Supporting Information

Fe$_2$P-decorated N, P Codoped Carbon Synthesized via Direct Biological Recycling for Endurable Sulfur Encapsulation

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Experimental procedures:

Materials Preparation

Preparation of Fe-containing electroplating sludge leaching solution

The raw electroplating sludge was dried at 80 °C for 12 h and ground to 200 mesh. Then, 20.0 g electroplating sludge dry powder was mixed with 100 mL hydrochloric acid (2 mol/L) followed by ultrasonic treatment for 3 h. The electroplating sludge leaching solution was collected by centrifugation at 10,000 rpm for 3 min.

Synthesis of Fe$^{3+}$/Bacillus cereus (BC) precursors

*Bacillus cereus* (BC) was obtained from Fujian Institute of Research on the structure of Matter, Chinese Academy of Sciences. BC was grown in Luria-Bertani (LB) culture medium which was comprised of 10 g of tryptone, 5 g of yeast extract, 10 g of NaCl and 1 L of distilled water under the temperature of 35 °C for 24 h and on a shaker at 200 rpm. Then, the cells were separated and collected by centrifugation at 5000 rpm for 5 min. The remaining pellets were washed twice with deionized (DI) water to eliminate the culture medium. Subsequently, the washed bacterial cells were added into the prepared electroplating sludge leaching solution and stirring for 12 h. Finally, the mixture was centrifuged at 5000 rpm for 5 min and washed twice with DI water to obtain the Fe$^{3+}$/BC precursors.

Synthesis of the Fe$_2$P@N, P codoped biological carbon (NPC) and NPC

The obtained Fe$^{3+}$/BC precursors were frozen by using liquid nitrogen, and subjected to a vacuum drying process for 24 h. After calcination at 800 °C for 3 h with a heating rate of 3 °C min$^{-1}$ under N$_2$ atmosphere, the Fe$_2$P@N, P codoped carbon (Fe$_2$P@NPC) sample was obtained. For comparison, pristine BC-derived hierarchical porous NPC has also been fabricated.

Synthesis of S/Fe$_2$P@NPC and S/NPC composites

A popular melt-diffusion method was carried out to achieve the sulfur encapsulation. Typically, the Fe$_2$P@NPC and sulfur (the weight ratio of Fe$_2$P@NPC : sulfur is set to be 1 : 3) were mixed and hand-milled in an agate mortar for 20 min, and then calcined at 155 °C for 6 h. After cooling down to room temperature, the
S/Fe\textsubscript{2}P@NPC composite was obtained. For comparison, the S/NPC composite has been prepared via the similar procedure.

**Lithium polysulfides adsorption experiments**

By dissolving stoichiometric amounts of sulfur (S, Alfa Aesar) and lithium sulfide (Li\textsubscript{2}S, Alfa Aesar) with a molar ratio of 5 : 1 in 1,3-dioxolane (DOXL) and 1,2-dimethoxyethane (DME) (v/v = 1 : 1) at 65 °C with vigorous stirring in an Ar-filled glovebox with H\textsubscript{2}O and O\textsubscript{2} content less than 0.1 ppm for 24 h, a 5 mM Li\textsubscript{2}S\textsubscript{6} solution was successfully prepared. Typically, for the visualized LiPSs adsorption experiment, 50 mg of the as-prepared Fe\textsubscript{2}P@NPC and NPC were added into 2.0 mL of the above fabricated Li\textsubscript{2}S\textsubscript{6} solution, respectively, and kept steady for 3 h.

**Materials characterizations**

Powder X-ray diffraction (XRD) measurements was conducted by using a Bruker D8 Advanced instrument with Cu K\textalpha radiation (\(\lambda=1.5418 \text{ Å}\)) within the range of 2\(\theta\) = 5-80 °. A field-emission scanning electron microscopy (FESEM, Hitachi SU8010) was used to characterize the morphology of the samples. A JEM-2100F transmission electron microscope (TEM) with an energy dispersive spectroscopy (EDS) detector operating at 200 kV is applied to acquire the Transmission Electron Microscope (TEM) images and elemental mappings. Surface chemistry of the samples was investigated by using an X-ray photoelectron spectroscopy (Thermo, K-Alpha \textsuperscript{+} spectrometer) apparatus with mono-chromatic Al K\textalpha radiation at room temperature. Vario EL III was applied to perform the CHNS elemental analysis and the sulfur content was determined by applying A SDT Q600 TG/DTA analyzer with a heating rate of 5 °C min\textsuperscript{-1} from room temperature (RT) to 800 °C under N\textsubscript{2} atmosphere.

**Electrochemical Performance Measurements**

**Li-S batteries electrochemical performance testing:** Firstly, to prepare a homogeneous cathode slurry, the fabricated sulfur hosts S/Fe\textsubscript{2}P@NPC or S/NPC (70 wt%), acetylene black (20 wt%), and water-soluble polymer n-lauryl acrylate (10 wt%, LA, Chengdu, China) were uniformly mixed and ball-milled for 6 h. Then, the sulfur cathodes were obtained by coating the as-prepared slurry to the aluminum (Al) foil collectors and dried at 60 °C overnight in a vacuum oven. Finally, the CR 2016 coin-
type cells were assembled in an argon-filled glovebox by using the as-obtained S/Fe$_2$P@NPC or S/NPC coated Al foil as the cathode, a lithium foil as the anode, a Cellgard 2400 as the separator, and 1.0 M lithium bis-(trifluoromethanesulfonyl) imide (LiTFSI, TCI Japan) + 2 wt% LiNO$_3$ dissolved in dioxolane (DOXL) and 1,2-dimethoxyethane (DME) (1:1, v/v) as the electrolyte. During the Li-S batteries assembly process, the electrolyte amount was set to be 40 μL, the electrode area was set to be 1.3 cm$^2$, and the areal sulfur mass loading on the electrode was controlled to be about 2.6 and 3.73 mg cm$^{-2}$. The ratio of electrolyte to sulfur (E/S) is about 12 and 7.5 μL/mg S. A CHI660E electrochemical workstation was applied to conduct Cycle voltammetry (CV) and electrochemical impedance spectra (EIS) tests. The rate capability and cycle performance were tested in the voltage window of 1.7-2.7 V at various current rates on the LAND2001CT system.

**Symmetric cells electrochemical performance testing**: Firstly, in order to obtain a homogeneous electrode slurry, 70 wt% of active materials (Fe$_2$P@NPC or NPC), 20 wt% of acetylene black and 10 wt% of LA were uniformly mixed and ball-milled for 6 h. Then, the electrodes were obtained by coating the as-prepared slurry to the Al foil collectors and then dried overnight in a vacuum oven at $60^\circ$C. The symmetric cells (CR 2016) were assembled in an argon-filled glovebox by using Fe$_2$P@NPC or NPC coated Al foil as both cathode and anode, a Cellgard 2400 as the separator and 40 μL electrolyte of 0.2 M Li$_2$S$_6$ and 1 M LiTFSI+ 2 wt% LiNO$_3$ in a DME/DOXL (1:1, v/v) mixture as the electrolyte. CV and EIS tests were carried out on a CHI660E electrochemical workstation, and the CVs were tested within the voltage window of -1.0-1.0 V with a sweep rate of 6.0 mV s$^{-1}$.

**Computational details**

The projector augmented wave method was performed to do all the calculations on the basis of density functional theory (DFT),$^{S1}$ as applied in the Vienna $ab$-initio Simulation Package (VASP). The generalized gradient approximation (GGA) and Perdew–Burke–Ernzerhof (PBE) exchange function were used.$^{S1}$ The plane-wave energy cut off was set to be 520 eV, and the Monkhorst–Pack method was employed
for the Brillouin zone sampling.\textsuperscript{S2} The convergence criterions of energy and force calculations were set to be $10^{-5}$ eV/atom and 0.01 eV Å$^{-1}$, respectively.

To explore the interactions between the ploysulfide (Li$_2$S and Li$_2$S$_6$) molecules and substrates, the adsorption energy of the ploysulfide molecules on the pure carbon, pyridine N-and pyrrole N-doped carbon, P- doped carbon and Fe$_2$P (111) surface were calculated, respectively. A vacuum region of 15 Å is applied to avoid interactions between the neighboring configurations. DFT-D2 method was used to account for the van der Waals interactions between the ploysulfide molecules and carbon surface.\textsuperscript{S3} Here, the adsorption energy ($E_a$) has been calculated by the energy difference of the system before and after Li$_2$S or Li$_2$S$_6$ adsorption. The energy barriers for Li$_2$S decomposition on the pure carbon, pyridine N-doped carbon, pyrrole N-doped carbon, P- doped carbon and Fe$_2$P (111) surface were calculated by using the nudged elastic band (NEB) method to evaluate their de-lithiation reaction kinetics.

\textbf{Safety Statement}

No unexpected or unusually high safety hazards were encountered.
Figure S1. SEM images of the *Bacillus cereus* (BC) (a) and Fe\textsuperscript{3+}/BC precursors (b).
Figure S2. High-magnification SEM image of Fe$_2$P@NPC sample.
Figure S3. The $\text{N}_2$ adsorption-desorption isotherm (a) and corresponding pore distribution (b) of NPC sample.
Figure S4. The XPS survey spectrum of Fe$_2$P@NPC sample.
Table S1. The ICP-OES analysis results of Fe$_2$P@NPC sample.

| Sample Weight (g) | Solution Volume (mL) | Element | Element Content in Solution (mg/L) | Dilution Ration | Element Content in Sample (mg/kg) | Element Content in Sample (%) |
|-------------------|----------------------|---------|-----------------------------------|-----------------|----------------------------------|-------------------------------|
| 0.0357            | 10                   | Fe      | 1.93                              | 100             | 53924,1                          | 5.39%                         |
|                   |                      | P       | 0.90                              |                 | 25298.5                          | 2.53%                         |
Table S2. The CHNS analysis results of Fe$_2$P@NPC and NPC samples.

| Materials | Weight (mg) | N (%) | C (%) | H (%) | S (%) |
|-----------|-------------|-------|-------|-------|-------|
| Fe$_2$P@NPC | 1.489       | 8.51  | 60.66 | 1.671 | 0.414 |
|           | 1.522       | 8.6   | 61.02 | 1.692 | 0.502 |
| NPC       | 3.041       | 7.35  | 63.96 | 1.295 | 0.224 |
|           | 2.657       | 7.48  | 64.12 | 1.314 | 0.316 |
Figure S5. SEM image of the S/Fe$_2$P@NPC composites.
Figure S6. The XRD patterns of the as-prepared S/Fe$_2$P@NPC and S/NPC composites.
Figure S7. CV profiles of S/NPC cathode in a voltage range of 1.7 to 2.7 V at a sweep rate of 0.1 mV s$^{-1}$. 
Figure S8. The CV profiles of the S/Fe$_2$P@NPC (a) and S/NPC (b) cathodes at increasing scan rates from 0.1 to 1.0 mV s$^{-1}$; the plots of log(current) versus log(scan rate) of peak 1, peak 2 and peak 3 in S/Fe$_2$P@NPC (c) and S/NPC (d) cathodes.
Table S3. The simulated results from the electrochemical impedance spectra (EIS) of fabricated coin cell with S/Fe$_2$P@NPC or S/NPC cathode.

| Materials    | $R_s$ (Ω) | $R_e$ (Ω) | $R_{ct}$ (Ω) | $D_{Li^+}$ (cm$^2$ s$^{-1}$) |
|--------------|-----------|-----------|--------------|-----------------------------|
| S/Fe$_2$P@NPC | 9.899     | 20.96     | 74.95        | 9.59×10$^{-10}$             |
| S/NPC        | 8.758     | 123.4     | 123.1        | 1.77×10$^{-10}$             |

Figure S9. The $\sigma$ value for S/Fe$_2$P@NPC and S/NPC cathodes determined by using Equation S2.

Simplified equivalent circuit model was constructed to analyze the impedance spectra (Figure 4b), the Li ion diffusion coefficient ($D_{Li^+}$) in S/Fe$_2$P@NPC and S/NPC cathodes can be calculated according to the following equations:\cite{S4,S5}

\[
D_{Li^+} = \frac{R^2T^2}{2A^2n^4F^4C^2\sigma^2} \quad (S1)
\]

where $R$ is the gas constant (8.314 J mol$^{-1}$ K$^{-1}$), $T$ is the Kelvin temperature (298.15 K), $A$ is the contacting area of the electrode/electrolyte, $n$ is the number of electronic
transfer, $F$ is the Faraday constant, $C$ is the concentration of Li ion, $\sigma$ is the Warburg factor which is relative with $Z'$.

$$Z' = R_s + R_e + R_{ct} + \sigma \omega^{-1/2} \quad (S2)$$

where $R_s$ is the ohmic resistance, $R_e$ is the solid electrolyte interface (SEI) resistance, $R_{ct}$ is the charge transfer resistance and $\omega$ is the angular frequency in the low frequency region. The graph of $Z'$ against $\omega^{-1/2}$ in the low-frequency region is a straight line with the slope of $\sigma$ (Figure S9).
Figure S10. Galvanostatic charge/discharge profiles of the S/NPC cathode under the current rate of 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 C.
Figure S11. Galvanostatic charge/discharge profiles of different cycles at 1.0 C for S/Fe$_2$P@NPC (a) and S/NPC (b) cathodes.
Figure S12. Rate capability of the S/Fe$_2$P@NPC cathode under the current rate of 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 C with a sulfur loading of 3.73 mg cm$^{-2}$.

Figure S13. Cycling performance of the S/Fe$_2$P@NC cathode under the current rate of 1.0 C with a sulfur loading of 3.73 mg cm$^{-2}$.
Figure S14. Rate capability of the S/Fe$_2$P@NPC cathode under the current rate of 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 C at an E/S value of 7.5 µL/mgs.

Figure S15. Cycling performance of the S/Fe$_2$P@NPC cathode under the current rate of 1.0 C at an E/S value of 7.5 µL/mgs.
Figure S16. Optimized structures based on DFT calculations showing the interactions of Li$_2$S and Li$_2$S$_6$ molecules adsorbed on pyrrole N-doped carbon and corresponded adsorption energy ($E_a$). The green, yellow, brown and blue balls donate Li, S, C and N atoms, respectively.
Figure S17. Digital photos of Li$_2$S$_6$ adsorption test for the blank Li$_2$S$_6$ solution, pure carbon (acetylene black, denoted as C), NPC and Fe$_2$P@NPC.
Figure S18. Li$_2$S decomposition energy barrier ($E_{\text{barrier}}$) in DFT calculations on the surface of pyrrole N-doped carbon.
References

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