Supporting Information

Frogspawn Inspired Hollow Fe$_3$C@N-C as an Efficient Sulfur Host for High-rate Lithium-sulfur Batteries

Huaiyue Zhang[a], Hongtao Cui[a], Jing Li[a*], Yuanyuan Liu[a], Yanzhao Yang[b] and Meiri Wang[a*]

[a] Shandong Collaborative Innovation Center of Light Hydrocarbon Transformation and Utilization, School of Chemistry & Chemical Engineering, Yantai University, Yantai 264005, China; E-mail: jli@ytu.edu.cn, wangmr@ytu.edu.cn

[b] Key Laboratory for Special Functional Aggregate Materials of Education Ministry, School of Chemistry and Chemical Engineering, Shandong University, Jinan 250100, China.

1. Experimental

1.1 Preparation

Synthesis of Fe$_3$C@N-C and N-C composites: The Prussian blue (PB) template was prepared by a liquid precipitation method. First, 25 mL of ferric chloride solution

(0.08 mol L^{-1}) and 1 mL of hydrochloric acid were dissolved in 50 mL deionized water in a 150 mL beaker. Then, it was added to a stirred solution of 25 mL of potassium ferricyanide (0.04 mol L^{-1}) at room temperature and with continuous stirring in a water bath at a temperature of 60 °C for 4 h. After that, it was transferred to a dark place for aging about 12 hours. After centrifugation (9000 r min^{-1}) and washed with anhydrous ethanol for three times successively, the PB powder was collected and dried in vacuum at 60 °C for 12 hours. Next, the corresponding products were used as template and coated with polydopamine (PDA) to form the core-shelled PB@PDA nanoboxes. Followed by calcinating to 800°C with heating ramp of 5°C min^{-1} for 2 h in N_2 atmosphere, the frogspawn-like $Fe_3C@N-C$ was obtained. The hollow N-C nanocage was also prepared for the reference sample.

Preparation of $Fe_3C@N-C/S$, N-C/S and SP/S composites: The $Fe_3C@N-C$ and sulfur powder was first mixed as a weight ratio of 3:7. Then, the mixture was heated to 155°C for 15 h in N_2 atmosphere at a tube furnace, and the $Fe_3C@N-C/S$ as cathode materials were obtained.

For comparison, the pristine N-C/S and SP/S composites were also prepared by the same method. For all the samples, the S content was 70 wt.%.

1.2 Characterization

XRD patterns were recorded on Rigaku SmartLab III diffractometer using Cu Kα radiation (λ = 1.5406 Å, 40 kV, 30 mA). The morphology and structure of the samples were observed on a JSM-7900F SEM (JEOL, Japan) and a JEM-2100F TEM (JEOL, Japan). Energy dispersive X-ray spectroscopy (EDS) mapping was carried out on Yalos F200X. N_2 adsorption/desorption isotherms of samples were measured by ASAP-2010 surface area analyzer. The X-ray photoelectron spectroscopy (XPS) analysis on the valance state and composition of samples were carried out on ESCALAB Xi+. The sulfur content was analyzed in Argon on a Pyris Diamond TGA/DTA analyzer (PerkinElmer) at a heating rate of 5 °C min^{-1}.

1.3 Electrode Fabrication and Electrochemical Characterization

The positive electrode consists of $Fe_3C@N-C/S$, Kejent Black (KB) and polyvinylidene fluoride (PVDF). The mixture at a weight ratio of 8: 1: 1 was

dispersed in N-methyl-2-pyrrolidinone (NMP). Then the slurry was coated onto Al foil and dried overnight at 65°C in vacuum. The electrode was cut into circular discs with a diameter of 7 mm. The electrolyte containing 1.0 M lithium bis-trifluoromethane sulfonimide (LiTFSI), 5 % $LiNO_3$ additives and a mixture of dimethoxyethane (DME) and 1,3-dioxolane (DOL) (1:1 by volume). Coin-type cells (CR 2016) were assembled in an Ar filled glove box with lithium foil as the anode and Celgard 2325 as the separator. The electrochemical tests were carried out by a LAND CT-2001A instrument (Wuhan Landian), with constant current and voltage ranging from 2.8 to 1.85 V. The cyclic voltammogram (CV) measurements were performed on a CHI660D electrochemical work station (Shanghai Chenhua) at a scanning rate of 0.1 mV/s in a potential range of 1.85 to 2.8 V (vs Li/Li^+). Electrochemical impedance spectroscopy (EIS) was conducted in the frequency range 3.0×10^5 Hz to 100 mHz at the open-circuit voltage with an amplitude of 10 mV using a IVIUMnSTAT electrochemical work station.

Adsorption Test of Li_2S_4: A 0.01 M of Li_2S_4 solution was prepared by adding sulfur powder and Li_2S at a molar ratio of 3: 1 in dimethoxyethane (DME). After vigorous magnetic stirring at 60 °C for 24 h, a uniform yellow solution of Li_2S_4 was obtained to perform adsorption test. SP and $Fe_3C@N-C$ with same mass of 3 mg were added to 3.0 ml of the Li_2S_4 solution respectively, and 3.0 ml Li_2S_4/DME solution was used as a comparison. The concentration of residual polysulfide in the solution was also determined by UV-vis adsorption A560.

1.4 DFT

First principle calculations were performed using CASTEP program to give an insight into mechanism.[1] In all calculations, the generalized gradient approximation (GGA) with the Perdew, Burke, and Ernzerhof (PBE) exchange-correlation function was used, [2] and a plane-wave cutoff energy was set to be 500 eV. For all geometry optimizations and single energy calculations, the convergence criterion for the force between atoms was 3×10^{-2} eV/Å, self-consistent convergence accuracy was set at 1×10^{-5} eV per atom, and the maximum displacement was 1×10^{-3} Å. Also, DFT

calculations were performed to observe the stable geometries, for revealing the optimal adsorption location of Li_2S_4 on Fe_3C. To better understand the surface state change, we calculated the charge density. In order to comprehend the interaction between Li_2S_4 and Fe_3C, the electron population was also calculated. The Arrhenius equation for calculating rate constant is expressed in eq(1). [3]

$$\ln(k) = \ln(A) - \frac{E_a}{RT}$$

Where k is the rate constant of adsorption, (g mg^{-1} min^{-1}); A is the Arrhenius factor; E_a is the activation adsorption energy (kJ mol^{-1}); $R = 8.314$ (J K^{-1}mol^{-1}) is the ideal gas constant; T is the temperature (K).

2. Results
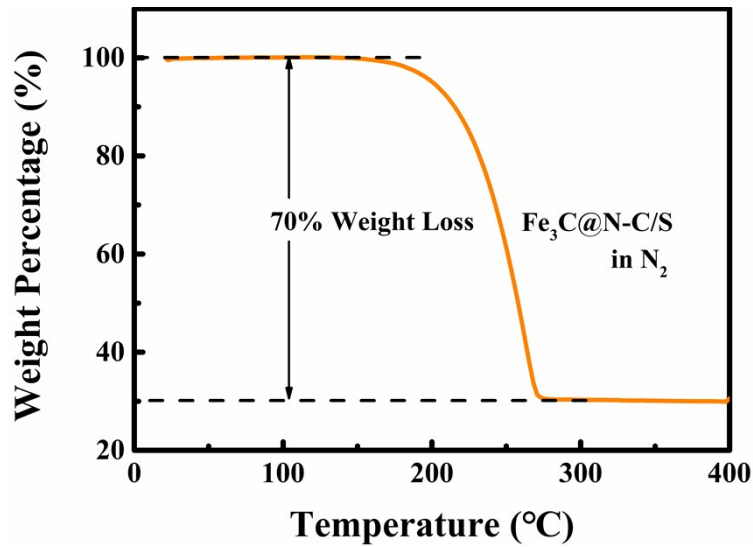

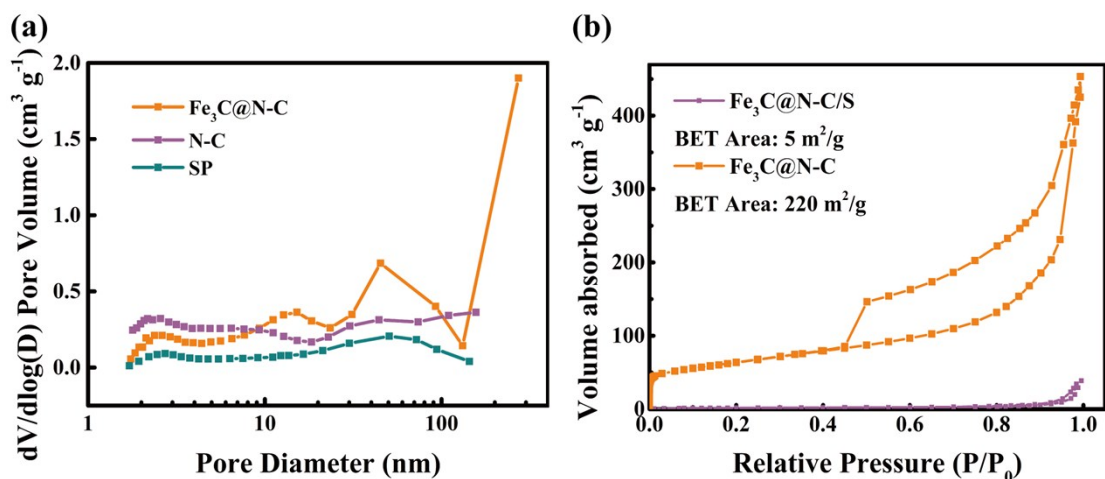Fig. S1. Thermogravimetric analysis (TGA) of the sulfur content of $Fe_3C@N-C/S$ electrode.

Fig. S2. a) Pore size distribution of $Fe_3C@N\text{-}C$, N-C and SP; b) N_2 adsorption/desorption isotherms of $Fe_3C@N\text{-}C/S$.
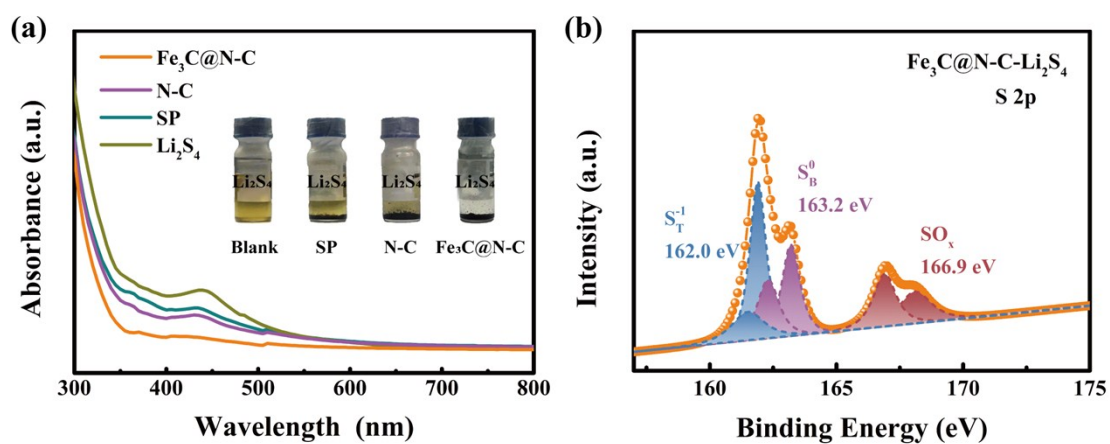

Fig. S3. a) Ultraviolet-visible (UV-vis) absorption spectroscopy for polysulfides based on $Fe_3C@N\text{-}C$, N-C and SP after visual adsorption test; XPS spectra of $Fe_3C@N\text{-}C\text{-} Li_2S_4$ b) N 1s; c) Fe 2p; d) S 2p.
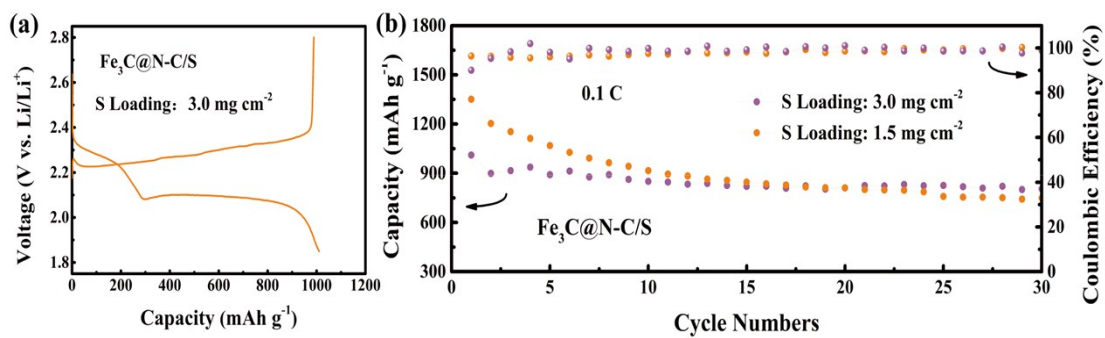
Fig. S4. a) First discharge-charge curves of Fe$_3$C@N-C/S electrode at 0.1C as the sulfur loading is 3.0 mg cm^{-2}; b) Cycle performance of Li-S batteries based on the Fe$_3$C@N-C/S electrode at 0.1C as the sulfur loading is 3.0 mg cm^{-2}.

References

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