

# Supplementary information

## Graphene Encircled $\text{KFeSO}_4\text{F}$ Cathode Composite for High Energy Density Potassium-Ion Batteries

Jiemin Dong, Jiaying Liao, Xiaodong He, Qiao Hu, Yifan Yu, Chunhua Chen\*

*CAS Key Laboratory of Materials for Energy Conversions, Department of Materials Science and Engineering & Collaborative Innovation Center of Suzhou Nano Science and Technology, University of Science and Technology of China, Hefei 230026, Anhui, China*

## Experimental section

Synthesis of  $\text{KFeSO}_4\text{F}$  (KFSF) and graphene wrapped KFSF (KFSF@G):

The  $\text{KFeSO}_4\text{F}$  (KFSF) sample was synthesized by a simple solvothermal process. Firstly, 5 mmol  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (A.R.) was dissolved into 50 ml of ethylene glycol solvent. After ultrasonically dispersed and stirred for a while, stoichiometric KF (A.R.) was added into the solution. After homogenization, the resulted solution was transferred to a 100 mL Teflon-lined stainless steel autoclaves and kept at 160 °C for 6 h in a thermostatic oil bath under stirring. Consequently, a grey colored precipitate as the KFSF precursor was obtained. Then this precursor powder was collected by centrifugation and washing for three times with alcohol. Subsequently, it was annealed at 350 °C under a flowing  $\text{H}_2(5\%)/\text{Ar}$  atmosphere for 3 h to obtain bare KFSF.

To improve the conductivity of the sample, a portion of the KFSF precursor powder was mixed with different amounts of commercial graphene dispersion (Carbon Century, Beijing) by ball-milling for 15 h and then annealed under the same conditions to obtain the final graphene wrapped  $\text{KFeSO}_4\text{F}$  powders, i.e. KFSF@G. For comparison, KFSF@SP was synthesized using Super P as another carbon source.

### Morphology and structure characterization

The phase compositions and crystallinity of KFSF and KFSF@G were analyzed by X-ray diffraction (Rigaku TTR-III, Cu  $\text{K}\alpha$  radiation) over a range of  $2\theta$  angles from 10° to 70° at a scanning rate of 10 °·min<sup>-1</sup>. Their morphologies were observed with a scanning electron microscope (FEI Apreo) and a transmission electron microscope

(TEM, JEM-2010). Thermogravimetric analysis (TGA, DTG-60H, Shinadzu) was performed at a heating rate of  $10\text{ }^{\circ}\text{C min}^{-1}$  in the temperature range of  $25\text{-}700\text{ }^{\circ}\text{C}$  under flowing  $\text{N}_2$  atmosphere. The specific surface area of the powder was measured by  $\text{N}_2$ -adsorption/desorption (ASAP 2020). The Raman spectra of KFSF and KFSF@G were recorded on the condition of 532 nm diode laser excitation (Renishaw inVia Raman Microscope). The carbon contents of the as-prepared samples were analyzed by an infrared carbon-sulfur analyzer (CS-8800C, Jinbo).

#### Electrochemical measurements

The electrochemical performances of the samples were evaluated using coin-type half-cells (CR2032 size). The working electrodes were prepared by mixing the active materials (70 wt. %), acetylene black (20 wt. %) and poly(vinylidene fluoride) (10 wt. %) binder in N-methyl-2-pyrrolidinone to obtain slurries, which were coated on an aluminium foil collector and vacuum dried at  $120\text{ }^{\circ}\text{C}$ . The mass loading of the active material in the electrode was  $1.4\text{ mg cm}^{-2}$ . The electrolyte was 0.1 M  $\text{KClO}_4$  dissolved in PC. A potassium foil acted as the counter electrode, and a Whatman glass-fiber was used as a separator. All the cells were assembled in an argon filled glove box (MBraun Labmaster 130) and tested at room temperature ( $25\pm 2\text{ }^{\circ}\text{C}$ ). The cyclic voltammetry (CV) of the cell was measured on a CHI 660C electrochemical workstation at the scan rate of  $0.1\text{-}0.7\text{ mV s}^{-1}$  between 1.5 and 4.8 V. The galvanostatic charge-discharge was also tested on a NEWWARE BTS-610 multichannel battery test system (Neware Co., Shenzhen, China) in the voltage range of 1.5-4.5 V. Also, in order to verify that the

graphene can improve the electronic conductivity of the electrode, we measured the electronic conductivity of KFSF and KFSF@G by a four-probe method (Powder Resistivity Tester, ST2722-SZ, Suzhou Jinge).

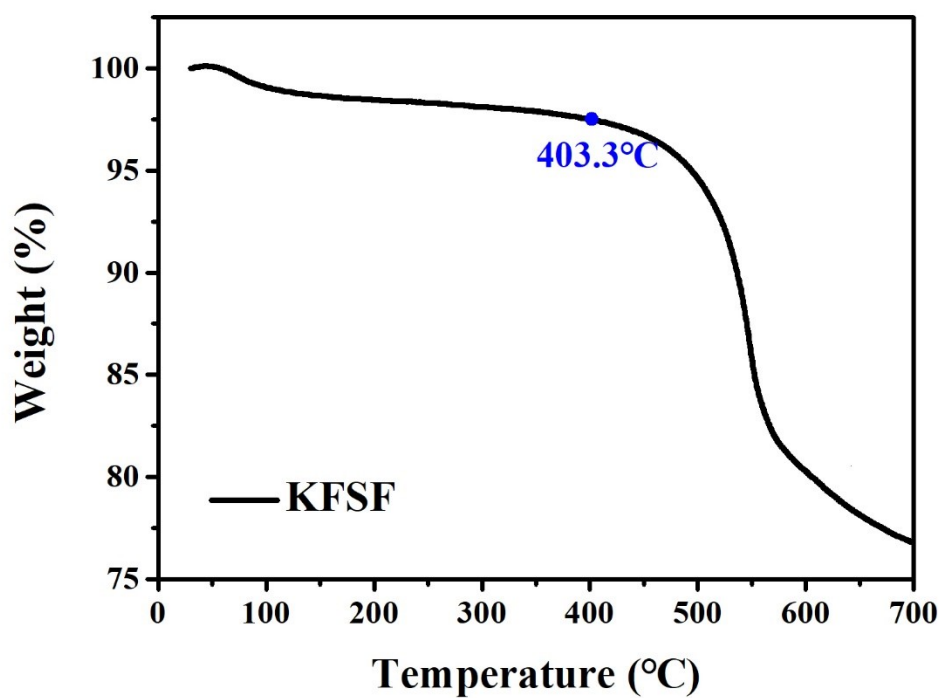


Fig. S1 Thermogravimetric analysis of KFSF@G.

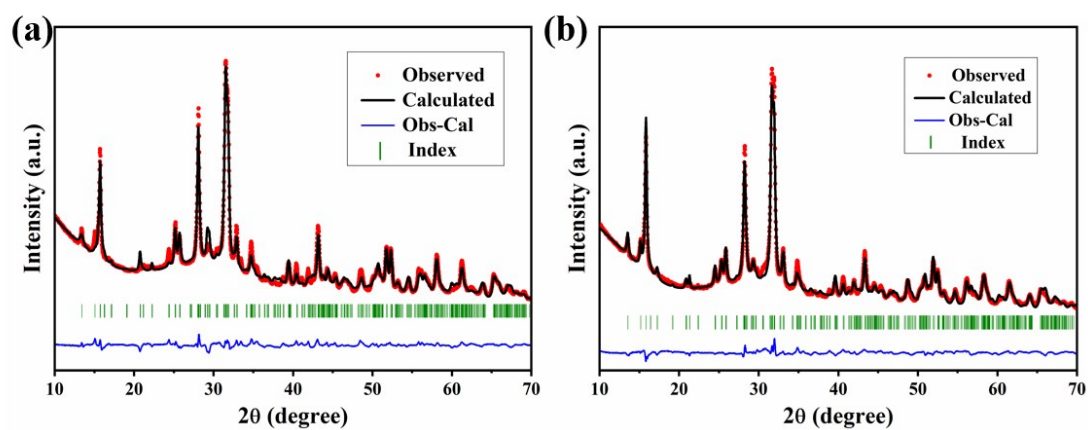


Fig. S2 Rietveld refinement of XRD patterns of KFSF (a) and KFSF@G (b).

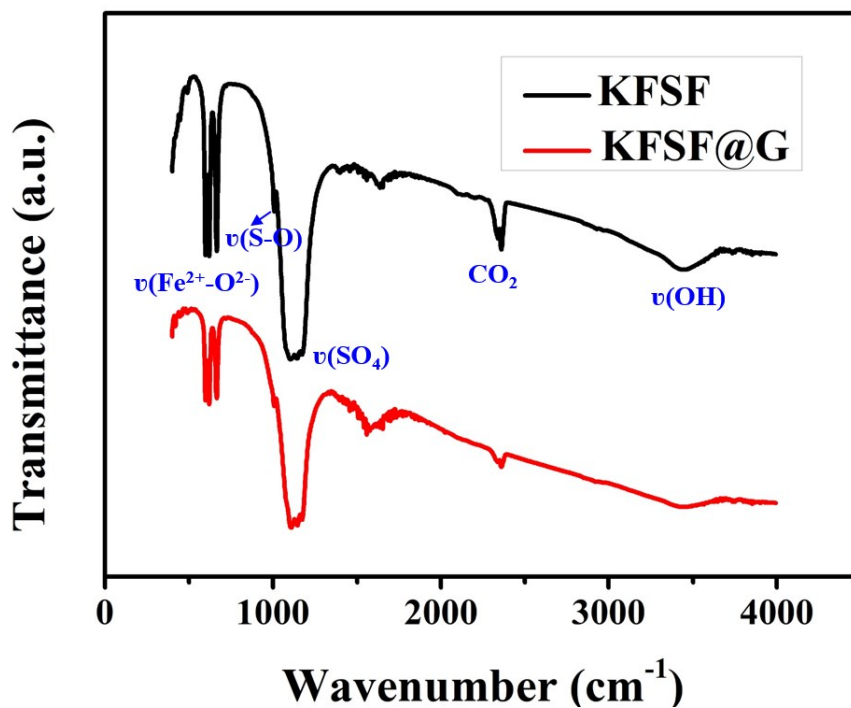


Fig. S3 FTIR spectra of KFSF and KFSF@G.

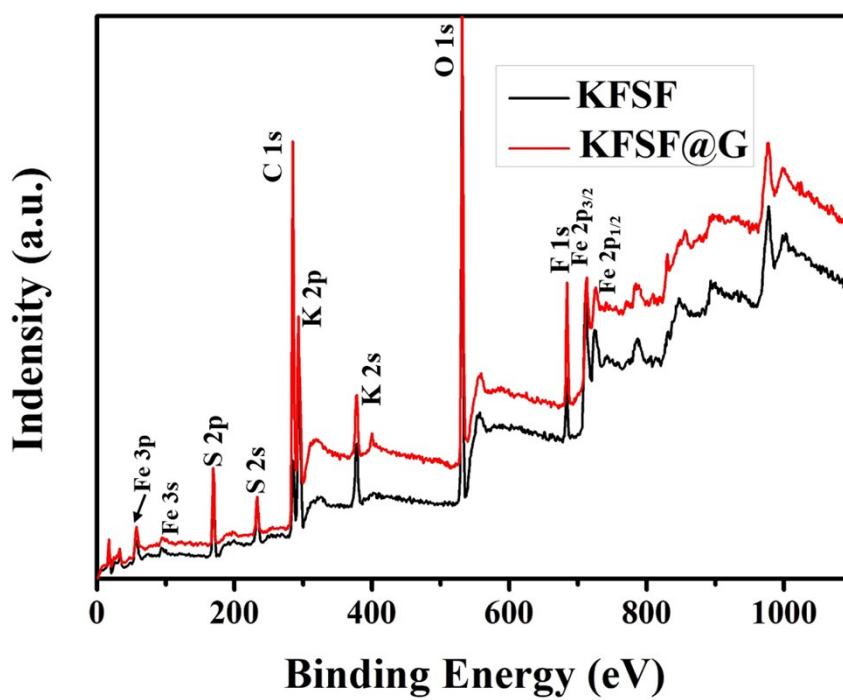


Fig. S4 XPS spectra of KFSF and KFSF@G.

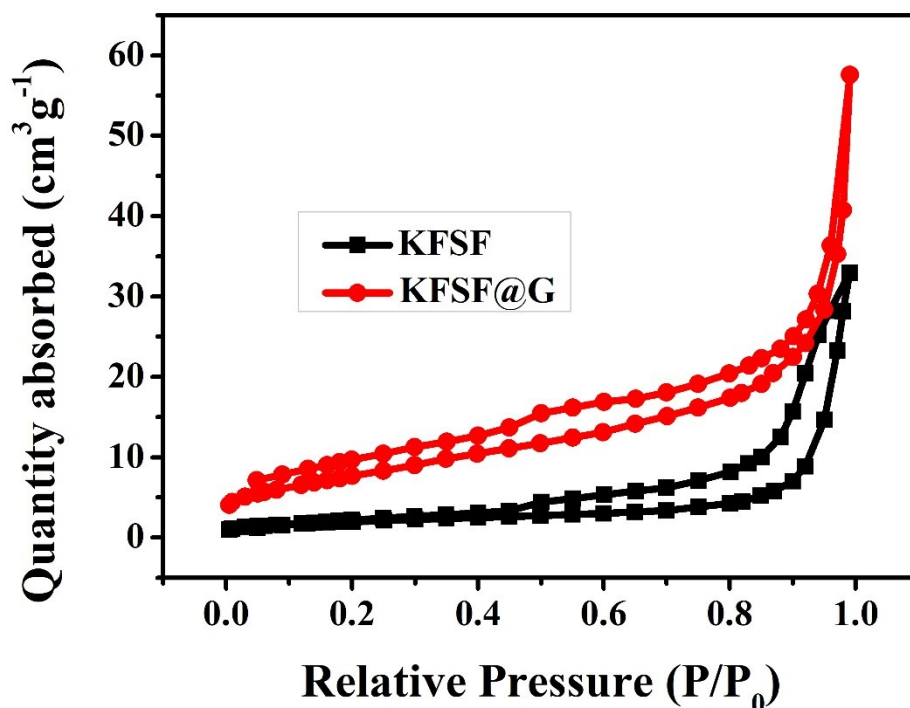


Fig. S5  $\text{N}_2$  adsorption–desorption isotherms of KFSF and KFSF@G.

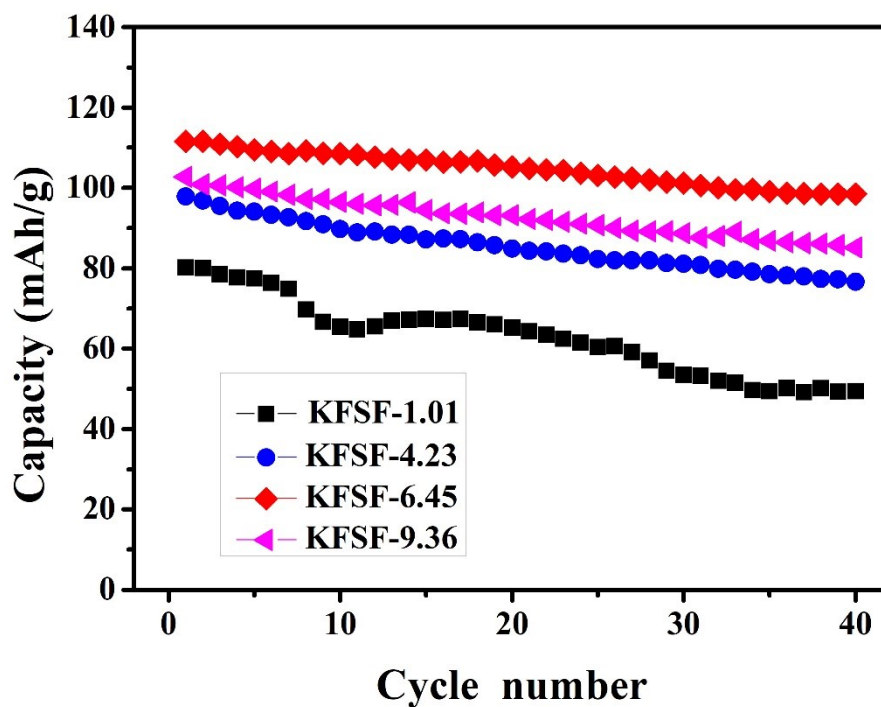
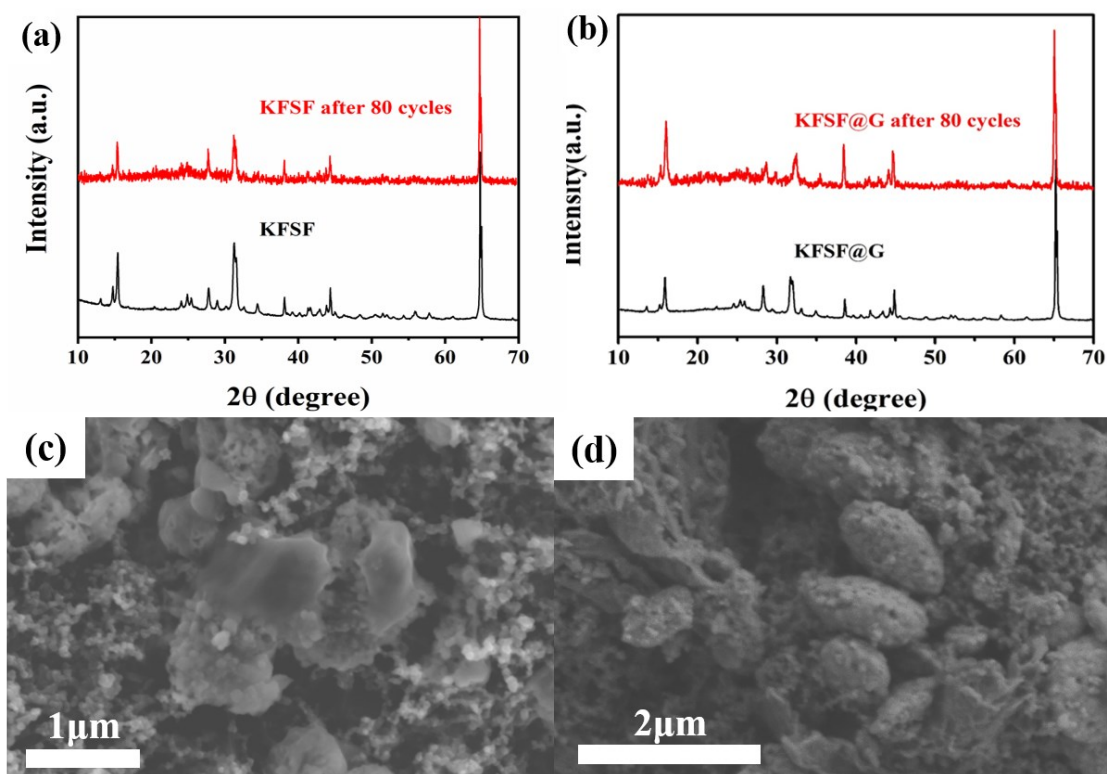
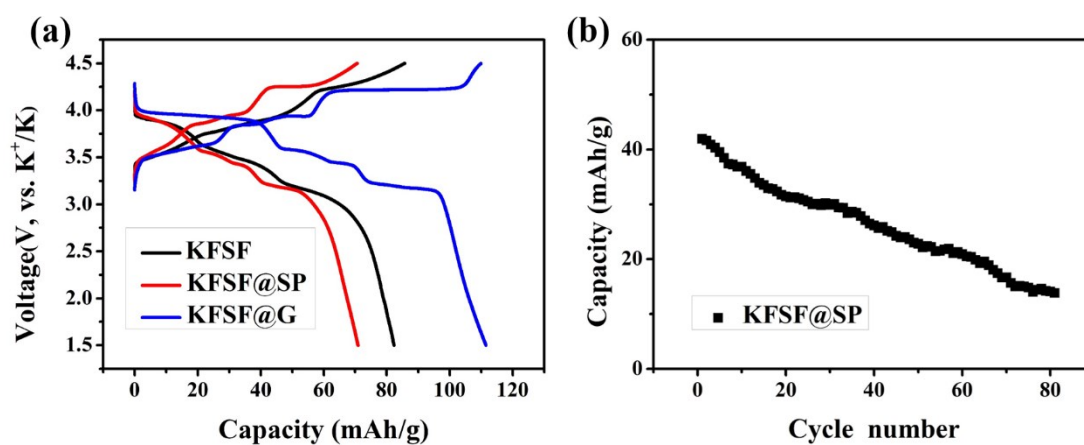


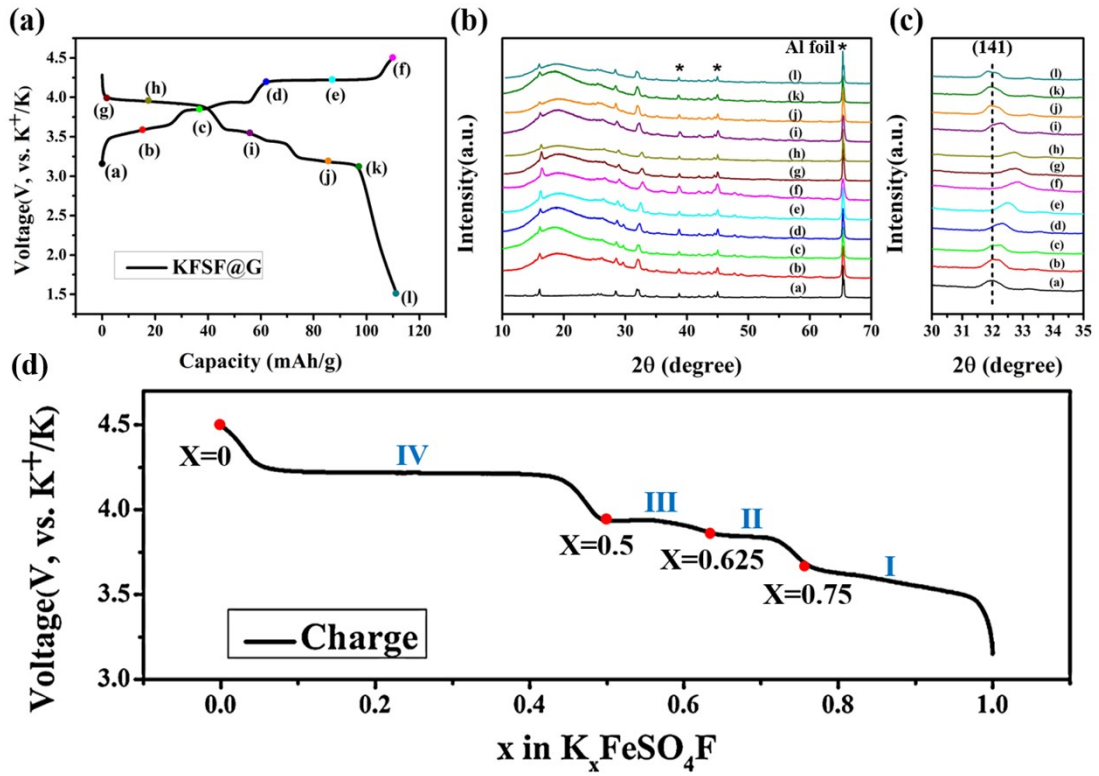
Fig. S6 Cycling performance of four samples with different carbon content at 0.05C.



**Fig. S7** Comparison of the XRD patterns of KFSF and KFSF@G after cycling (a,b); SEM images of KFSF and KFSF@G after 80 cycles (c,d).



**Fig. S8** Electrochemical performances of KFSF materials: the initial charge-discharge curves of KFSF, KFSF@SP and KFSF@G at 0.05C (a); cycling performance of KFSF@SP at 0.5C (b).



**Fig. S9** Ex-situ XRD patterns of KFSF@G electrode during the first charge-discharge process: selected different states (a); ex-situ XRD patterns (b, c). Initial charge curve at 0.05C of KFSF@G (d).