

Supporting information

Carbon with hierarchical pores from carbonized metal-organic frameworks for lithium sulphur batteries

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Experimental

SI-1: Reagents and Chemicals

Zn(OAc)₂·2H₂O, Zn(NO₃)₂·4H₂O, Zn(NO₃)₂·6H₂O, 2-methylimidazole, terephthalic acid, triethylamine (TEA), and fumaric acid were purchased from *Acros Organics*. *N, N'*-dimethylformamide (DMF), *N, N'*-diethylformamide (DEF) and anhydrous chloroform were purchased from *Fisher Scientific*. All chemicals were used as received without further purification.

SI-2: Preparation of MOFs

ZIF-8. Zn(OAc)₂·2H₂O (0.66 g, 2 mmol) was mixed with 2-methylimidazole (2.46 g, 20 mmol) inside a small Teflon cup. This cup was then placed inside a 125 mL Teflon-lined stainless steel autoclave, with 12 mL of H₂O added at the bottom of the autoclave. Crystallization was then carried out at 125 °C for 24 h, followed by natural cooling to room temperature. The synthesized ZIF-8 crystals were collected by filtration and washed several times with de-ionized H₂O.¹

Solvo-MOF-5. Zn(NO₃)₂·4H₂O (0.523 g, 2 mmol) and terephthalic acid (0.111 g, 0.67 mmol) were dissolved in DEF (20 mL) in a Teflon-lined vial. The reaction mixture was heated in an oven at 105 °C for 24 h. The autoclave was removed from the oven and allowed to cool to room temperature. The synthesized large cubic crystals were collected by filtration and repeatedly washed with DMF and anhydrous chloroform, then soaked in anhydrous chloroform for 24 h. Then, the crystals were filtered and vacuum-dried at pressures less than 5 μBar at room temperature.²

RT-MOF-5. Terephthalic acid (1.013g, 6.1 mmol) and TEA (1.7 mL, 12.2 mmol) were dissolved in 80 mL of DMF in a conical flask. Zn(OAc)₂·2H₂O (3.398 g, 15.48 mmol) was dissolved in 100 of DMF. The two above solutions were rapidly mixed together under vigorous stirring at room temperature and continuously stirred for 2.5 h. The precipitates were collected by centrifugation and repeatedly washed with DMF, and

soaked in anhydrous chloroform for 5 days. The precipitates were then vacuum-dried at pressures less than 5 μ Bar at room temperature.³

ZnFumarate. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (3 g, 10.1 mmol) and fumaric acid (1.17 g, 10.1 mmol) were dissolved in 60 DMF in a Teflon-lined autoclave. The autoclave was sealed and heated to 100 °C for 2 days. The autoclave was removed from the oven and allowed to cool to room temperature. The synthesized products were collected by filtration and washed several times with DMF.⁴

SI-3: Preparation of hierarchical porous carbon through pyrolyzing MOFs

The as-prepared respective MOFs were placed inside an alumina crucible and transferred to a tube furnace. The sealed tube furnace was heated to a target temperature of 900 °C^{2,5} (ZIF-8, solvo-MOF-5 and RT-MOF-5) or 1000 °C⁴ (ZnFumarate) under continuous Ar flow of 40 mL/min. After reaching the target temperature, the material was held at this temperature for 9 hours and then cooled to room temperature.

SI-4: Preparation of sulfur/hierarchical porous carbon composites

Elemental sulfur powder (99.98%, Aldrich) and porous carbon materials were dried at 80 °C for 24h under vacuum before use. Then they were mixed, and heated to 155 °C for 12 h in a sealed vessel to facilitate diffusion of the melted sulfur into the porous space of as-prepared porous carbon materials. Final composites were found to contain different mass ratio of sulfur, in which sulfur content was calculated by weighing and assuming no weight loss for porous carbon materials. In contrast, sulfur/ZIF-8 and sulfur/solvo-MOF-5 composites were prepared by the same process.

SI-5: Instrumental Analysis

X-ray diffraction patterns were collected by using Bruker D8-advance powder X-ray diffractometer. The source of the X-rays was Cu K- α which was operated at a power of 1600 W (40 mA, 40 kV). Porosity was measured by N₂ sorption isotherm at 77 K on a Micromeritics ASAP 2020 instrument. Samples were outgassed in vacuum (\sim 5 μ bar) for at least 5 hours at 453 K before starting the sorption measurements. The surface areas were estimated using the Brunauer–Emmett–Teller (BET) equation for the relative pressure range (P/P_0) of 0.002 to 0.3. The saturation pressure, P_0 , corresponds to ca. 103.4 kPa. The t_{HJ} -plot micropore volume is the calculated total pore volume with dimensions < 20 Å, using the Harkins and Jura method. Non-local density functional theory (NLDFT) calculation was used to generate the pore size distribution data, based on the carbon slit pores geometry assumption. The SEM instruments FEG 6400 were used for scanning the samples. Energy dispersive X-ray spectroscopy (EDS) was carried out using a JEOL 5800 LV scanning electron microscope (SEM) with an energy dispersive X-ray spectroscopy (EDS) detector. Transmission electron microscope (TEM) was carried out at FEI Tecnai F20-G2 FEGTEM. A dilute ethanol suspension of as-prepared samples was prepared via an ultrasonic dispersion and dropped onto a copper grid

covered with a carbon film to make a specimen for TEM. Raman data were obtained on a Dilor XY-800 spectrometer, using a 514 nm wavelength from an argon-ion laser.

SI-6: Preparation and electrochemical testing of the cathodes

The working electrode was prepared by compressing the mixture of active materials, conductive carbon black (99+%, metals basis, Super P) and binder (poly(tetrafluoroethylene) (PTFE)) in a weight ratio of 70:20:10. After dropping a small amount of ethanol as a dispersant and stirring 30 min, the paste was pressed into a film, cut into a disk of 0.5 cm² and quality 2.5-3 mg. After this process, the cathode material was dried at 80 ° C for 24 h.

A Li battery was assembled in a glove box filled with pure argon. Lithium metal (99.99%, Sigma-Aldrich) was used as the anode and reference electrode. The separator was a commercial microporous polypropylene product (Celgard 2400). Aluminium foil was used as the cathode current collector while a copper foil served as the anode current collector. The electrolyte is LiN(CF₃SO₂)₂ (1 M) (99.95%, trace metals basis, Sigma-Aldrich) salt dissolved in a mixture of dioxolane (DOL) (99.8%, Sigma-Aldrich) and 1,2-dimethoxyethane (DME) (99.5, Sigma-Aldrich) in a volume ratio of 1:1. The galvanostatic charge/discharge tests were performed at a specific current of 400 mA g⁻¹ to evaluate the electrochemical capacity and cycle life of the electrodes at room temperature using a LAND-CT2001A instrument (Wuhan, China). The cut-off potentials for charge and discharge were set at 3.0 and 1.5 V vs Li⁺/Li, respectively.

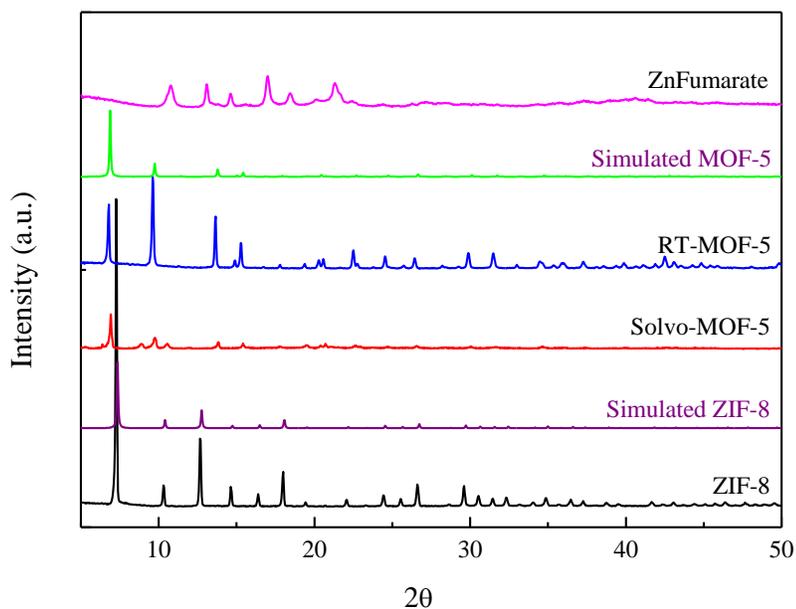


Fig. S1 X-ray diffraction patterns of as-prepared ZIF-8, solvo-MOF-5, RT-MOF-5 and ZnFumarate; simulated patterns for ZIF-8 and MOF-5 are shown for comparison.

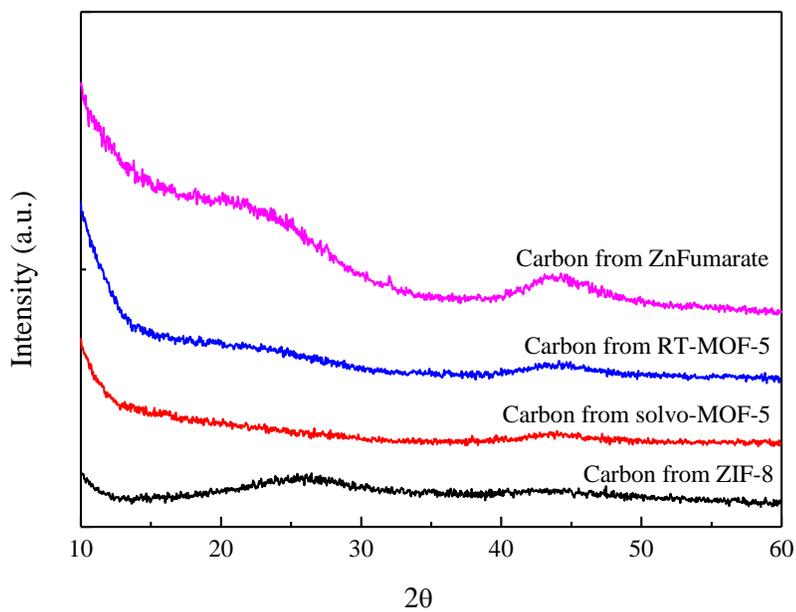


Fig. S2 X-ray diffraction patterns of as-prepared carbons from ZIF-8, RT-MOF-5, solvo-MOF and ZnFumarate.

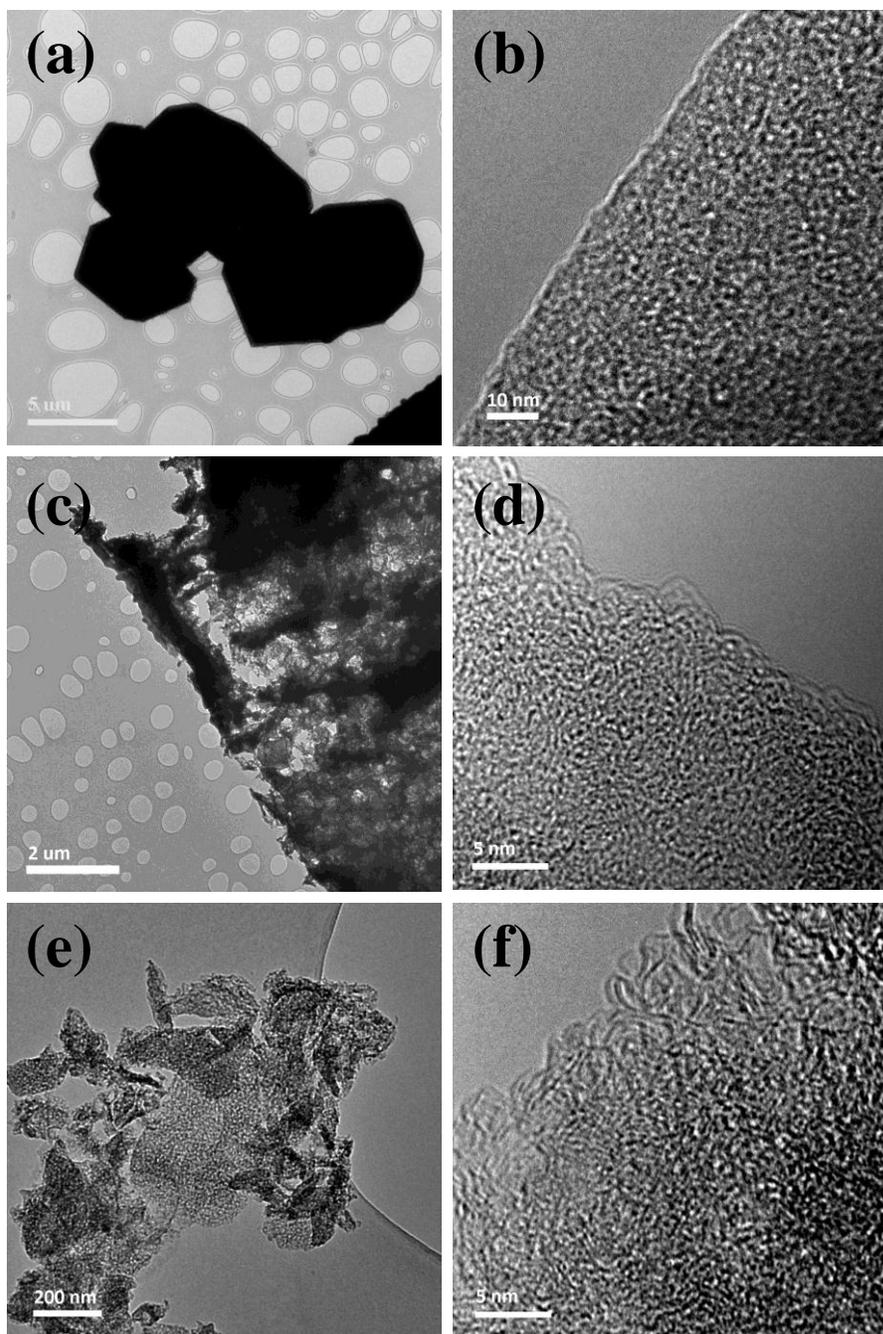


Fig. S3 TEM images of carbon from ZIF-8 (a, b), carbon from solvo-MOF-5 (c, d) and carbon from ZnFumarate (e, f).

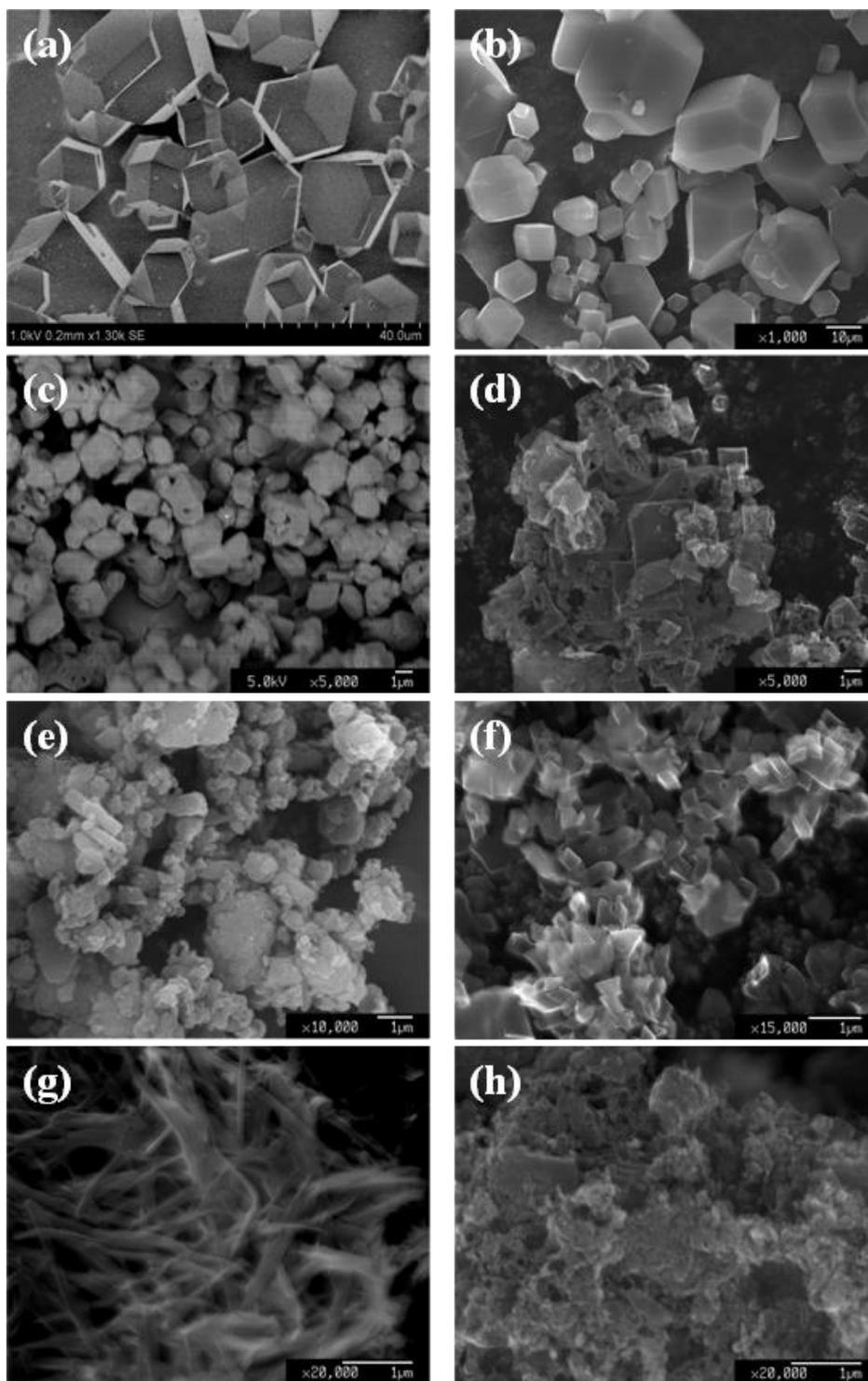


Fig S4 SEM images of ZIF-8 (a), carbon from ZIF-8 (b), solvo-MOF-5 (c), carbon from solvo-MOF-5 (d), RT-MOF-5 (e), carbon from RT-MOF-5 (f), ZnFumarate (g) and carbon from ZnFumarate (h).

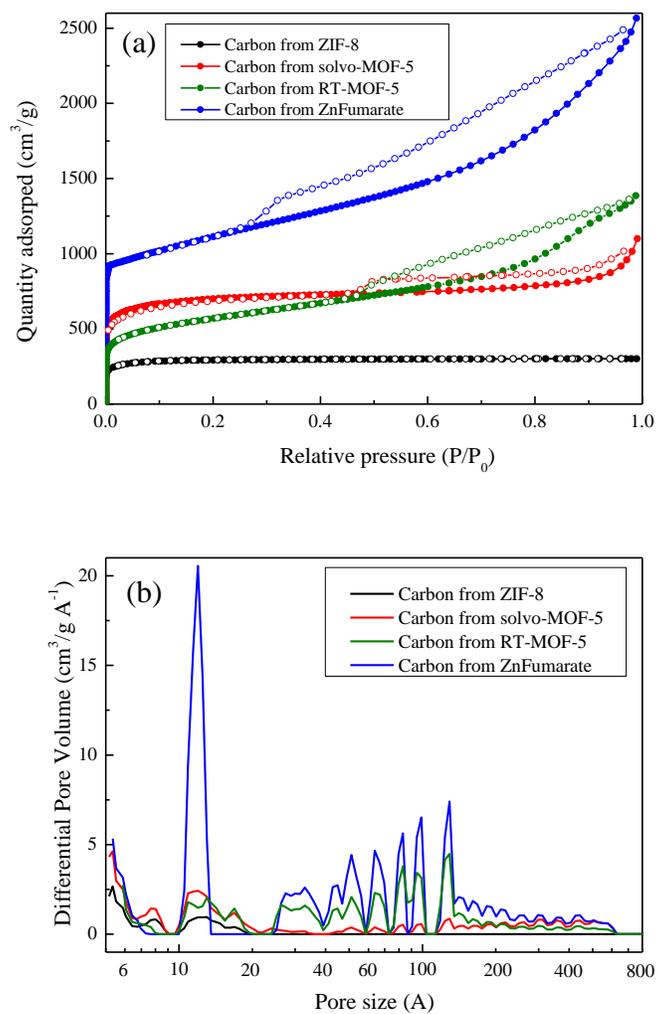


Fig. S5 N₂ adsorption-desorption isotherms the as-prepared samples (adsorption: ●; desorption: ○) (a), and the pore size distribution of as-prepared samples calculated from the desorption branches (b).

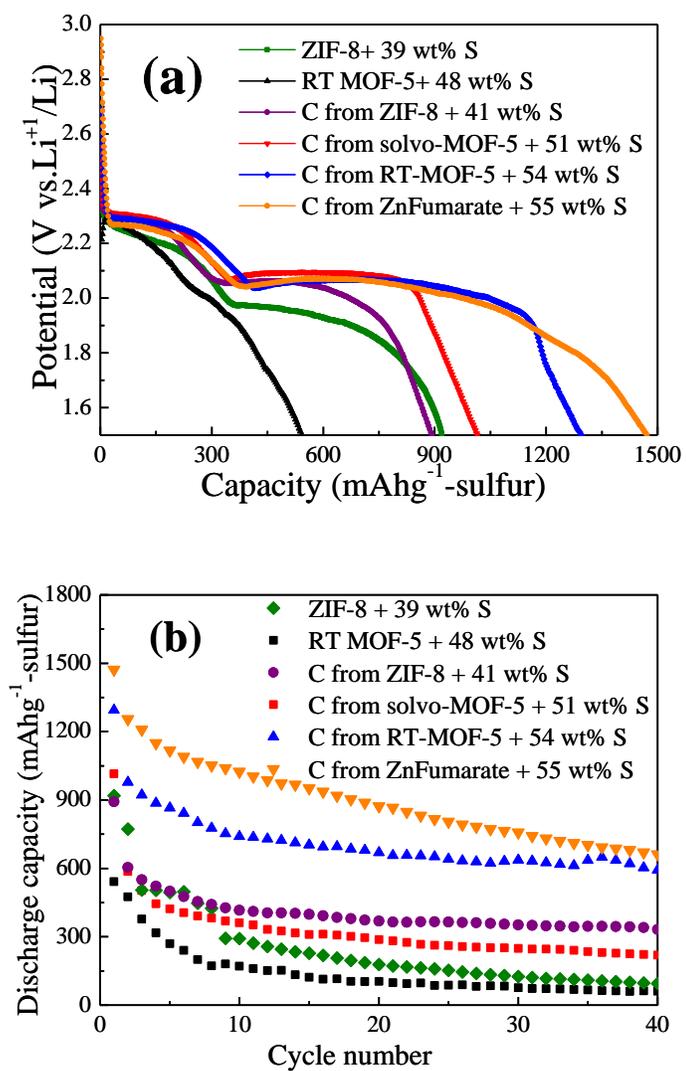


Fig. S6 The first discharge curves (a) and cycle performance (b) of samples at specific current of 400 mA g^{-1} between 1.5 and 3.0 V (vs Li^+/Li) in the electrolyte ($\text{LiN}(\text{CF}_3\text{SO}_2)_2$ / DOL:DME=1:1(v/v)) (C: Carbon)

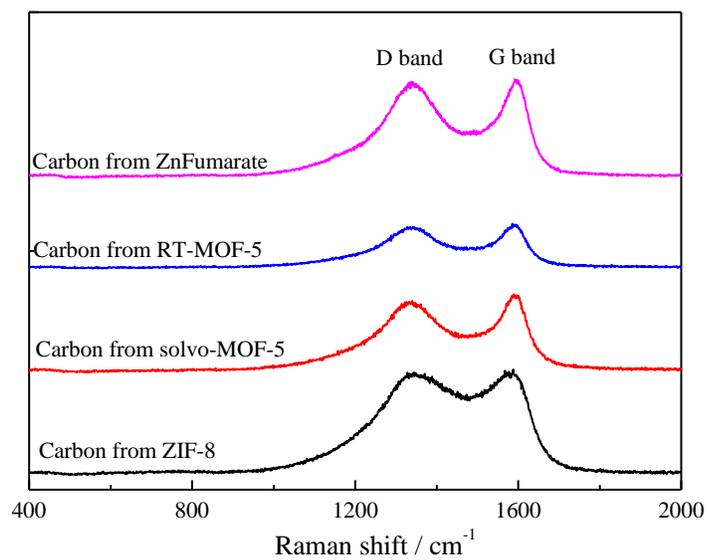
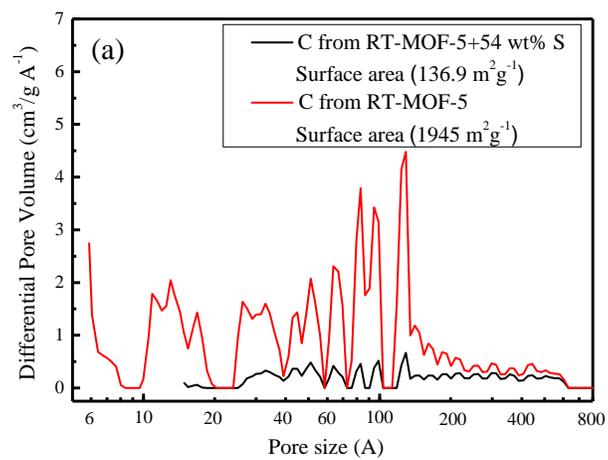


Fig. S7 Raman spectra of the carbon samples.



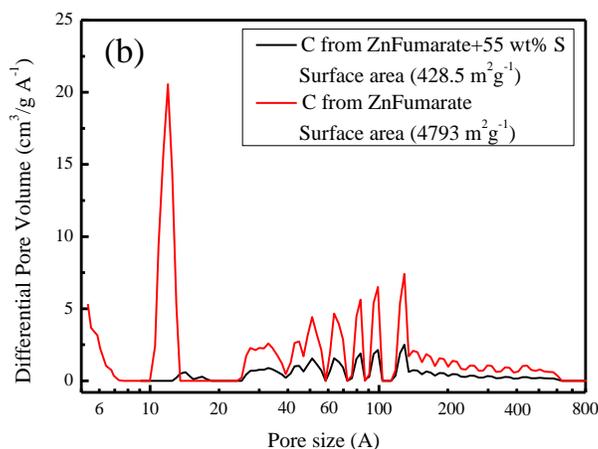


Fig. S8 Pore size distributions of carbon from RT-MOF-5 (a) and carbon from ZnFumarate (b) before and after sulphur loading, and their corresponding BET surface areas.

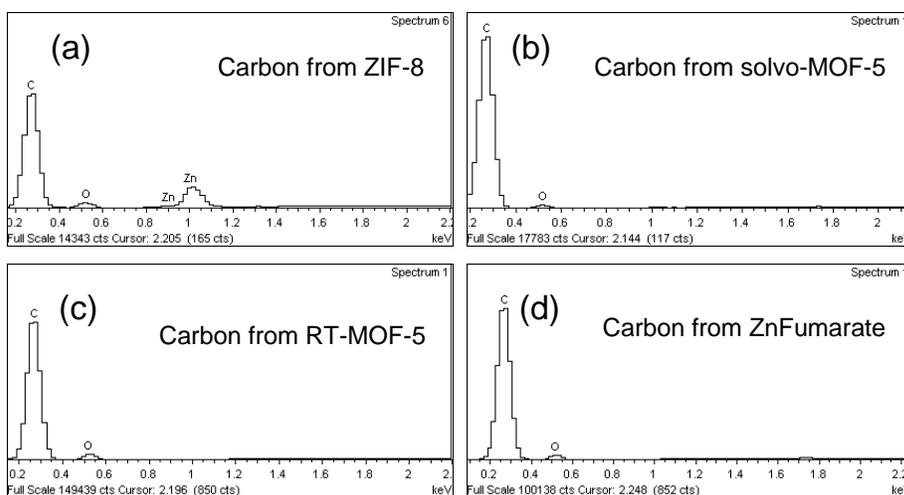


Fig. S9 EDS spectra of carbons from ZIF-8, solvo-MOF, RT-MOF-5 and ZnFumarate.

Note and reference

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