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Supplementary Information

Synthesis of iron-fluoride materials with controlled nanostructures and composition through a template-free solvothermal route for lithium ion batteries

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Fig. S1 Thermogravimetric analyses of the products prepared at 85 °C for 4 h under nitrogen. (Fe source: 1.5 mmol of $Fe(NO_3)_3 \cdot 9H_2O$)



Fig. S2 The XRD patterns of the products prepared at 85 °C for various time. (Fe source: 1.5 mmol of $Fe(NO_3)_3 \cdot 9H_2O$)



Fig. S3 The SEM images of the products prepared at 85 °C for various time. (Fe source: 1.5 mmol of $Fe(NO_3)_3 \cdot 9H_2O$, a: 1 h; b: 2 h; c: 4 h; d: 8 h; e: 10 h; f: 24 h)



Fig. S4 The SEM images of the samples prepared with various amount of $Fe(NO_3)_3$ •9H₂O at 85 °C for 4 h. (a: 0.625 mmol; b: 1.25 mmol; c: 2.0 mmol; d: 2.5 mmol)



Fig. S5 The XRD patterns of the products prepared with various amounts of $Fe(NO_3)_3 \cdot 9H_2O$ at 85 °C for 4 h.



Fig. S6 The SEM images of the products prepared at 85 °C for 4 h with different amounts of H₂O. (Fe source: 1.5 mmol of Fe(NO₃)₃•9H₂O, a: 0.3 mL; b: 0.5 mL; c: 0.7 mL; d: 0.9 mL)



Fig. S7 The SEM images of the samples prepared with various amount of $FeCl_3 \cdot 6H_2O$ at 85 °C for 4 h (a: 0.625 mmol; b: 1.25 mmol; c: 1.5 mmol; d: 2.0 mmol; e: 2.5 mmol) and (f) the SEM image of the product prepared with NH₄F.



Fig. S8 The XRD patterns of the products prepared at 85 °C for 4 h with various amounts of $FeCl_3 \cdot 6H_2O$.



Fig. S9 The XRD pattern of the products prepared at 85 °C for 4 h with NH₄F.



Fig. S10 Cyclic voltammograms of the first cycles of the $FeF_3 \cdot 0.33H_2O$ hollow nanospheres (vs Li/Li⁺ at a scanning rate of 0.5 mV s⁻¹)



Fig. S11 The SEM image of the products prepared with 5 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ at 85 °C for 4 h after 100 cycles at 0.2C.



Fig. S12 Coulombic efficiency of the $FeF_3 \cdot 0.33H_2O$ hollow nanospheres prepared with 1.5 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ at 0.2C.



Fig. S13 Cycling performance of the hollow nanospheres prepared with (a) 2.5 mmol and (b) 0.625 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ at 0.2C rate. (c) Cycling performance of the hollow nanospheres prepared with 1.5 mmol of $Fe(NO_3)_3 \cdot 9H_2O$ and 0.9 mL of H_2O at 0.2C rate.

Table S1 BET surface areas and pore volumes of the hollow nanospheres prepared

 with various reactant concentrations.

Amounts of Fe(NO ₃) ₃ •9H ₂ O	Surface area	Pore volume	
(mmol)	$(m^2 g^{-1})$	$(cm^3 g^{-1})$	
0.625	4.6	0.069	
1.25	12.9	0.088	
1.5	14.9	0.046	
2.5	11.8	0.054	

Table S2 Comparison of electrochemical performance of $FeF_3 \cdot 0.33H_2O$ hollownanospheres with other $FeF_3 \cdot 0.33H_2O$ nanomaterials

Materials	Charge capacity (mAh g ⁻¹)	Reference
FeF ₃ •0.33H ₂ O hollow nanospheres	120 mAh g ⁻¹ at 0.1C (100th)	This work
	105 mAh g ⁻¹ at 0.2C (100th)	
	70 mAh g ⁻¹ at 1C (100th)	
Mesoporous FeF ₃ •0.33H ₂ O	115 mAh g ⁻¹ at 0.1C (50th)	5
Pure $FeF_3 \cdot 0.33H_2O$	42 mAh g ⁻¹ at 0.1C (30th)	7
FeF ₃ /V ₂ O ₅ (milled 30 min)	108 mAh g ⁻¹ at 0.1C (30th)	7
FeF ₃ /MoS ₂	141 mAh g ⁻¹ at 0.1C (30th)	8
FeF ₃ •0.33H ₂ O/C	145 mAh g ⁻¹ at 0.1C (25th)	9
FeF ₃ •0.33H ₂ O nanoparticles	<75 mAh g ⁻¹ at 50 mA g ⁻¹ (30th)	12
FeF ₃ •0.33H ₂ O/reduced graphitic oxide	<75 mAh g ⁻¹ at 0.1C (50th)	24
FeF ₃ •0.33H ₂ O solid crystals	56 mAh g ⁻¹ at 0.5C (50th)	30
FeF ₃ •0.33H ₂ O/C composites	130 mAh g ⁻¹ at 0.5C (100th)	30
FeF ₃ •0.33H ₂ O particles	64 mAh g ⁻¹ at 0.5C (100th)	31
FeF ₃ •0.33H ₂ O/C composites	136 mAh g ⁻¹ at 0.5C (100th)	31