# **Supporting information**

# Three-Dimensionally Ordered Macroporous FeF<sub>3</sub> and its In Situ Homogenous Polymerization Coating for High Energy and Power Density Lithium Ion Batteries

De-long Ma, Zhan-yi Cao, Heng-guo Wang, Xiao-lei Huang, Li-min Wang, and Xin-bo Zhang\*

#### **Chemicals and Materials**

Ferric trichloride hydrate [FeCl<sub>3</sub>·6H<sub>2</sub>O, Aladdin Reagent, AR], Sodium hydroxide (NaOH, Aladdin Reagent, AR), Hydrofluoric acid (HF, Aladdin Reagent, AR), Styrene (C<sub>8</sub>H<sub>8</sub>, Aladdin Reagent, CP), Potassium peroxydisulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, Aldrich Reagent, AR), Toluene (C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, Beijing Chemical Work, AR), Methanol (CH<sub>4</sub>O, Aladdin Reagent, GR), Lithium Bis(Trifluoromethanesulfonyl)imide (LiTFSI, Aldrich Reagent, AR), 3, 4-ethylenedioxythiophene (C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>S, Aladdin Reagent, 99%), Polyvinylidenefluoride (PVDF, DuPont Company, 99.9%), Acetylene black (Hong-Xin Chemical Works), N-methyl-2-pyrrolidinone (NMP, Aladdin Reagent, AR), Separator (polypropylene film, Celgard 2400), Electrolyte (1 M LiPF<sub>6</sub> in ethylene carbonate (EC)/dimethyl carbonate (DMC) with the weight ratio of 1:1, Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd).

### **Experimental Section**

*Synthesis of Polystyrene Spheres*: All water in the forthcoming synthetic steps was deionized. Monodispersed polystyrene sphere (PS) dispersions were prepared by emulsion polymerization<sup>[1]</sup> using styrene (CP), sodium dodecyl sulfate (SDS), potassium persulfate (KPS) and anhydrous alcohol. Before use, the spheres were close-packed into colloidal crystals by centrifugation (2500 rpm, 20 h) followed by drying at 60 °C for 8 h. The obtained dried pieces were used as templates in the synthesis of 3DOM FeF<sub>3</sub>.

Synthesis of  $\alpha$ -FeF<sub>3</sub>·3H<sub>2</sub>O: All fabrication process was performed by using Teflon or plastic wares. Firstly, a certain amount of FeCl<sub>3</sub> solution was added to the NaOH solution (10% mass excess) with violently stirring for 20 min and the obtained precipitation was then washed and separated by centrifugation. Secondly, the above precipitation was added to excessive HF solution with continued stirring for 12 h at room temperature, and then the solution was freezed in refrigerator. After that, the  $\alpha$ -FeF<sub>3</sub>·3H<sub>2</sub>O was obtained by freeze drying.

Synthesis of 3DOM  $FeF_3 \cdot 3H_2O$ : Precursor solutions were obtained by dissolving desired amount of above synthesized  $\alpha$ -FeF<sub>3</sub>·3H<sub>2</sub>O in a methanol-water (10 vol%) mixture at room temperature to achieve the concentration of  $\alpha$ -FeF<sub>3</sub>·3H<sub>2</sub>O to be ca. 150-200 mg mL<sup>-1</sup>. Then, the PS colloidal crystals were soaked in the produced solution for 1-2 h, and the excess solution was removed from the impregnated PS template by vacuum filtration. The obtained sample was allowed to dry in air at 60 °C for 10 h. The dried composites were soaked in toluene for 12 h. After that, the 3DOM

 $FeF_3 \cdot 3H_2O$  was obtained by centrifugation. Finally, heat treatment under Ar atmosphere was performed to remove  $H_2O$  in  $FeF_3 \cdot 3H_2O$  at 140 °C for 15 h according to the result of TG/DSC (Fig. S9).

*Synthesis* 3DOM  $FeF_3$ lithium of coated by PEDOT: bis(trifluoromethanesulfonyl)imide (LiTFSI) (200 mg) was dissolved in ethanol (10 mL) in a petri dish. Then, 3, 4-ethylenedioxythiophene (EDOT) (25 mg) and 3DOM  $FeF_3$  (200 mg) were added to the solution. The petri dish was placed in an oven at 60 °C for 2 h. A blue color appeared upon solvent evaporation. The mixture was then transferred to a filter and rinsed with ethanol. The PEDOT-3DOM FeF<sub>3</sub> was dried at 60 °C overnight in vacuum oven. The weight ratio between PEDOT and FeF3 was determined by measuring the weight loss in the PEDOT-3DOM FeF<sub>3</sub> after removing the FeF<sub>3</sub> by washing in diluted HCl solution.

*Material Characterization*: The morphology and crystalline structure of as-obtained samples were characterized using scanning electron microscopy (SEM Hitachi S-4800) and transmission electron microscope (TEM) recorded on a Tecnai G2 operating at 200 kV. X-ray diffraction (XRD) patterns were recorded on a Rigaku-Dmax 2500 diffractometer with Cu Kα radiation using a glass substrate. N<sub>2</sub> adsorption/desorption was determined by BET measurements using an Autosorb-1 Surface Area Analyzers (Quantachrome Instrument Corporation). Thermogravimetric analysis was performed on a NETZSCH STA 449 F3 Simultaneous TGA-DSC Instrument. Fourier transform infrared spectroscopy (FT-IR) was obtained with BRUKER Vertex 70 FT-IR spectrometer. *Electrochemical Evaluation*: The electrodes were prepared by mixing active materials (70 wt%), acetylene black (20 wt%), and polyvinylidene fluoride (PVDF, 10 wt%) in N-methyl-2-pyrrolidone (NMP). After the above slurries were uniformly spread onto an aluminum foil, the electrodes were dried at 70 °C in vacuum for 12 h. Then the electrodes were pressed and cut into disks before transferring into an Argon-filled glove box. Coin cells (CR2025) were laboratory-assembled using lithium metal as the counter electrode, Celgard 2400 membrane as the separator and LiPF<sub>6</sub> (1 M) in ethylene carbonate/dimethyl carbonate (EC/DMC, 1:1 vol%) as the electrolyte. The galvanostatic charge-discharge tests were carried out on a Land Battery Measurement System (Land, China). Cyclic voltammetry (CV) was performed using a VMP3 Electrochemical Workstation (Bio-logic Inc.).



Fig. S1. XRD patterns of (a)  $FeF_3 \cdot 3H_2O$  and (b) 3DOM  $FeF_3$ .



**Fig. S2.** SEM images of PS colloidal crystal (a, b), 3DOM  $FeF_3$  (c, d), and 3DOM  $FeF_3$  after coating with PEDOT (e, f).



**Fig. S3**. TEM images of PEDOT after completely dissolving 3DOM FeF<sub>3</sub> with diluted HCl solution.

After completely dissolving the  $FeF_3$  with diluted HCl solution, the porous network of PEDOT can be obtained. Due to the relatively low mechanical strength of PEDOT, the 3DOM framework can't be well maintained after dissolving the FeF<sub>3</sub>.



**Fig. S4**. Nitrogen adsorption/desorption isotherms of 3DOM  $FeF_3$ , inset: BJH pore size distribution from the adsorption branch.



**Fig. S5.** Charge-discharge profiles of 3DOM  $FeF_3$  coated by PEDOT of first cycle within the voltage range of 1.5-4.5 V at a current density of 50 mA g<sup>-1</sup>.



Fig. S6. CV curves of PEDOT-3DOM FeF<sub>3</sub> within a voltage range of 1.5-4.5 V at a scan rate of 0.1 mV s<sup>-1</sup>.

During the cathodic/anodic reaction, two peaks are observed in each reaction. The cathodic peak near 3.0 V and the anodic peak near 3.3 V are related to insertion reaction, and the cathodic peak near 1.7 V and the anodic peak near 2.8 V are related to conversion reaction.



Fig. S7. Discharge profiles of 3DOM  $FeF_3$  without coating at different current densities.

Fig. S7 shows the rate capability of 3DOM  $\text{FeF}_3$  without coating. It can deliver 135 mAh g<sup>-1</sup> at a current density of 50 mA g<sup>-1</sup>. However, under a high current density of 1000 mA g<sup>-1</sup>, only a capacity of 40 mAh g<sup>-1</sup> can be obtained.



**Fig. S8.** SEM (a, b) and TEM (c, d) images of 3DOM FeF<sub>3</sub> after 20 cycles at a current density of 150 mA  $g^{-1}$ .

Fig. S8a and b show the SEM images of 3DOM  $FeF_3$  after 20 cycles at a current density of 150 mA g<sup>-1</sup>. Interestingly, it can be found that the 3DOM structure can be preserved. However, the wall of 3DOM structure is found to be made up of little nanoparticles after cycling (Fig. S8c and d), which might be caused by the volume expansion/contraction in the process of discharging/charging.



**Fig. S9.** TG/DSC curves of 3DOM  $FeF_3 \cdot 3H_2O$  measured from 0 to 600 °C at a heating rate of 10 °C min<sup>-1</sup> in Ar.

The existence of hydration water in  $FeF_3 \cdot 3H_2O$  is demonstrated from the thermogravimetric results shown in Figure S9. From 30 to 100 °C, the weight loss could be ascribed to the adsorbed water at the surface of samples. In the temperature range between 100 and 400 °C, a maximum derivative peak is located at 140 °C. The weight loss corresponds to the removal of hydration water.



Fig. S10. The SEM image of commercial nonporous FeF<sub>3</sub>.

As shown in Figure S10, the commercial  $FeF_3$  is nonporous and consist of little particles with a diameter about 200 nm.

## Reference

(1) J. Zhang, Z. Chen, Z. Wang, W. Zhang, N. Ming, Mater. Lett. 2003, 57, 4466.