M lithium bis-trifluoromethanesulphonylimide (LiTFSI) in 1, 3-dioxolane (DOL) and 1, 2-dimethoxyethane (DME) (1:1 by volume) with 1 wt.% LiNO<sub>3</sub>. The ratio of electrolyte to active substance SeS<sub>2</sub> was around 10  $\mu$ L mg<sup>-1</sup>. The galvanostatic discharge and charge of Li-S cells were tested at a voltage range of 1.7-2.8 V using a LAND CT2001A battery test system. The cyclic voltammetry (CV) was measured on a CHI 660E electrochemical workstation in the voltage range of 1.7-2.8 V with the scan rate of 0.1 mV s<sup>-1</sup>. The electrochemical impedance spectroscopy (EIS) was tested from 1 Hz to 100 KHz.

#### 3. Experimental procedures

#### 3.1 Synthesis of COF-F

To a glass tube (5 mL, the outer diameter is 10 mm and the inner diameter is 8 mm) was added 2,3,5,6-tetrafluoroterephthalaldehyde 1 (15 mg, 0.075 mmol) 4,4',4"- (1,3,5-triazine-2,4,6-triyl)tria-niline 2 (18 mg, 0.05 mmol), 3 M acetic acid (0.1 mL), dioxane (1.8 mL), and mesitylene (0.2 mL). The tube was flash frozen at 77 K in liquid nitrogen and evacuated to the internal pressure of ~100 mTorr, and then sealed under an open flame. The mixture was first warmed to room temperature and then the temperature was slowly raised to 120 °C over 2 h. The reaction was kept at this temperature for 3 days and cooled to room temperature over 12 h. The orange precipitate was collected by vacuum filtration, washed with a large amount of acetone and CH<sub>2</sub>Cl<sub>2</sub>, and dried under vacuum to yield the fluorinated COF (COF-F, 24 mg, 74%).

### 3.2 Synthesis of COF-F-SeS<sub>2</sub>

The COF-F-SeS<sub>2</sub> was synthesized using similar procedures as reported.<sup>1</sup> COF-F and the commercial SeS<sub>2</sub> were mixed in a glass tube (10 mL, 10 mm outer diameter and 8 mm inner diameter) with a polymer/SeS<sub>2</sub> weight ratio of 1:4. The tube were degassed and sealed under an open flame. The tube was heated at 380 °C for 8 h, after cooling to room temperature, the obtained black powder was COF-F-SeS<sub>2</sub>. Carbon material (COF-F) was prepared in a similar way.

The formation mechanism of COF-F-SeS<sub>2</sub> during synthetic process can be explained as follows:

(1) During the heating process, the eight-membered ring was changed into linear chain compound at 155 °C which was similar to sulfur. At this stage, homogenous mixture of COF-F and the linear chain  $SeS_2$  was formed.<sup>2</sup>

(2) The heat treatment at 380 °C facilitated the formation of linear ionic chain which can act as nucleophiles for the chemical impregnation of SeS<sub>2</sub> via  $S_NAr$  reaction. During this process, C-S or C-Se bonds were formed and the SeS<sub>2</sub> was chemically confined in the porous structures of the COF-F.<sup>3</sup>

(3) As the temperature drops, the unreacted  $SeS_2$  was left on the surface or in the pore of COF-F and finally confined in the frameworks.

#### 3.3 Synthesis of COF-F@SeS<sub>2</sub>

To explore the structure stability of COF-F during preparation of COF-F-SeS<sub>2</sub>, the stored SeS<sub>2</sub> in COF-F-SeS<sub>2</sub> was removed as far as possible by CS<sub>2</sub> washing at room temperature for 12 h and Soxhlet extracted at 100 °C for another 12 h. After 72 h freeze drying, COF-F@SeS<sub>2</sub> was obtained and sent to TEM experiment.



Fig. S1 The probable formation mechanism of COF-F-SeS<sub>2</sub>.



Fig. S2 FT-IR spectra of COF-F and COF-F-SeS<sub>2</sub>.



Fig. S3 Raman spectrum of COF-F-SeS<sub>2</sub>.



Fig. S4 The HRTEM image of COF-F@SeS<sub>2</sub>.



Fig. S5 N<sub>2</sub> adsorption-desorption profiles and pore size distribution of COF-F-SeS<sub>2</sub>.



**Fig. S6** Charge-discharge curves of host materials (COF-F post treated similar as preparation of COF-F-SeS<sub>2</sub>) repeated for 4 time.

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Active	Initial capacity	Rate capacity	long-term cycling	SeS <sub>2</sub>	re
material	$(mAh g^{-1})$	$(mAh g^{-1})$	stability	conte	f
				nt	
				(wt%)	
S-SeS <sub>2</sub> -	1218 mAh g <sup>-1</sup> at	585, 812	0.0549% capacity	SeS <sub>2</sub> :	4
DIB@KB600	100 mA g <sup>-1</sup>	mAh g <sup>-1</sup> at	decay per cycle	S=1:9	4

Table S1 Comparison with other reported SeS<sub>2</sub> cathode materials.

		2000 100mA	(500 cycles at		
		α <sup>-1</sup>	$(300 \text{ cycles at} 1000 \text{ m} \text{ s}^{-1})$		
Costal BC/Sos	$868 \text{ mAh } \alpha^{-1}$ at	5	0.10% capacity		
C052@LIC/5C5		1090,1038,	dagay par avala		
2	0.3 A g <sup>-</sup>	$526 \text{ m Ab } \text{s}^{-1}$	(400 explagat 0.5		
		526 mAn g		70.	5
		at	A g <sup>-1</sup> )		
		0.1, 0.2, 0.5,			
		1, and 2 A $g^{-1}$			
Co–N–C/SeS <sub>2</sub>	1153.5 mAh g <sup>-</sup>	760, 604.1,	0.08% capacity		
	<sup>1</sup> at 0.2C	and 439.7	decay per cycle		
		mAh g <sup>-1</sup> at 1,	(200 cycles at	66.5	6
		2 and 4C	0.2C)		
SeS <sub>2</sub> @MCA	1150, 816mAh	1129,1012	0.49% capacity		
	g <sup>-1</sup> at 50, 500	and 846 mAh	decay per cycle		
	mA g <sup>-1</sup>	g <sup>-1</sup> at 100,	(130 cycles at 500	49.3	7
	e	250 and 500	$mA g^{-1}$		
		mA g <sup>-1</sup>			
SeS <sub>2</sub> /DLHC	930 mAh g <sup>-1</sup> at	1070 800	0.012% capacity		
5052/DEIIC	020	and 400 mAh	decay per cycle		
	0.2 C	$\sigma^{-1}$ at 0.1.0.5	(900 cycles at 1	75	8
		g at 0.1, 0.5	() of cycles at 1	15	0
			C)		
COF-F-SeS <sub>2</sub>	1633 mAh g <sup>-1</sup>	1703, 1318,	0.276% capacity		Т
-	at 0.1 C	1157, 983	decay per cycle		hi
		and 270 mAh	(200  cycles at  1)		S
		g <sup>-1</sup> at 0 1 0 2	() ()	40	w
		0.5 1  and  2	2)		or
		C			k
SeS <sub>2</sub> /DLHC COF-F-SeS <sub>2</sub>	930 mAh g <sup>-1</sup> at 0.2 C 1633 mAh g <sup>-1</sup> at 0.1 C	250 and 500 mA g <sup>-1</sup> 1070, 800 and 400 mAh g <sup>-1</sup> at 0.1, 0.5 and 6 C 1703, 1318, 1157, 983 and 270 mAh g <sup>-1</sup> at 0.1, 0.2, 0.5, 1 and 2 C	mA g <sup>-1</sup> ) 0.012% capacity decay per cycle (900 cycles at 1 C) 0.276% capacity decay per cycle (200 cycles at 1 C)	75 40	8 T hi s w or k



Fig. S7 The equivalent circuit used to fit the measured impedance spectra.

**Tab. S2** The  $Li^+$  ion diffusion coefficient of different cathodes.

Sample	σ	$D_{Li^+} (cm^2 s^{-1})$
$SeS_2$	81.97125	2.5751×10 <sup>-19</sup>

COF-F@SeS <sub>2</sub>	31.39111	1.7559×10 <sup>-18</sup>
COF-F@SeS <sub>2</sub> after cycle	37.77852	1.2124×10 <sup>-18</sup>

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