Electronic Supplementary Material (ESI) for Chemical Communications.
This journal is © The Royal Society of Chemistry 2024

Supporting Information

Construction of heterostructured Fe_2O_3/Fe_7S_8 hollow fibers to boost the electrochemical kinetics of lithium storage

Kaitao Liu,‡[a] Qiaoling Li,‡[ab] Yingying Song,[a] Yifei Song,[a] Zhiming Yan,[a] Junzhe Wang,[a] Xueda Li,[a] Hongqiang Wang*[a] and Jiao Li*[a]

[a]School of Materials Science and Engineering, Shandong University of Technology, Zibo, 255049, Shandong, China

[b]School of Materials Science and Engineering, Hebei University of Technology, 300130, Tianjin, China

‡ These authors have contributed equally to this work.

* Corresponding authors.

E-mail: hwang@sdut.edu.cn (H. Wang);

haiyan9943@163.com (J. Li)

1. Experimental section

1.1 Preparation of as-spun PVP/Fe fibers

To begin with, the as-spun PVP/Fe fibers were prepared by using electrospinning technique. A well-mixed spinning solution was obtained by combining a certain amount of PVP (1.9 g, M_w=1,300,000) and $Fe(NO_3)_3 \cdot 9H_2O$ (2.0 g) in a mixture of ethanol absolute (10 mL) and DMF (8 mL) through vigorous stirring overnight. Subsequently, the solution was loaded into a 5 mL syringe and attached to the spinneret for electrospinning. The parameters, including feeding speed, drum speed, spinning distance, and low/high voltage, were set at 0.07 mm/min, 120 rpm, 15 cm, and -5/15 kV, respectively. Finally, the collected membrane on the aluminum foil was dried to obtain the as-spun PVP/Fe fibers.

1.2 Preparation of Fe_2O_3, Fe_7S_8, Fe_2O_3/Fe_7S_8 hollow fibers, and Fe_2O_3/Fe_7S_8 nanoparticles

The as-spun PVP/Fe fibers were pre-oxidized at 200 ^oC for 2 h, followed by calcination at 600 ^oC for 2 h with a heating rate of 5 ^oC min^{-1}, resulting in hollow Fe_2O_3 fibers. The heterostructured Fe_2O_3/Fe_7S_8 and Fe_7S_8 hollow fibers were prepared by sulfidation process, which stems from the thermal decomposition of thiourea at high temperature. The hollow Fe_2O_3 fibers was firstly mixed with a certain amount of thiourea (1:2 by weight), and then heated at 400 ^oC and 500 ^oC for 30 min in the Ar atmosphere to obtain Fe_2O_3/Fe_7S_8 and Fe_7S_8 hollow fibers, respectively. The control sample of Fe_2O_3/Fe_7S_8 nanoparticles was prepared following the same procedure without electrospinning technique.

1.3 Materials characterization

The morphology and structure of samples were examined by using scanning electron microscope (JEOL, JSM-7500), transmission electron microscope (JEOL, JSM 2100 F), and powder X-ray diffractometer (XRD, Bruker D8 Advanced). X-ray photoelectron spectroscopy (XPS) was collected on Thermo Scientific ESCALAB 250Xi.

1.4 Electrochemical characterization

The electrode slurry was prepared by mixing the active material, carbon black, and sodium carboxymethyl cellulose (CMC) (7:2:1 by weight) in deionized water, which was then coated on copper foil and dried in vacuum at 90 ℃ for 24 h. Coin-type (CR2032) cells were assembled in an argon-filled glove box, with lithium metal foil as the anode, membrane Celgard 2400 as separator, and 1 M $LiPF_6$ in a solution of Ethylene carbonate (EC), Dimethyl carbonate (DMC), and Ethyl Methyl Carbonate (EMC) (1:1:1 by volume) containing 5% Fluoroethylene carbonate (FEC) as electrolyte. The LAND CT2001A battery test system was used to evaluate electrochemical performance of electrodes in the voltage range of 0.01-3 V. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out under the CHI 660E electrochemical workstation.

1.5 Computational Method

Density functional theory (DFT) calculations were performed by using the Vienna *ab initio* simulation package (VASP). The exchange-correlation interaction was described by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof

(PBE) functional. The energy cut-off was set to 400 eV. The convergence thresholds of the total energy and the force on an atom were 10^{-5} eV and 0.001 eV·Å^{-1}, respectively. The Brillouin zone was sampled by a Monkhorst-Pack 5×5×1 k-point grid. The adsorption energies (E_{ads}) were calculated by Equation (1):

$$E_{ads} = E_{Li/host} - E_{Li} - E_{host} \quad (1)$$

where $E_{Li/host}$ represents the total energy of the optimized adsorption system, while E_{Li} and E_{host} are the energies for the isolated Li and Fe_2O_3/Fe_7S_8, respectively.

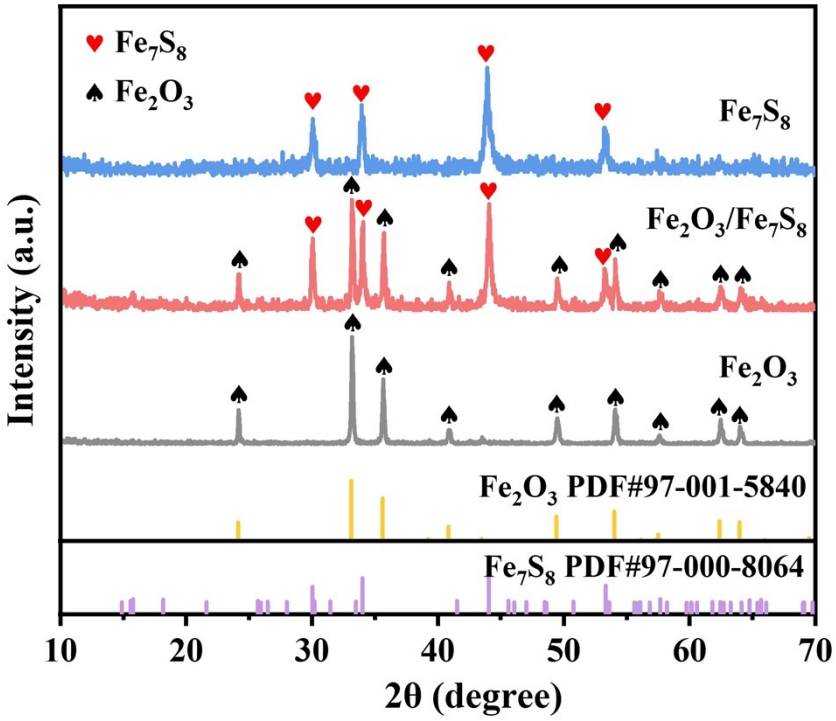

Figure S1. XRD patterns of Fe_2O_3, Fe_7S_8, and Fe_2O_3/Fe_7S_8 hollow fibers.

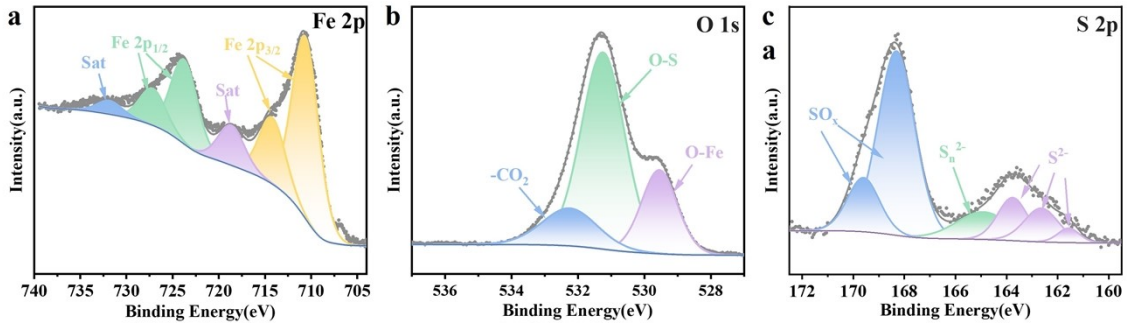

Figure S2. XPS spectra of Fe_2O_3/Fe_7S_8 hollow fibers: (a) Fe 2p, (b) O 1s, and (c) S 2p.

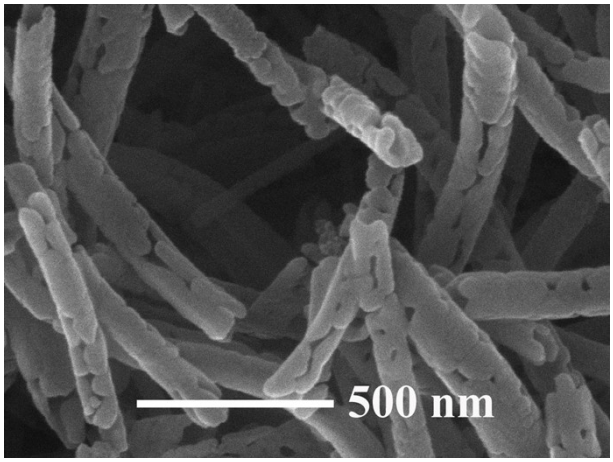

Figure S3. SEM image of Fe_7S_8 hollow fibers.

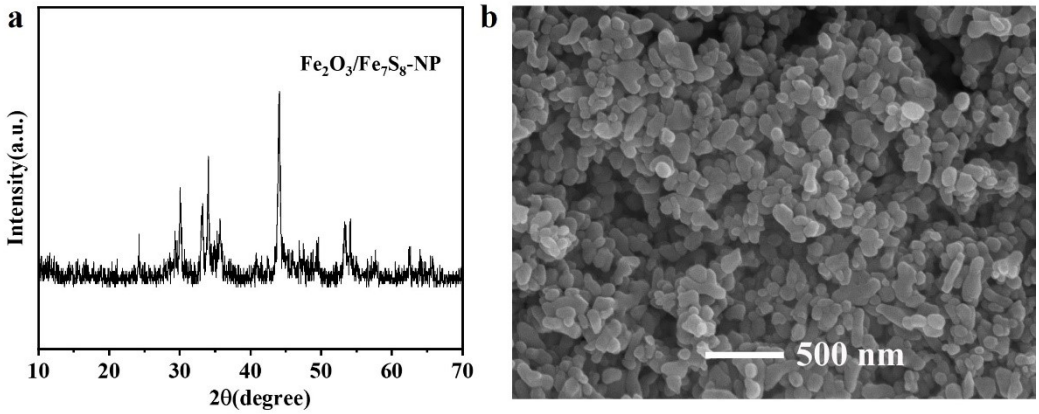

Figure S4. (a) XRD pattern and (b) SEM image of Fe_2O_3/Fe_7S_8 nanoparticles.

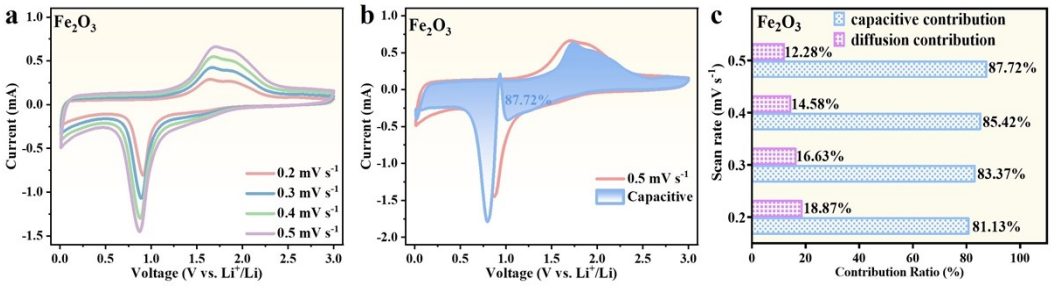

Figure S5. (a) CV curves of Fe_2O_3 electrode at different scan rates, (b) capacitance contribution at 0.5 mV s^{-1} and (c) ratios of capacitance contribution at different rates for Fe_2O_3 electrode.

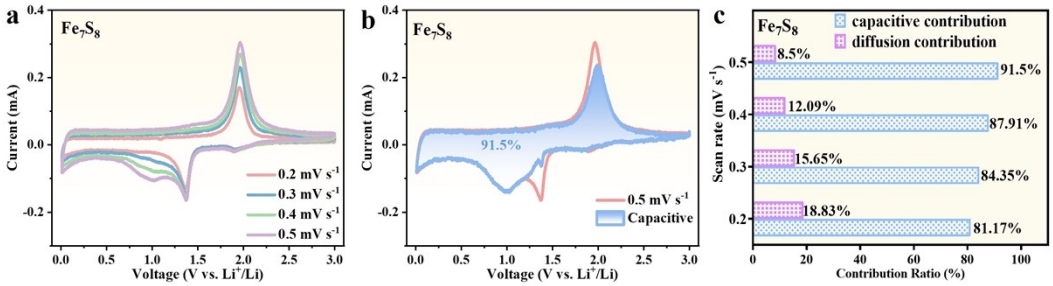

Figure S6. (a) CV curves of Fe_7S_8 electrode at different scan rates, (b) capacitance contribution at 0.5 mV s^{-1} and (c) ratios of capacitance contribution at different rates for Fe_7S_8 electrode.