Inverse-Vulcanization of Vinylic Functionalized Covalent Organic Frameworks as Efficient Cathode Materials for Li-S Batteries

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Section 1. Materials and Methods

All starting chemical materials were directly used from commercial suppliers without further purification. Solvents were purified according to the standard procedures.

High resolution scanning electron microscopy (SEM) images of the COF morphologies was obtained using a Hitachi S-4800 cold field emission scanning electron microscope. High resolution transmission electron microscopy images (HRTEM) was obtained on a JEOL JEM-2100F electron microscope with a LaB6 filament operated at 200 kV. FT-IR-ATR spectra were recorded on a VERTEX 70v FTIR spectrometer (Bruker Optics). ¹H NMR spectra were recorded on a Bruker Advance DPX 400. ¹³C cross-polarization magic angle spinning (CP/MAS) spectra were recorded with a 4 mm double resonance MAS probe and at a MAS rate of 10.0 kHz with a contact time of 2 ms (ramp 100) and a pulse delay of 3 s. Elemental analysis (C, H, N, S) were performed on a Elementar Vario macro cube elemental analyzer. Thermal gravimetric analyses (TGA) was carried out on a TA Instruments TGA Q50-1918 analyzer under nitrogen atmosphere with a heating rate of 10 °C min⁻¹ from ambient temperature to 800 °C using an empty Al₂O₃ crucible as reference. Surface areas and pore size distributions were measured by nitrogen sorption at 77.3 K using a BELSOPR-max analyzer and the samples were degassed at 100 °C for 6 h under vacuum (10^{-5} bar) before analysis. The pore size distribution was calculated from the adsorption branch with the nonlocal density functional theory (NLDFT). The Powder X-ray diffraction (PXRD) spectra were recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA with a Cu-target tube and a graphite monochromator.

The vulcanization of COF-V were performed in a two-step manner. The activated COF-V and elemental Sulphur were uniformly mixed in a weight ratio of 1/3 by grounding. Subsequent thermal treatment at 155°C for 10 h under vacuum in a sealed tube enable the fluid of molten liquid sulphur infiltrated into the pores. Further heat treatment at elevated temperature of 200 °C for additional 6 h ensured the ring-opening

polymerization (ROP) of S_8 and fully copolymerization between the polysulphur diradicals and vinyl groups. The obtained material was then transferred into tubular furnace and heated at 200 °C under nitrogen for 2 h to evaporate the surface Sulphur.

The sulfur cathode was prepared by mixing 60 wt% S-COF-V, 30 wt% acetylene black and 10 wt% sodium alginate (SA) into a paste and pasted onto an aluminum film. The film disks were dried at 50 °C for 24 h. The resulted cathode foil was pressed and cut into circular sheets with a diameter of 9 mm. The mass loading of active sulfur was ~ 0.7 mg cm⁻². All electrochemical tests for the sulfur electrode were carried out by using coin cells with lithium sheet as counter electrode and reference electrode and a mixed solution of 1,3-dioxolane and 1,2-dimethoxyethane (1:1 v/v) containing 1.0 M lithiumbis(trifluoromethanesulfonyl)imide (LiTFSI) and 0.1 M LiNO₃ as the electrolyte. A microporous membrane (Celgard 2300) was used as the separator. A carbon nanofiber interlayer was put among the cathode and separator as upper collector. The coin cells were assembled in an argon-filled glove box with oxygen and moisture contents of less than 0.1 ppm. The adding amount of the electrolyte in a single coin cell is ~ 30 uL. In addition, conventional sulfur cathodes were also prepared at a sulfur/conductive carbon black/SA mass ratio of 50:40:10. The galvanostatic discharge/charge experiments were performed at a voltage interval of 1.7- 2.8 V (vs Li⁺/Li) on a programmable computer-controlled battery tester (Land CT 2001A). The specific capacity was calculated on the basis of the active sulfur material. Cyclic voltammetry (CV) measurement was conducted on a CHI 660E electrochemical workstation with a scan rate of 0.1 mV S⁻¹ in the potential range of 1.7-2.8 V (vs Li^+/Li). The impedance spectra were recorded using a frequency response analyzer (1400, Solartron Analytical) coupled with an electrochemical interface (1470, Solartron Analytical) at a sinusoidal perturbation of 5 mV and in the frequency range 1 mHz-100 kHz.

Section 2. Synthetic Procedures

The detailed synthetic methods including the monomers and COFs are given as follows:

2, 5-divinylterephthalaldehyde was synthesized according to literature.¹



2,5-dibromobenzene-1, 4-dicarbaldehyde:

To a mixture of 2,5-dibromo-*p*-xylene (8.0 g), acetic acid (40 mL), acetic anhydride (80 mL) at 0 °C, sulfuric acid (28 mL) was added dropwise. CrO_3 (12.0 g) was then added to the mixture in small portions. The resultant mixture was stirred at 0 °C overnight. The greenish slurry was poured into ice water, filtrated, and washed with water and methanol. The obtained diacetate was then hydrolyzed by refluxing with a mixture of water (40 mL), ethanol (40 mL) and sulfuric acid (4 mL) overnight. The product was obtained by filtration, which was used directly for the next step without further purification. Yield: 2.5 g (28%).¹H NMR (400 MHz, CDCl₃, 298 K): \Box 10.34 (s, 2H), 8.15 (s, 2H) ppm.

2, 5-divinylterephthalaldehyde:

Potassium vinyltrifluoroborate (4.57 g, 33.1 mmol), K₂CO₃ (11.3 g, 82.2 mmol), and Pd(PPh₃)₄ (0.456 g, 0.41 mmol) were dissolved in a mixture of toluene (50 mL), THF (50 mL) and H₂O (10 mL), the resulting mixture was refluxed at 90 °C under N₂ atmosphere for 24 h. The residue was extracted with ethyl acetate, washed with brine, dried over Na₂SO₄, and evaporated under reduced pressure. The crude compound was purified by flash chromatography with hexane/ethyl acetate (5:1) as eluent to afford the target compound as yellow solid. Yield: 2.0 g (78%). ¹H NMR (400 MHz, *d*₆-DMSO, 298 K): δ 10.34 (s, 2H), 8.19 (s, 2H), 7.59-7.66 (m, 2H), 5.97 (d, 2H), 5.58 (d, 2H) ppm.

1, 3, 5-tris-(4-aminophenyl)benzene was synthesized according to literature.^{2,3}



1, 3, 5-Tris(4'-nitrophenyl)benzene:

SiCl₄ (20 mL, 0.18 mol) was added dropwise to a solution of *p*-nitroacetophenone (10 g, 0.06 mol) in absolute ethanol (60 mL) at 0 °C. A yellow precipitate was formed immediately and then the mixture was refluxed for 10 h. After the mixture was cooled to room temperature, saturated NH₄Cl (100 mL) was added and stirred for 10 min. The obtained yellow precipitate was filtered and dried.

1, 3, 5-Tris(4'-aminophenyl)benzene:

To a slurry of 1, 3, 5-tris-(4'-nitrophenyl)benzene (8.8 g, 20 mmol) and tin granules (47 g, 0.40 mol) in ethanol (20 mL), concentrated HCl (12 N, 200 mL) was added slowly with vigorous stirring under reflux. After 8 h, the reaction mixture was cooled to RT and the precipitate was collected by filtration. The solid was dissolved in water (200 mL) and filtered to remove residual tin. The filtrate was treated with NaOH solution (30%). The product was precipitated by triturating the solution, collected by filtration, washed with water repeatedly, and dried under vacuum. Pale yellow product was obtained (6.0 g, 87%). ¹H NMR (400 MHz, d_6 -DMSO, 298 K): δ 7.48 (s, 3H), 7.46 (m, 6H), 6.67 (m, 6H), 5.22 (s, 6H).

Synthesis of COF-V1

A Pyrex tube (o.d.×i.d. = $9.5 \times 7.5 \text{ mm}^2$) was charged with 2, 5divinylterephthalaldehyde (22.3 mg, 0.12 mmol) and 1,3, 5-tris(4aminophenyl)benzene (28.0 mg, 0.08 mmol) in 1.1 mL of a 5:5:1 v/v/v solution of *o*dichlorobenzene/1-butylalcohol/6 M aqueous acetic acid. The tube was flash frozen at 77 K (liquid N₂ bath), evacuated, and flame-sealed. Upon sealing, the length of the tube was reduced to ca. 15 cm. The reaction mixture was heated at 100 °C for 3 days to afford a yellow precipitate which was isolated by filtration and washed with anhydrous tetrahydrofuran using Soxhlet extraction for 24 h. The product was dried under vacuum at 100 °C.

Synthesis of the COF without vinyl groups⁴

A Pyrex tube (o.d.×i.d. = $9.5 \times 7.5 \text{ mm}^2$) was charged with terephthalaldehyde (16 mg, 0.11 mmol), tris(4-aminophenyl)benzene (28 mg 0.08 mmol), *o*-dichlorobenzene (0.5 mL), 1-butanol (0.5 mL) and aqueous acetic acid (100 µL, 6M). The tube was flash frozen at 77 K (liquid N₂ bath), evacuated, and flame-sealed. Upon sealing, the length of the tube was reduced to ca. 15 cm. The mixture was heated at 120 °C for 3 days to afford a yellow precipitate which was isolated by filtration and washed with acetone using Soxhlet extraction for 24 h. The product was dried under vacuum at 100 °C.

Section 3. TEM Images



Figure S1. The TEM images of (a) COF-V, (c) S-COF-V and HRTEM images of (b) COF-V, (d) S-COF-V.

Section 4. Element Analysis and Thermal Gravimetric Analysis

Sample	C (%)	H (%)	N (%)	S (%)
COF-V	82.23	6.53	5.55	
S-COF-V	27.79	3.26	2.30	67.42

Table S1. Elemental analysis of COF-V and S-COF-V (Wt %)



Figure S2. The TGA curves of COF-V and S-COF-V.

Section 5. Solid State ¹³C CP/MAS NMR Spectra



Figure S3. ¹³C MAS NMR spectra of COF-V and S-COF-V.

Section 6. X-ray Photoelectron Spectroscopy (XPS)



Figure S4. XPS spectra of S-COF-V: (a) Full spectrum; (b) N 1s spectrum.



Figure S5. XPS spectra of COF-V: (a) Full spectrum; (b) N 1s spectrum; (c) C 1s spectrum.



Section 7. Electrochemical Performance

Figure S6. The first four CV cycling curves of the control samples: (a) S/COF and (b) S/C.



Figure S7. The discharge and charge capacity of the COF-V substrate at 0.2 C.



Figure S8. The typical charge-discharge curves of S-COF-V during long cycles at 0.2C.



Figure S9. (a) Nyquist plots of S-COF-V at different cycles and (b) The comparison of Nyquist plots of S/C, S/COF and S-COF-V, the resistance.



Table S2. Comparison of the resistance of XXX for S-COF-V, S/COF and S/C.

	S-COF-V	S/COF	S/C	
$R_{s}(\Omega)$	5.1	6.2	3.7	
$R_{CT}(\Omega)$	51.9	65.1	32.5	

battery cathode.							
	Sulfur	Init	ial spec	ific	Cycle	Fading	
COF	Content	capac	ity (m A	(h g1)	performance	Rate	Ref.
	(wt %)	0.2C	0.5C	1C	(m Ah g-1)	(%)	
					100th, 959@0.2 C	0.31%	This
S-COF-V	67%	1400	1045	946	200th, 670@0.5 C	0.11%	work
					1000th, 416@1 C	0.057%	WUIK
Azo-COF	39%	1121	976	874	100th, 602@1 C	0.42%	[5]
CTF-1	34%	848	686	541	50th, 762@0.1 C	0.72%	[6]
Por-COF	55%	850	730	670	200th,633@0.5 C	0.16%	[7]
COF-1	40%	1062	822	620	200th,770@0.5 C	0.13%	[8]
TpPa-COF @MWCNT s	40%	1079	966	861	450th,525@0.5C	0.099%	[9]

Table S3. Comparison of the performance of reported COFs composite as Li-S

Section 8. Pore Size Distribution



Figure S10. Pore size distribution profiles of COF-V using (a) the nonlocal density functional theory and (b) BJH methods. The NL-DFT method afford better pore size distribution results, the main pore size at ca. 3.0 nm is also in accordance with the results of PXRD diffraction at *d*-spacing of 3.12 nm.





Figure S11. (a) PXRD profiles of COF-V (red: experimental, blue: Pawley refinement, black: their difference, pink: AA stacking mode and violet: AB stacking mode). Graphic view of the slipped structure of COF-V: (b) AA stacking (c) AB stacking.

120).			
Atom	x/a	y/b	z/c
H1	0.62000	1.09739	0.50000
H2	0.58589	0.99639	0.50000
Н3	0.65402	1.08399	0.50000
H4	0.40979	0.89351	0.50000
H5	0.48708	0.83545	0.50000
H6	0.33049	0.76302	0.50000
H7	0.37757	0.84592	0.50000
H8	0.44275	0.75509	0.50000
Н9	0.71088	1.41144	0.50000

Table S4. Atomistic coordinates for the AA-stacking mode of COF-V optimized using Forcite method (space group P6/M, a = b = 37.4778 Å; c = 3.5621 Å, $\alpha = \beta = 90^{\circ}$ and $\gamma = 120^{\circ}$).

N10	0.88662	-2.57287	0.50000
C11	0.91176	-2.53327	0.50000
C12	0.95693	-2.51551	0.50000
C13	0.97294	-2.54235	0.50000
C14	1.01542	-2.52773	0.50000
C15	1.43352	-2.15740	0.50000
C16	1.39022	-2.17624	0.50000
C17	1.36574	-2.21928	0.50000
C18	1.38401	-2.24424	0.50000
C19	1.42732	-2.22518	0.50000
C20	1.45183	-2.18212	0.50000
C21	1.35805	-2.28988	0.50000
C22	1.31481	-2.30890	0.50000
C23	0.97234	-2.44022	0.50000
C24	1.06627	-2.55250	0.50000

Section 10. Supporting References

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