

N-Rich Porous Carbon Nanocube Anchored with Co/Fe Dual Atoms: An Efficient Bifunctional Catalytic host for Li-S batteries

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Experimental

1. Sample preparation

1.1 Synthesis of PCN-224

Add pyrrole (3.0 g, 0.043 mol), methyl p-formylbenzoate (6.9 g, 0.042 mol) and propionic acid (100 ml) into a 250 ml three-necked flask. The solution was refluxed at 160 °C for 12 h, cooled to room temperature, and filtered to obtain a precipitate. Subsequently, wash the above-mentioned precipitate with ethanol, ethyl acetate, tetrahydrofuran, and vacuum dry overnight. The precipitate was dissolved in THF tetrahydrofuran (60 mL) and MeOH methanol (60 mL), and KOH solution (6.82 g KOH dissolved in 80 ml deionized water) was added. The mixture was refluxed at 80 °C for 12 h and gradually cooled to room temperature. Add additional deionized water to ensure complete dissolution, acidify with 1M Hydrogen chloride (HCl) until no more purple precipitate is formed. The purple precipitate (H₂TCP) was filtered out and dried in vacuum. Zirconium (IV) chloride (ZrCl₄) (120 mg), H₂TCP (50 mg) and benzoic acid (1200 mg) were dissolved in N, N-Dimethylformamide (DMF) (8 mL) and heated at 120 °C for 24 h. After cooling to room temperature, cubic dark purple crystals were collected by filtration.

Synthesis of PCN-224-CoFe

Add different proportions of Ferrous chloride tetrahydrate (FeCl₂·4H₂O) and Cobalt chloride hexahydrate (CoCl₂·6H₂O), and mixed with PCN-224. Heat and stir at 120 °C for 12 h. After that, centrifuge the mixture and pour out the liquid to obtain a solid precipitate. Wash the remaining solid precipitate twice each with fresh DMF and acetone and dry in an oven.

1.2 Synthesis of CoFe-NC

100 mg sample was heated to 650 °C at a rate of 5 °C/min under a nitrogen (N₂) atmosphere and pyrolyzed at 650 °C for 2 h to obtain a porous carbon composite material, named PCN-CoFe-650. Then, the metal or metal oxide nanoparticles contained in the product obtained were etched with HF solution at 80 °C for 12 h and then washed thoroughly with a large amount of deionized water to obtain CoFe-NC. Dry overnight at 120 °C before use.

1.3 Synthesis of S@CoFe-NC

The S@CoFe-NC composite was prepared via a simple melting-diffusion strategy. Firstly, CoFe-NC and sublimed S were fully mixed according to a weight ratio of 2:8 in a gate mortar for 30 min, respectively. And the mixture was put in a porcelain boat and further took them to a quartz tube for heating treatment at 155 °C for about 12 h under the argon atmosphere in the tube furnace.

2. Characterization

Scanning electron microscopy (FESEM; JEOL JSM-6701F, Japan) equipped with energy-dispersive X-ray

spectroscopy (EDS) mapping was used to characterize the morphology and the distribution of the elements of three samples. High-resolution transmission electron microscopy (HRTEM, JEOL JEM 2100F, 200 kV) was used to characterize the internal microstructure of the sample. The pore size distribution and the specific surface area of the product were tested by the Brunauer-Emmett-Teller (BET; ASAP 2020 HD88, USA). The crystal architecture was measured via X-ray diffraction (XRD; D/max 2500, Japan) with Cu K α radiation from 10° to 80°. The valence state information for the element characterization of the samples was characterized using X-ray photoelectron spectroscopy (XPS; ESCALAB250XI, USA). The S content of the sample was measured via thermogravimetric analysis (TGA, Diamond TG-DTA, USA) which heated from 30 to 800 °C at a heating rate of 10 °C/min in N₂ atmosphere. The adsorption effect of the composite on Li₂S₆ was further measured via ultraviolet-visible diffuse reflection spectroscopy (UV-vis-DRS, Lambda 1050+ USA).

3. Electrochemical test

The cathode was prepared by coating the N-methyl pyrrolidone (NMP) slurries on the Al foil (as current collectors), which contains 70 wt% composites, 20 wt% super P and 10 wt % polyvinylidene fluoride (PVDF) binder, followed by dried at 60 °C for 12 h. Electrochemical measurements were characterized using 2032-type coin cells with the working electrode and lithium metal as the counter electrode. The electrolyte used solution of 1, 3-dioxolane (DOL) and 1, 2-dimethoxymethane (DME) (v/v = 1:1) with 1 mol bis (trifluoromethane) sulfonamide lithium salt (LiTFSI) and 1 wt % lithium nitrate (LiNO₃) as electrolyte additive which could reduce the shuttle effect of the long-chain lithium polysulfides between the cathode and anode. The ratio of electrolyte/sulfur (E/S) was 10 μ l/mg under the S loading of 2.5-3.2 mg/cm². The galvanostatic charge-discharge characterization was operated between 1.7 and 2.8 V (versus Li⁺/Li) with different current densities via a Land battery test system (the specific capacity was calculated based on the mass of S₈). Cyclic voltammetry (CV) tests were measured under a scan rate of 0.1 mV/s and a cut-off voltage of 2.80 - 1.70 V. The symmetrical cell was subjected to CV tests to analyze the redox behavior of Li₂S₆ in a voltage window from -1 to 1 V at a scan rate of 1 mV/s. All current densities and specific capacities mentioned in this paper are calculated based on the sulfur. Electrochemical impedance spectra (EIS) (frequency range: 100 kHz - 5 MHz) were measured with an electrochemical workstation (Autolab). All the electrochemical measurements were completed at room temperature.

4. Synthesis of Li₂S₆ solution and adsorption test

Lithium polysulfides solution with an overall stoichiometric ratio matching Li₂S₆ was synthesized according to the literature reported before. Typically, the sublimed S and Li₂S with a molar ratio of 5:1 was dissolved in DOL/DME (v/v=1:1) via stirring for 24 h, obtaining a deep yellow solution. And synthesis procedure was in an argon gas-filled glove box. The adsorption ability of NC, Co-NC, Fe-NC and CoFe-NC composites on lithium polysulfides were qualitatively tested via using ultraviolet and UV-vis-DRS.

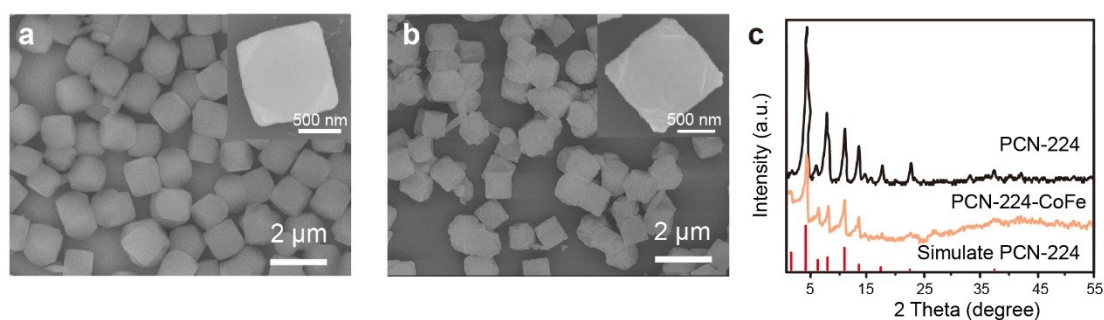


Figure. S1 (a) SEM images of PCN-224. (b) SEM images of PCN-224-CoFe. (c) XRD patterns of PCN-224, PCN-224-CoFe and simulate PCN-224.

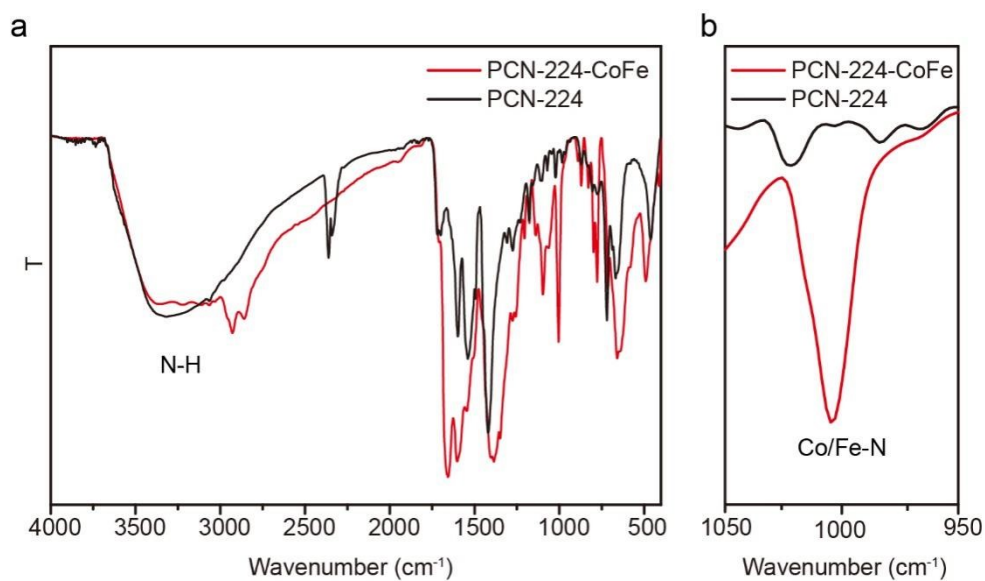


Figure. S2 FT-IR spectra of PCN-224 and PCN-224-CoFe.

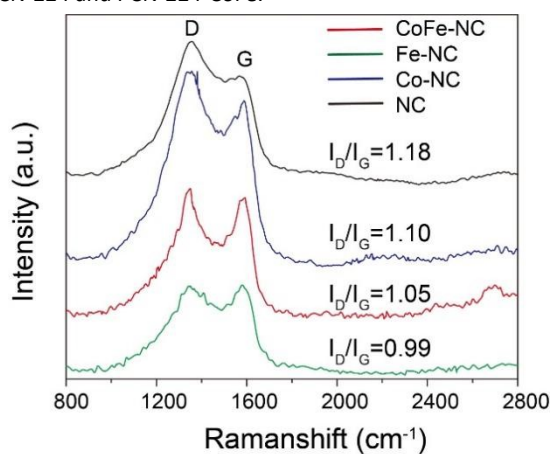


Figure. S3 Raman spectra for NC, Co-NC, Fe-NC and CoFe-NC.

Co	Fe
0.5 wt%	0.8 wt%

Table S1 Concentration of Cobalt and Iron.

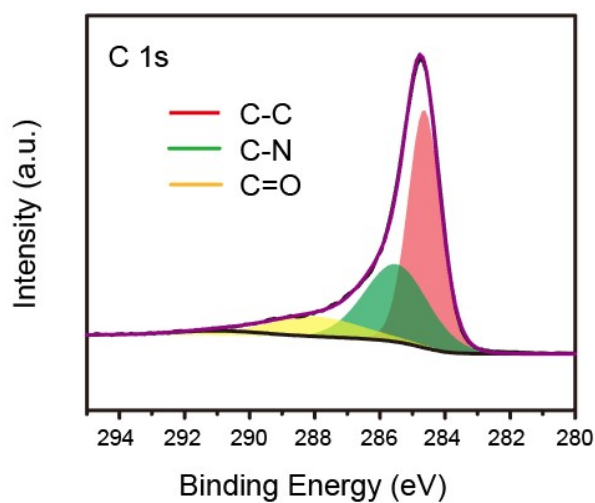


Figure. S4 High-resolution C 1s XPS spectra of CoFe-NC.

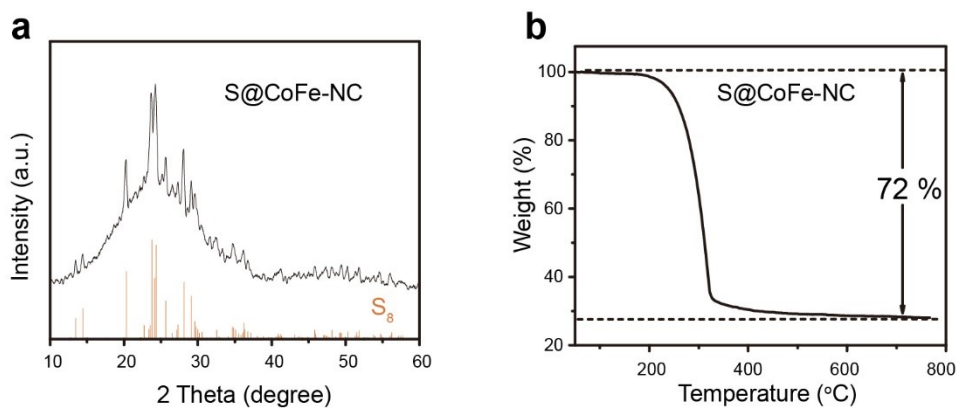


Figure. S5 (a) XRD patterns of S@CoFe-NC, (b) TGA of S@CoFe-NC in N₂.

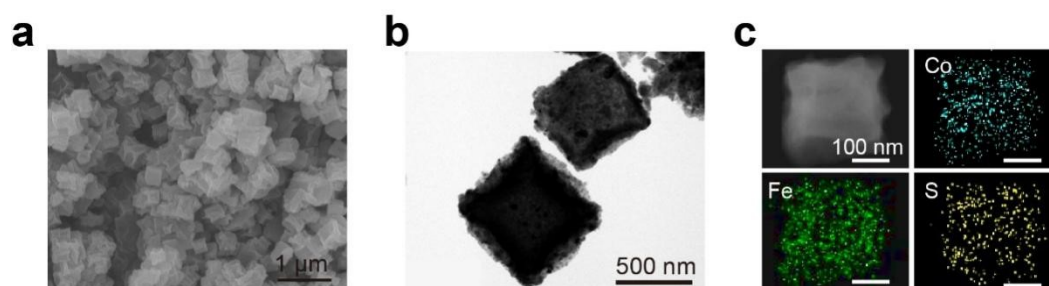


Figure. S6 (a-b) SEM and TEM images of S@CoFe-NC, (c) elemental mapping images of a single S@CoFe-NC.

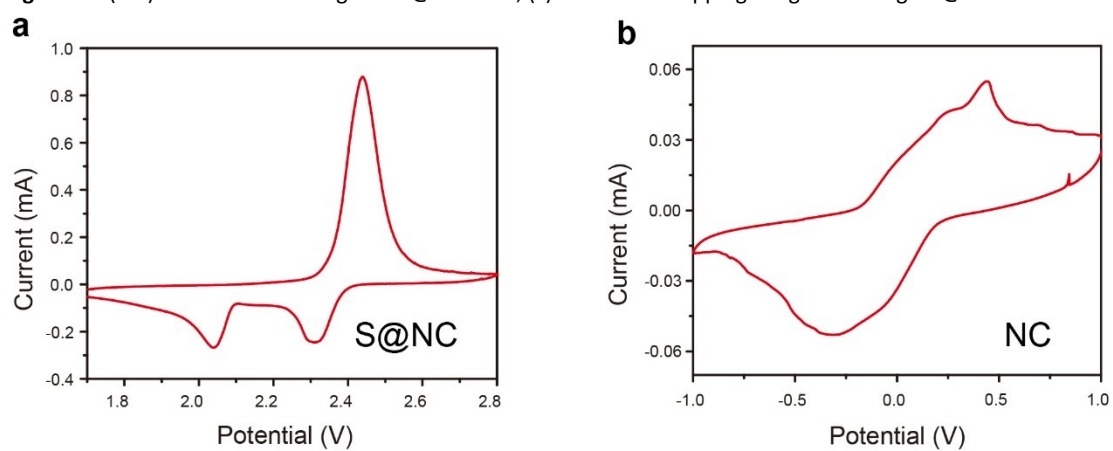


Figure. S7 (a) CV curves of S@NC at 0.1 mV/s. (b) CV curves of symmetric cells using NC without Sulfur as an electrode with 0.5 M Li₂S₆ in electrolyte at a scan rate of 50 mV/s within a voltage window of -1.0 to 1.0 V.

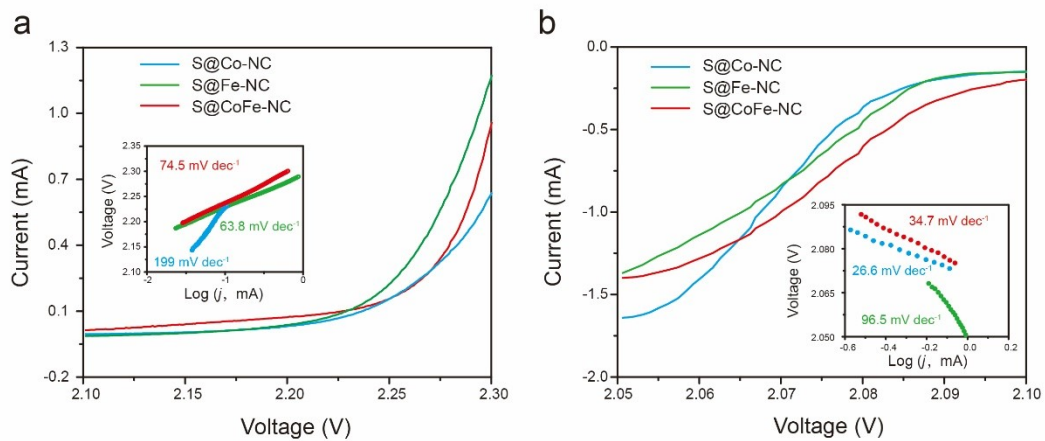


Figure. S8 (a,b) Linear sweep voltammetry curves obtained from fig.3(e) and the insets are corresponding Tafel plots.

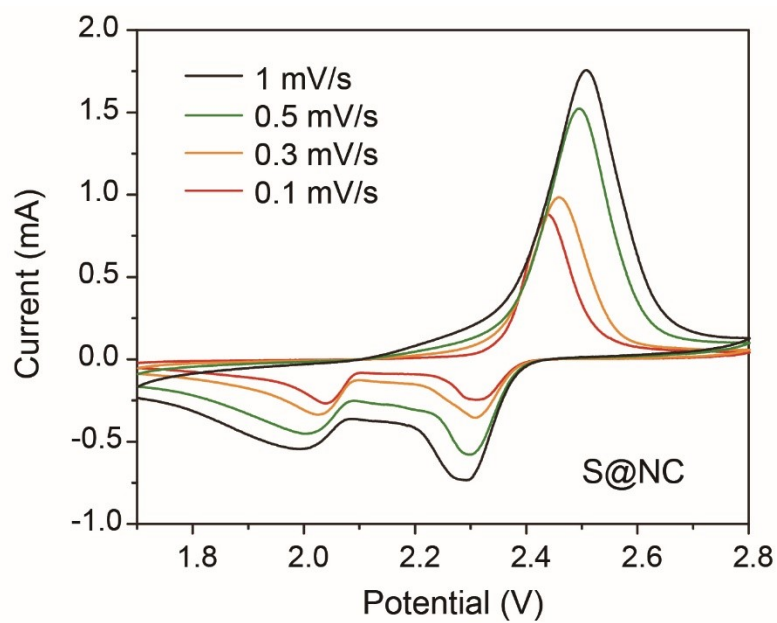


Figure. S9 CV curves of S@NC at different scan rates.

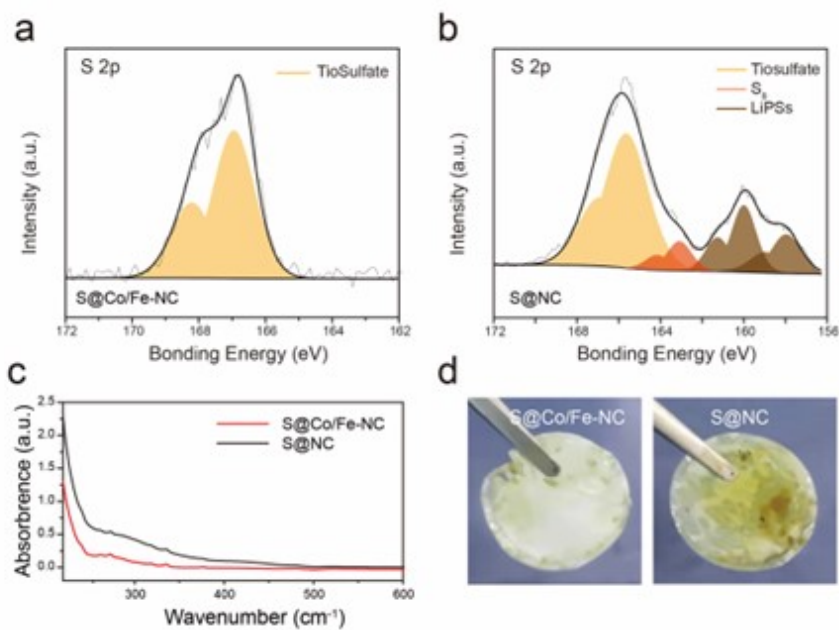


Figure S10 (a-b) S 2p XPS spectra of Li anode surface after 100 cycles of S@Co/Fe-NC and S@NC. (c) UV-vis absorption spectra of electrolytes after 100 cycles of S@Co/Fe-NC and S@NC. (d) Optical photographs of the separators after 100 cycles of S@Co/Fe-NC and S@NC.