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# **Supporting Information**

# A Novel Synergistic Composite with Multi-Functional Effects for High-

# **Performance Li-S Batteries**

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# **Experimental Section**

# **Materials Preparation**

#### Synthesis of ZIF-67 and ZIF-8 crystals.

All the chemicals were directly used after purchase without further purification. In a typical preparation, 4mmol of  $Co(NO_3)_2 \cdot 6H_2O$  or  $Zn(NO_3)_2 \cdot 6H_2O$  was dissolved in 50mL of methanol to form a clear solution, which was subsequently poured into 50mL of methanol containing 16mmol of 2-methylimidazole (MeIM). After thorough mixing, the solution was incubated at room temperature for 24h. The as-obtained precipitates were collected by centrifugation, washed with methanol for 3 times and dried at 80°C for 12h, resulting in the purple ZIF-67 crystals and the white ZIF-8 crystals.

### Synthesis of Co-N-GC composites.

The as-prepared ZIF-67 crystals were thermally converted to Co-N-GC composites through carbonization under a N<sub>2</sub> flow at 700°C for 3h, with a heating rate of 5°C·min<sup>-1</sup>.

### Synthesis of N-GC composite.

The as-prepared Co-N-GC composites were immersed in 2M HCl solution, ultra-sonicated for 2h and continuously stirred for 6h. Then the as-obtained precipitates were collected by centrifugation, washed with water and ethanol and dried at 80°C for 12h, resulting in the N-GC composite.

#### Synthesis of Co-GC composite.

The as-prepared ZIF-67 crystals were thermally converted to Co-GC composite through carbonization under a N<sub>2</sub> flow at 1000°C for 3h, with a heating rate of  $5^{\circ}$ C·min<sup>-1</sup>.

### Synthesis of Co/ACN and Co/Super P composites.

Firstly, the as-prepared ZIF-8 crystals were thermally converted to ACN composites through carbonization under a N<sub>2</sub> flow at 1000°C for 3h, with a heating rate of  $5^{\circ}$ C·min<sup>-1</sup>.

Next, 400 mg ACN composite and 1062.43mg  $Co(NO_3)_2 \cdot 6H_2O$  were dispersed in 40mL deionized water, magnetic stirrer mixing overnight. Then the mixed solution was rotary evaporated, dried at 80°C for 12h and thermally converted to Co/ACN composite through carbonization under a N<sub>2</sub> flow at 700°C for 3h, with a heating rate of 5°C·min<sup>-1</sup>. The Co/Super P composites were prepared via the same procedure as above except that Super P replaced ACN.

Synthesis of S@Co-N-GC, S@N-GC, S@Co-GC, S@Co/ACN, S/Super P and S/Co/Super P

#### composites.

Sulfur encapsulation was performed by a melt-diffusion method. A mixture of sulfur (70 wt%) with Co-N-GC composites was hand-milled for 20 min, and then transferred to the electric oven at 155°C for 6h. Upon cooling down, the powder was collected as S@Co-N-GC. The S@Co/ACN, S@N-GC, S@Co-GC, S/Super P and S/Co/Super P composites were prepared via the same procedure as above.

## Structure characterizations.

Powder X-ray diffraction (XRD) measurements were performed by using a Rigaku Ultima IV instrument using Cu K $\alpha$  radiation ( $\lambda$ =1.5418 Å) at a range of 5-80°. The detailed morphologies of the as-prepared materials were determined by scanning electron microscopy (SEM, HITACHI S-4800), transmission electron microscopy (TEM, JEM1400) and high-resolution transmission electron microscopy (HRTEM, F30). The specific surface area and average pore diameter were measured by static N<sub>2</sub> physisorption at 77 KonaM icromeritics TriStar II3020 surface area and pore analyzer. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a XPS apparatus (PHI QUAN-TUM 2000) and elemental analysis was performed on Vario EL III. A Pryis Diamond TG/DTA analyzer (Perkin Elmer) was employed to determine the mass content of sulfur and the content of Co in the composites under a N<sub>2</sub>/O<sub>2</sub> atmosphere at a heating rate of 10 °C·min<sup>-1</sup>.

### **Electrochemical Measurements**

70 wt% sulfur composites mentioned above, 20 wt% acetylene black, 10 wt% water-soluble polymer n-lauryl acrylate (LA, Chengdu, China) were mixed and ball-milled into homogeneous slurry. Then the black slurry was coated on aluminum foil collectors and dried at 60°C under vacuum overnight to obtain cathodes. Coin cells (CR 2016) were assembled in an argon-filled glovebox with a lithium foil as the anode, Cellgard 2400 as the separator and 0.5 M LiCF<sub>3</sub>SO<sub>3</sub> + 0.5 M LiNO<sub>3</sub> dissolved in dioxolane (DOXL) and 1,2-dimethoxyethane (DME) (1:1, v/v) as the electrolyte. The electrolyte amount was 35µL. The electrode area was 1.3 cm<sup>2</sup> (diameter of 13 mm). The areal mass loading on the electrode was about 2.0 mg/cm<sup>2</sup> and 2.5 mg/cm<sup>2</sup> for rate capability test and cycle stability test, respectively. The cycle voltammetry was tested by using an IVIUM Multichannel Electrochemical Analyzer. The cycling performance and rate tests were carried out on a NEWARE BTS-5V/50mA type charger (Shenzhen, China) within the voltage range of 1.7-2.7 V. Specific capacity values were calculated with respect to the mass of sulfur. All experiments were conducted at room temperature.



**Fig. S1** a) The XRD patterns of simulated ZIF-67 and the as-prepared ZIF-67; b) The corresponding DFT pore size distribution of the Co-N-GC composite.



Fig. S2 a) The TG curve of the S@Co-N-GC composite; b) The XRD pattern of the S@Co-N-GC composite.



**Fig. S3** a) The cyclic voltammetry curves of the S@Co-N-GC composite electrode at a rate of 0.05 mV/s in the potential range of 1.7-2.7 V; b) The voltage profiles of the S@Co-N-GC composite electrode at different cycles at the current rate of 0.05C



**Fig. S4** The voltage profiles of the S@Co-N-GC composite electrode at different cycles at the current rate of a) 0.2C and b) 1C.



**Fig. S5** a) The XRD pattern of the Co/Super P composite; b) Cycling performance and coulombic efficiency comparisons between the S/Super P and the S/Co/Super P composite electrodes at 0.2C.



**Fig. S6** Cycling performance and coulombic efficiency comparisons between the S@ACN and the S@ Co/ACN composite electrodes at 0.2C.



**Fig. S7**. The rate capability and coulombic efficiency comparisons between the S@Co-N-GC and S@N-GC composite electrodes at increasing current rates from 0.05C to 5C.



**Fig. S8**. a) The voltage profiles of the S@Co-GC composite electrode at different cycles at the current rate of 0.05C; b) Cycling performance and coulombic efficiency comparisons between the S@Co-GC and the S@Co-N-GC composite electrodes at 1C.



Fig. S9  $\mathsf{N}_2$  adsorption–desorption analysis of the Co/ACN and Co-N-GC composites.

Sample	C content <sup>1</sup> [wt%]	N content <sup>1</sup> [wt%]	H content <sup>1</sup> [wt%]	Co content <sup>2</sup> [wt%]
N-GC	86.46	9.18	2.66	1.4
Co-GC	56.26	0.29	0.60	43.8
Co/ACN	60.51	2.44	3.07	33.9
Co/Super P	65.56	0.01	0.96	33.5