Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Core-shell oxygen-deficient Fe_2O_3 polyhedron serves as an efficient host for sulfur cathode

Jun Pu,[1,*] *Ziyang Huang,*[1] *Jie Wang,*[2,*] *Yun Tan,*[1] *Shanshan Fan,*[1] *Zhenghua Wang,*[1]

[1] Key Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Provincial Engineering Laboratory for New-Energy Vehicle Battery Energy-Storage Materials, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241002, China.

[2] College of Chemistry and Chemical Engineering, Anqing Normal University, Anqing 246000, China.

* *Prof. Jun Pu, jpu@ahnu.edu.cn*

* *Dr. Jie Wang, wangjie@aqnu.edu.cn*

1. Experimental

1.1 Synthesis of ZIF-C

First, 2.195 g of $Zn(CH_3COO)_2 \cdot 2H_2O$ and 2.464 g of 2-methylimidazole were dissolved into 50 ml methanol, then mixed, stirred overnight and precipitated, the white solid (zeolitic imidazolate framework-8, ZIF-8) was collected, washed with methanol, and dried under vacuum. Under Ar atmosphere, ZIF-8 was heated to 700 °C and held for 1 h. After cooling, it was dispersed into 1 M HCl, left overnight, centrifuged, washed, and dried to obtained porous carbon polyhedron.

1.2 Fabrication of Fe_2O_{3-x}@C polyhedron and Fe_2O_{3-x}@C@S composite

30 mg of ZIF-C was dispersed in 40 ml NaCl solution (1 M), ultrasonic for 10 min. About 1 mL Poly (sodium 4-styrenesulfonate) (PSS) was added, stirred at room temperature for 30 min, centrifuged, precipitated, washed, and vacuum dried. The PSS@C was dispersed in 60 mL aqueous solution containing 0.065 g $FeCl_3 \cdot 6H_2O$ and stirred in an oil bath at 80 °C for 30 min to obtain FeOOH@C. After this hydrothermal treatment, the Fe_2O_3@C composite was obtained by heating FeOOH@C to 400 °C under Ar atmosphere. Finally, above Fe_2O_3@C polyhedron were heated to 200 °C at Ar/H_2 (95:5) gas mixture for 30 min, and cooled to room temperature. The flow rate of hydrogen was about 25 standard cubic centimeter per minute. The content of iron oxide in Fe2O3@C and Fe2O3-x@C samples was about 37%.

For Fe_2O_{3-x}@C@S composite, the method is the classical sulfur melting technology. Fe_2O_{3-x}@C and sublimed sulfur were heated at 155 °C for 12 h at a mass ratio of 3:7. For comparison, Fe_2O_3@C@S and ZIF-C@S (C@S) with the same sulfur content composite cathode materials were prepared in the similar way.

1.3 Materials characterization

Scanning electron microscopy (SEM) was obtained with Hitachi S-8100. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), high-angle annular detector dark-field (HAADF) based scanning transmission electron microscopy (STEM), and corresponding energy dispersive X-ray spectroscopy (EDS) element mapping were attained at high operated voltage with FEI Talos F400x at an acceleration voltage of 200 kV. X-ray powder diffraction (XRD) was measured with Rigaku D/Max III (Cu Kα radiation). X-ray photoelectron spectrum (XPS) was utilized by ESCA Lab MKII with a monochromic Al Kα X-ray source.

1.4 Visual adsorption test

Visual polysulfide adsorption test was done with brown-yellow Li_2S_6 solution. Firstly, the Li_2S_6 solution were prepared by sulfur and Li_2S (5:1 in molar ratio) co-dissolved in 1,3-ioxolane/1,2dimethoxyethane (DOL/DME, 1:1) solution. The equivalent amount of Fe_2O_{3-x}@C and Fe_2O_3@C was added into as-obtained Li_2S_6 solution respectively. Subsequently, the mixture was shaken slightly and set aside to observe the change in color.

1.5 Cell assembly and electrochemical measurements

The compound sulfur cathode slurry was attained compositing Fe_2O_{3-x}@C sample, acetylene black, and polyvinylidene fluoride (PVDF) were mixed in N-methy-pyrrolidinone (NMP) with a weight ratio of 8:1:1. Then, above slurry was cast on Al foil using a film applicator. The sulfur loading was controlled to 1.0 and 3.0 mg cm^{-2}.

After drying, the cathode was loaded into CR2032 cell with Celgard separator and Li metal anode. The electrolyte was 1 M LiTFSI in DOL/DME with 2 wt% $LiNO_3$. It should be noted that the assembly of the battery was completed in a water-free, oxygen-free glove box filled with Ar gas.

For electrochemical measurements, in addition to high loading test (3.0 mg cm^{-2}), the sulfur loading of a normal battery was 1.0 mg cm^{-2}. For former, the ratio of electrolyte *vs.* sulfur (E/S) was 20 μL mg^{-1}. For high loading, this value was reduced to 8 μL mg^{-1}. All galvanostatic charge-discharge cycling and rate tests were performed using a Land Battery Tester. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) at frequencies ranging from 100 kHz to 0.01 Hz were measured with a CHI660D electrochemical workstation and a Bio-Logic VSP potentiostat. Thermogravimetric analysis (TGA) data were performed by NETZSCH ASAP2020 thermal analyzer.

1.6 Theoretical Calculations

The dissolubility LiPSs adsorption on different hosts was modeled using DFT calculation with the CASTEP code.[1] The Perdew-Burke-Ernzerhof (PBE) version of the generalized gradient approximation was employed to describe exchange-correlation effects.[2,3] The plane-wave basis cutoff energy for geometric optimization and energy calculation was 450 eV. The Brillouin zone was used with a 2×2×1 Monkhorst-Pack mesh k-points. The binding energy (Eb) of LiPSs on the substrate was defined as:[4]

$$E_b = E_{sub} + E_{ps} - E_{sub+ps}$$

where the E_{sub+ps}, E_{sub}, and E_{ps} represent the ground-state energies of the substrate-

LiPSs, substrate, and LiPSs, respectively.

The theoretical calculations have been done on the computing facilities in the High-Performance Computing Center (HPCC) of Nanjing University.

Figures

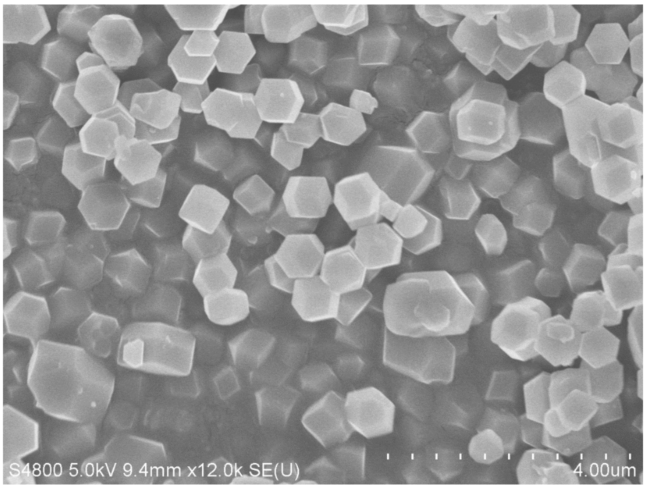

Figure S1. The SEM image of ZIF-8.

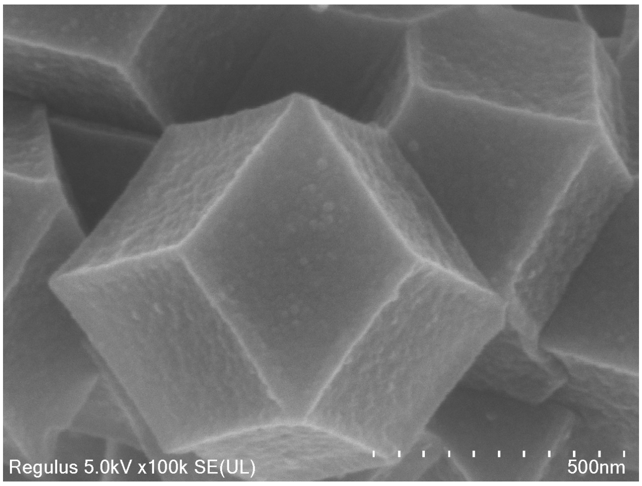

Figure S2. The SEM image of ZIF-C with high magnification.

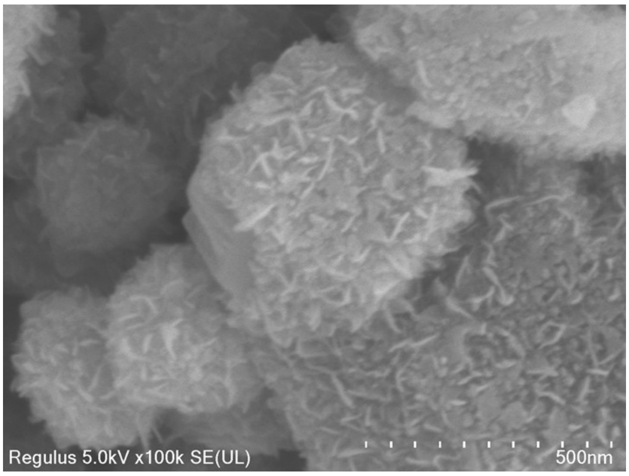

Figure S3. The SEM image of FeOOH@C.

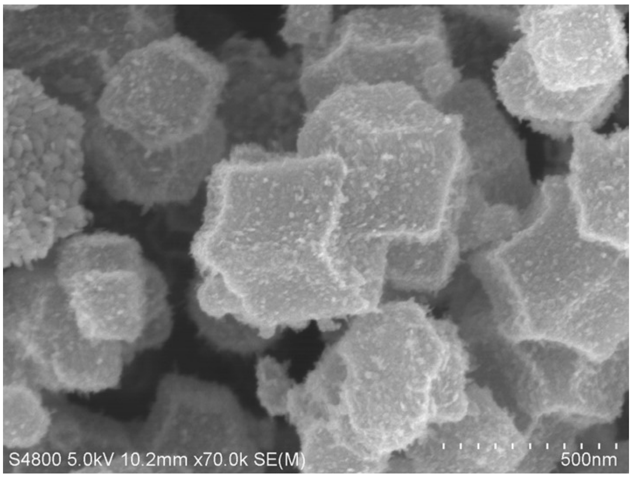

Figure S4. The SEM image of Fe_2O_3@C.

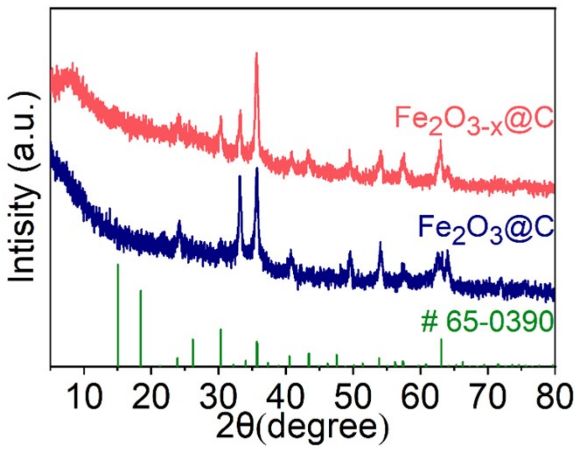

Figure S5. The XRD results of the Fe_2O_3@C and Fe_2O_{3-x}@C.

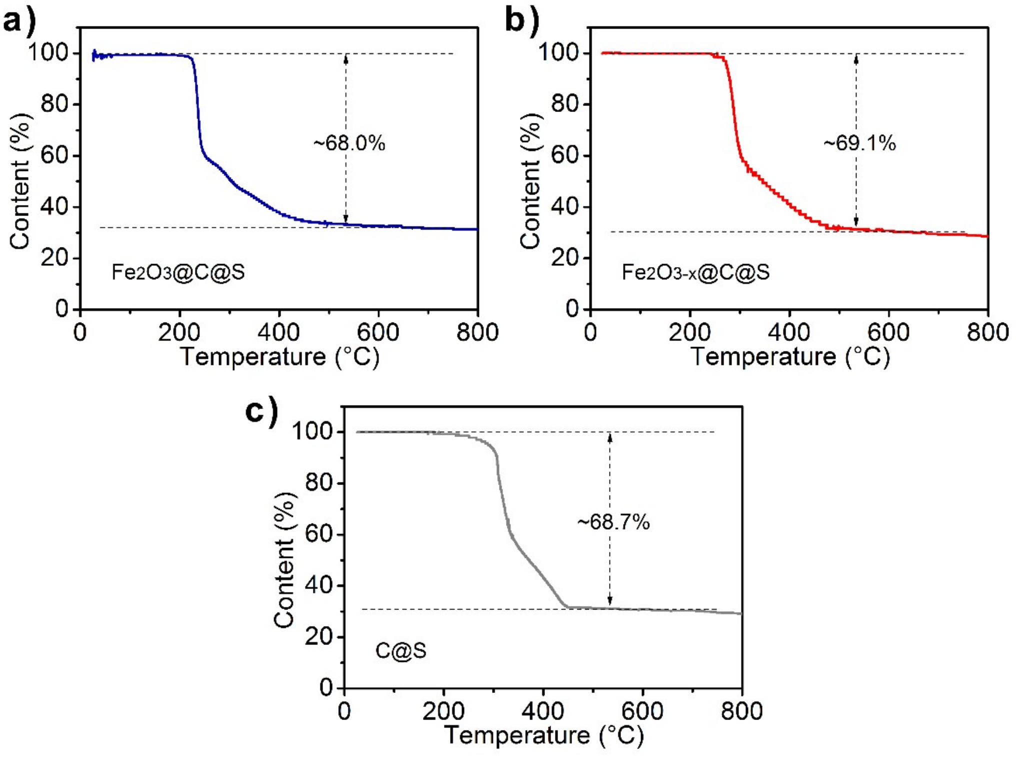

Figure S6. TGA results of (a) Fe_2O_3@C@S, (b) Fe_2O_{3-x}@C@S and (c) C@S.

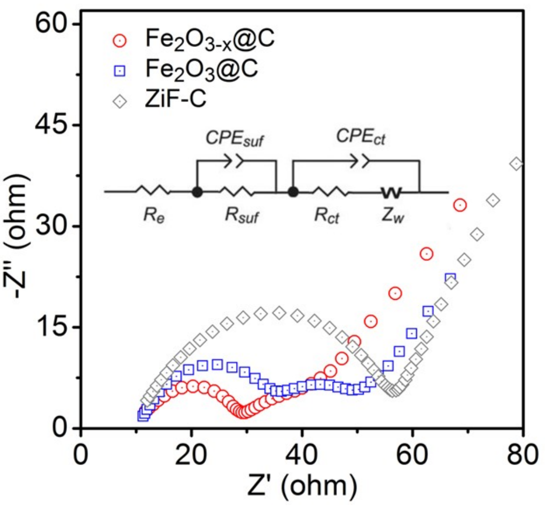

Figure S7. EIS results and corresponding fitted equivalent circuit model of Fe_2O_{3-x}@C@S, Fe_2O_3@C@S, and ZiF-C@S cathodes.

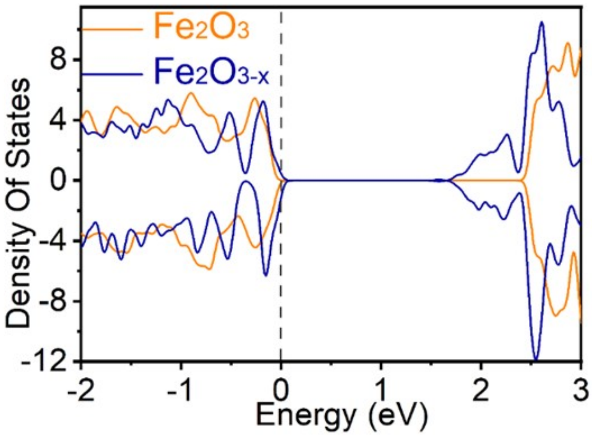

Figure S8. DOS profiles of Fe_2O_3 and Fe_2O_{3-x}.

Reference

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[4] Z. Yuan, H.-J. Peng, T.-Z. Hou, J.-Q. Huang, C.-M. Chen, D.-W. Wang, X.-B. Cheng, F. Wei, Q. Zhang, Powering Lithium-Sulfur Battery Performance by Propelling Polysulfide Redox at Sulfiphilic Hosts. Nano Lett. **2016**, 16, 519–527.