Supplementary Information

Uniform Li$_2$S Precipitation on N, O-Codoped Porous Hollow Carbon Fibers for High-energy-density Lithium-sulfur Batteries with Superior Stability

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Experimental section:

Synthesis of polypyrrole (PPy) hollow fiber paper: Polypyrrole hollow fibers were prepared via the chemical oxidation of pyrrole with FeCl$_3$ as an oxidant and methyl orange as a structure-guiding agent. Typically, 0.62 g of FeCl$_3$ was dissolved in 40 mL of de-ionized water. Then 0.12 g of methyl orange was added. After stirring for 0.5 h, 0.14 mL of pyrrole monomer was added drop by drop to the as-formed template solution. The reaction was carried out at room temperature for 4 h, and small black precipitates (hollow PPy fibers) were formed in the solution. To form the paper, the suspension was directly vacuum filtered and washed with 5% HCl solution, de-ionized water, and ethanol for several times until the filtrate became colorless and neutral. Finally, the PPy hollow fiber paper was peeled off from the filter and dried at 50 ºC for 24 h.

Synthesis of NCHF: Porous carbon hollow fiber paper was prepared via a CO$_2$-activation of PPy hollow fiber paper. At first, the as-obtained PPy hollow fiber paper was punched out into circular disks with diameters of 12 mm. Then, the disks were heated under a CO$_2$ atmosphere with a heating rate of 10 ºC/min to 850 ºC for 2 h to obtain the porous carbon hollow fiber paper. After carbonization, the diameters of the disks reduced to ~ 7 mm and the weight of a disk was ~ 1.6 mg.

Characterization: Scanning electron microscopy (SEM) and elemental mapping results were performed on an FEI Quanta 650 SEM. Transmission electron microscopy (TEM) images were obtained with a JEOL TEM 2010F microscope at an acceleration voltage of 200 kV. Nitrogen
adsorption and desorption isotherms were determined by nitrogen physisorption at 77 K on AutoSorb iQ2 (Quantachrome Instruments). The specific surface area was calculated with the BET method and the pore size distribution (PSD) was calculated with the density functional theory (DFT) method by using nitrogen adsorption data and assuming a slit-pore model. Pore volume was estimated from the adsorbed amount at a relative pressure \( P/P_0 = 0.975 \). XRD patterns were collected on a Rigaku X-ray diffraction instrument with Cu Kα radiation at a scan rate of 10 ° min\(^{-1}\). X-ray photoelectron spectroscopy (XPS) tests were performed with a Kratos X-ray Photoelectron Spectrometer.

**Electrochemical measurements:** The lithium-sulfur batteries were assembled in CR2032-type coin cells with polysulfide-impregnated porous carbon hollow fiber paper as cathode, Celgard 2400 as separator, lithium-metal chips with a diameter of 15.6 mm and thickness of 0.45 mm as anode, and 1.0 M LiCF\(_3\)SO\(_3\) salt and 0.1 M LiNO\(_3\) in a mixture of 1,2-dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1 : 1 by volume) as electrolyte. The polysulfide solution was prepared by dissolving stoichiometric sulfur and Li\(_2\)S powders into the electrolyte at 55 ºC overnight to form Li\(_2\)S\(_6\) solution (3.6 M, calculated based on S atom in the solution). The cathodes were prepared by dropping 21.2 μL of the as-prepared polysulfide solution (~ 2.4 mg S) onto the NCHF paper sheets (diameter: 0.7 cm). An additional 30.0 μL blank electrolyte was added to the cell during the cell assembly process (20.0 μL to the NCHF paper sheets and 10.0 μL to the separator), leading an electrolyte to sulfur ratio of around 20 for the whole cell. Charge-discharge and CV tests were performed with an Arbin battery test station at 1.8 – 2.8 V. All the specific capacities were calculated based on the amount of sulfur, \( 1C = 1675 \text{ mAh g}^{-1} \). Electrochemical impedance spectroscopy (EIS) data were collected with a Solartron 1260A impedance analyzer in the frequency range of 100 kHz to 10 mHz at the open-circuit voltage.
Fig. S1 FTIR spectra of PPy hollow fiber and NCHF.
Fig. S2 Low-magnification SEM image of NCHF.
Fig. S3 XRD pattern of NCHF.
Fig. S4 Impedance spectra of Li$_2$S$_6$-impregnated NCHF electrode after a various number of cycles.
Fig. S5 SEM image of the carbon fiber used in the control cell.
**Fig. S6** Cycling performance of the control cell using the carbon fiber as current collector.

**Fig. S7** SEM image, and N, O, and S distributions of Li$_2$S$_6$-impregnated NCHF electrode after 400 cycles at C/3.