

Supporting Information

Carbon Nanotube-Encapsulated FeF₂ Nanorods for High-Performance Lithium-Ion Cathode Materials

Jisheng Zhou,^{†,‡} Di Zhang,[†] Xiaoting Zhang,[†] Huaihe Song,^{,†} and Xiaohong Chen[†]*

[†] State Key Laboratory of Chemical Resource Engineering, Key Laboratory of Carbon Fiber and Functional Polymers, Ministry of Education, Beijing University of Chemical Technology, Beijing, P. R. China.

[‡] Changzhou Institute of Advanced Materials, Beijing University of Chemical Technology, Jiangsu, P. R. China.

Supporting Data:

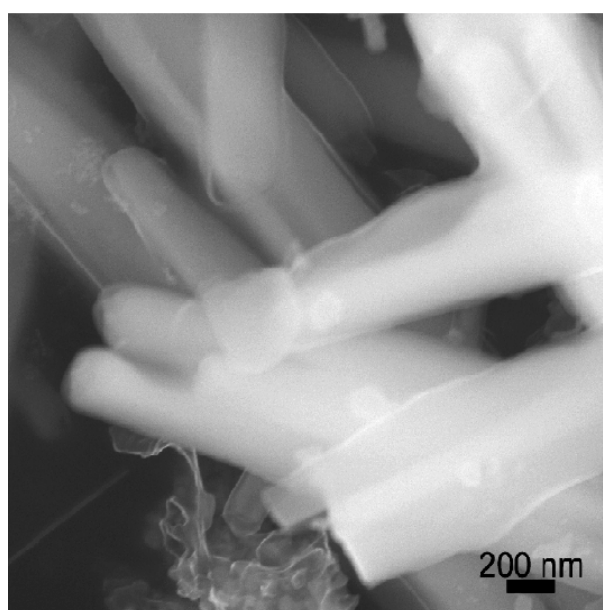


Figure S1. SEM image of FeF₂@CNT obtained at 500 °C for 3 h.

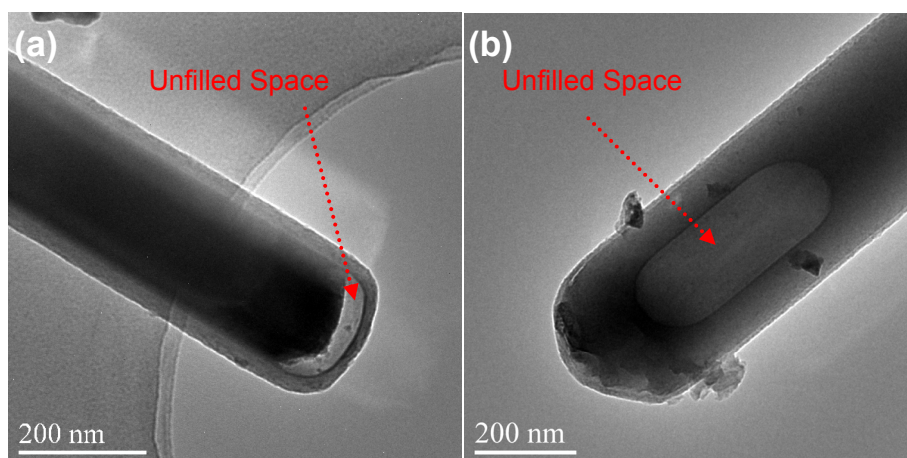


Figure S2. TEM images of $\text{FeF}_2@\text{CNT}$ with (a) unfilled space and (b) hollow interior obtained at 500 °C for 3 h.

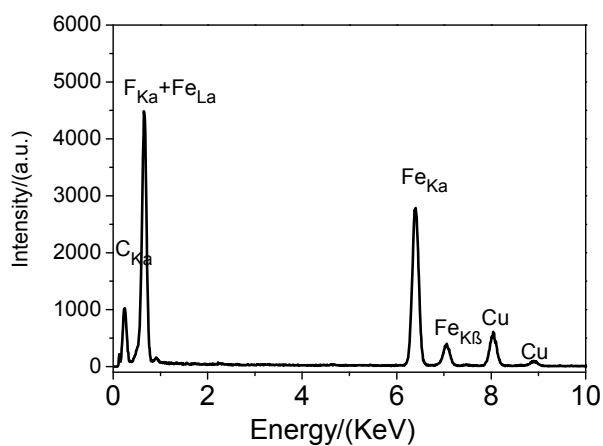


Figure S3 EDS spectrum of $\text{FeF}_2@\text{CNT}$ nanorods obtained at 500 °C for 3 h.

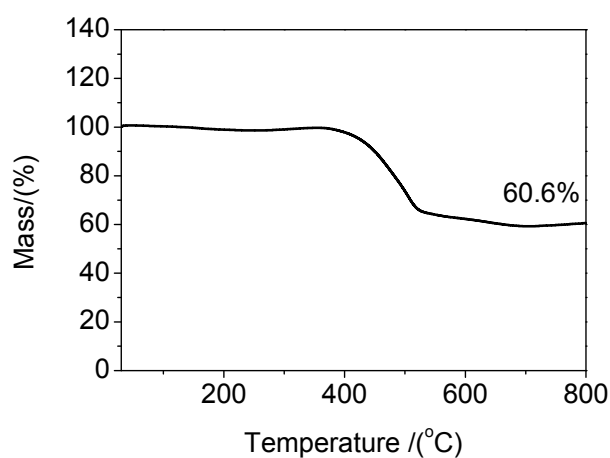


Figure S4 TG curve obtained by heating $\text{FeF}_2@\text{CNT}$ from room temperature to 800 °C in air atmosphere. (Note: It means that the content of FeF_2 in the composite is ca. 71.22 wt%.)

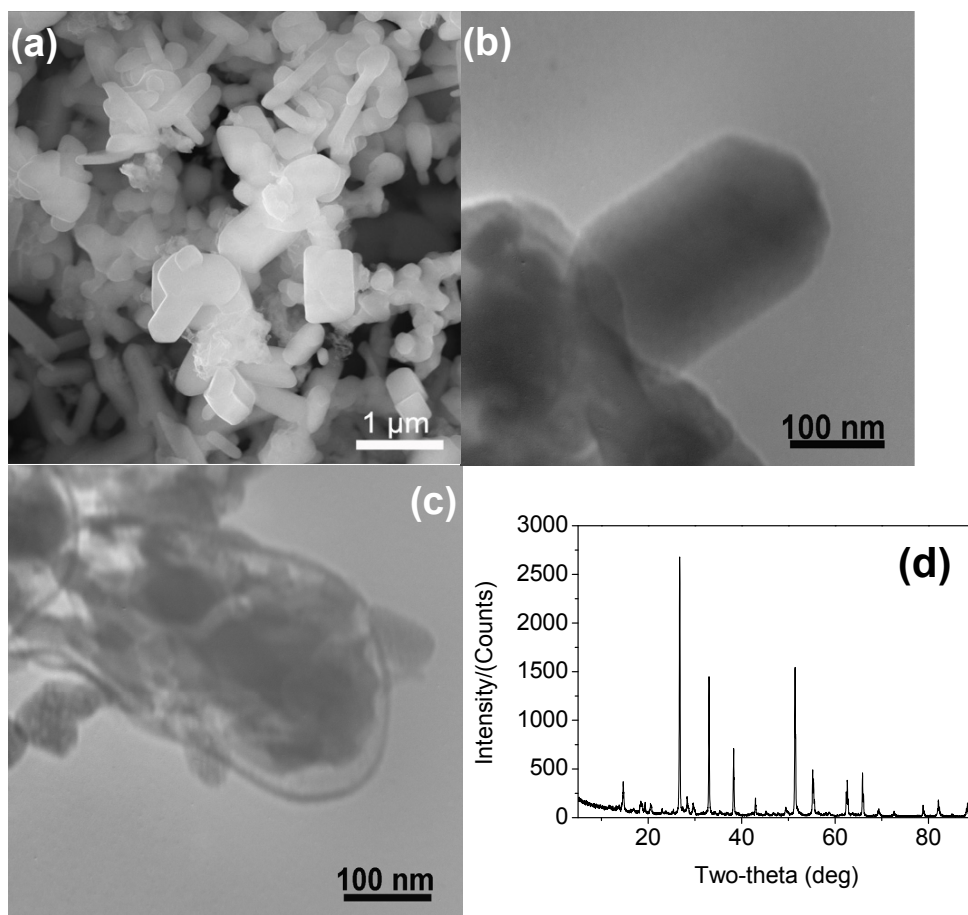


Figure S5 (a) SEM, (b,c) TEM images and (d) XRD pattern of the sample obtained by co-pyrolysis of ferrocene and NH_4F at 450°C for 3 h, (b) TEM image of a FeF_2 nanoparticle without carbon shell, (c) TEM image of a FeF_2 nanoparticle with thin carbon shell.

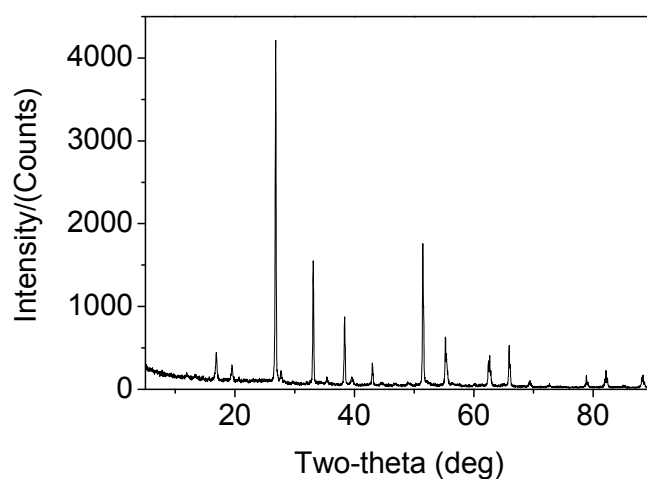


Figure S6. XRD pattern of the sample obtained by co-pyrolysis of ferrocene and NH_4F at 700°C for 10 min, which shows that the obtained sample is mainly composed of FeF_2 .

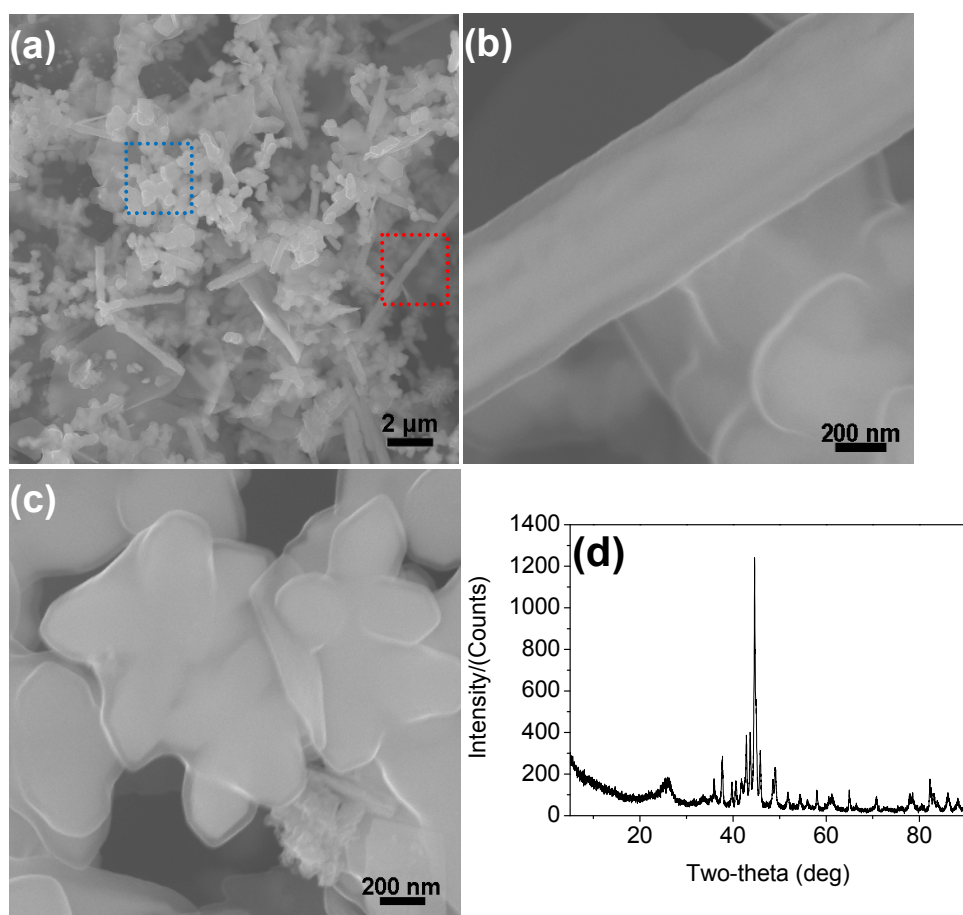


Figure S7 (a-c) SEM images and (d) XRD pattern of the sample obtained by co-pyrolysis of ferrocene and NH_4F at 700°C for 30 min, (b) magnified SEM image of a nanowire in red box in the image (a), and (c) magnified SEM image of aggregated nanoparticles in blue box in the image (a)

Fig. S7(a) exhibits that the sample obtained at 700°C for 3 h is composed of mainly aggregated nanoparticles and less nanorods/nanowires. And, both nanoparticles (Fig. S7(c)) and nanorods/nanowires (Fig. S7(b)) are coated by carbon shells. XRD pattern shows that Fe element in the sample exist in the form of Fe_3C and $\alpha\text{-Fe}$, and no any FeF_2 is found, indicating that FeF_2 is decomposed and reacted with carbon by long-period annealing at high temperature.

Table S1. Comparison of the electrochemical performance of FeF₂@CNT nanorods synthesized in this work with those of iron fluoride reported in the literatures

Samples		voltage range /(V)	Current density	Initial capacity /(mAhg ⁻¹)	Cycle number	Capacity after cycling/(mAhg-1)	Ref	
FeF ₃	FeF ₃ :C(50:50 wt%)	2.5-4.5	7.58 mAg ⁻¹	ca. 250	30	210	1	
	FeF ₃ •0.33H ₂ O	1.6-4.5	14 mAg ⁻¹	154	30	130	5	
			71 mAg ⁻¹	126	30	105		
	FeF ₃ •0.33H ₂ O with mesoporous structure	1.6-4.5	0.1 C	150	50	115	6	
			0.25 C	ca. 140	--	--		
			0.5 C	ca. 130	--	--		
			1 C	120	--	--		
	FeF ₃ nanoflowers on CNT	2.0-4.5	20 mAg ⁻¹	210	30	ca. 210	7	
			100 mAg ⁻¹	180	70	ca. 150		
			500 mAg ⁻¹	150	--	--		
			1000 mAg ⁻¹	ca. 125	--	--		
	FeF ₃ /ordered mesoporous carbon	2.0-4.5	0.1C	178	30	150	8	
			0.25C	156	--	--		
			0.5C	143	--	--		
			1C,	131	--	--		
			1C=237mA g ⁻¹					
			2C	117	--	--		
			5C	90	--	--		
			10C	69	--	--		
	FeF ₃ /graphene	1.0-4.5	20 mAg ⁻¹	587	10	300	9	
			100 mAg ⁻¹	ca.580	80	200		
			200mAg ⁻¹	ca.200	--	--		
			1000 mAg ⁻¹	ca.80	--	--		
	FeF ₃ /graphene	1.7-4.5	50 mAg ⁻¹	190	--	--	10	
			500 mAg ⁻¹	150	50	134		
			1000mAg ⁻¹	146	50	123		
	FeF ₃ nanowires	1.5-4.5	50 mAg ⁻¹	543	50	223	34	
			200 mAg ⁻¹	ca.470	50	147		
C/iron lithium fluoride nanocomposite (C/FeF ₃ /FeF ₂ /Fe ₃ C/LiF)		0.5-4.3	20.83 mAg ⁻¹	324	200	275	12	
			105 mAg ⁻¹	175	30	ca.175		
			1050 mAg ⁻¹	120	30	ca.120		
			2100 mAg ⁻¹	ca.100	30	ca.100		
FeF ₂	FeF ₂ -C nanocomposites	1.5-4.5	4 mAg ⁻¹	ca.480 (24 °C)	5	ca.480	4	
			50 mAg ⁻¹	ca.480 (60 °C)	5	ca.420		
	C(FeF ₂)0.55	1.3-4.3	22.7 mAg ⁻¹	538 (25 °C)	25	171	11	
			22.7 mAg ⁻¹	603(25 °C)	25	235		
	C(FeF ₂)0.55 after ball milling		22.7 mAg ⁻¹	576(25 °C)	25	327		
			22.7 mAg ⁻¹	637(25 °C)	25	425		
	FeF ₂ @C core/shell structures	1.3-4.2	30 mAg ⁻¹	314	50	217	23	
			100 mAg ⁻¹	ca.200	--	--		
			200 mAg ⁻¹	ca.160	--	--		
			500 mAg ⁻¹	ca.100	--	--		
			1000 mAg ⁻¹	ca.50	--	--		
			2000 mAg ⁻¹	ca.25	--	--		
	FeF ₂ @CNT	1.0-4.2	50 mAg ⁻¹	263	50	263	this work	
			100 mAg ⁻¹	221	50	181		
500 mAg ⁻¹			153	50	124			
1000 mAg ⁻¹			133	50	92			

Note: "--" means that the measurements were not carried out in the corresponding references.

Reference:

- (1) Badway, F.; Pereira, N.; Cosandey, F.; Amatucci, G. G. Carbon-Metal Fluoride

Nanocomposites Structure and Electrochemistry of FeF_3/C . *J. Electrochem. Soc.*, **2003**, *150*, A1209-A1218.

- (4) Wang, F.; Robert, R.; Chernova, N. A.; Pereira, N.; Omenya, F.; Badway, F.; Hua, X.; Ruotolo, M.; Zhang, R.; Wu, L.; Volkov, V.; Su, D.; Key, B.; Whittingham, M. S.; Grey, C. P.; Amatucci, G. G.; Zhu, Y.; Graetz, J. Conversion Reaction Mechanisms in Lithium Ion Batteries: Study of the Binary Metal Fluoride Electrodes. *J. Am. Chem. Soc.* **2011**, *133*, 18828-18836.
- (5) Li, C.; Gu, L.; Tsukimoto, S.; Tsukimoto, S.; Aken, P. A.; Maier, J. Low-Temperature Ionic-Liquid-Based Synthesis of Nanostructured Iron-Based Fluoride Cathodes for Lithium Batteries. *Adv. Mater.*, **2010**, *22*, 3650-3654.
- (6) Li, C.; Gu, L.; Tong, J.; Tsukimoto, S.; Maier, J. A Mesoporous Iron-Based Fluoride Cathode of Tunnel Structure for Rechargeable Lithium Batteries. *Adv. Funct. Mater.* **2011**, *21*, 1391-1397.
- (7) Kim, S.-W.; Seo, D.-H.; Gwon, H.; Kim, J.; Kang, K. Fabrication of FeF_3 Nanoflowers on CNT Branches and Their Application to High Power Lithium Rechargeable Batteries. *Adv. Mater.* **2010**, *22*, 5260-5264.
- (8) Jung, H.; Shin, J.; Chae, C.; Lee, J. K.; Kim, J. FeF_3 /Ordered Mesoporous Carbon (OMC) Nanocomposites for Lithium Ion Batteries with Enhanced Electrochemical Performance. *J. Phys. Chem. C* **2013**, *117*, 14939-14946.
- (9) Zhao, X.; Hayner, C. M.; Kung, J. C.; Kung, H. H. Photothermal-Assisted Fabrication of Iron Fluoride-Graphene Composite Paper Cathodes for High-Energy Lithium-Ion Batteries. *Chem. Commun.* **2012**, *48*, 9909-9911.
- (10) Chu, Q.; Xing, Z.; Ren, X.; Asiri, A. M.; Al-Youbi, A. O.; Alamry, K. A.; Sun, X. Reduced Graphene Oxide Decorated with FeF_3 Nanoparticles: Facile Synthesis and Application as a High Capacity Cathode Material for Rechargeable Lithium Batteries. *Electrochim. Acta*

2013, *III*, 80-85.

- (11) Reddy, M. A.; Breitung, B.; Chakravadhanula, V. S. K.; Wall, C.; Engel, M.; Kübel, C.; Powell, A. K.; Hahn, H.; Fichtner, M. CF_x Derived Carbon- FeF_2 Nanocomposites for Reversible Lithium Storage. *Adv. Energy Mater.* **2013**, *3*, 308-313.
- (12) Prakash, R.; Mishra, A. K.; Roth, A.; Kübel, C.; Scherer, T.; Ghafari, M.; Hahn, H.; Fichtner, M. A Ferrocene-Based Carbon-Iron Lithium Fluoride Nanocomposite as a Stable Electrode Material in Lithium Batteries. *J. Mater. Chem.* **2010**, *20*, 1871-1876.
- (23) Zhang, J.; Wang, L.; Li, J.; Wen L.; He X. A one-pot approach towards FeF_2 -carbon core-shell composite and its application in lithium ion batteries. *J. Alloys Comp.* **2014**, *606*, 226-230.
- (34) Li, L.; Meng F.; Jin, S. High-Capacity Lithium-Ion Battery Conversion Cathodes Based on Iron Fluoride Nanowires and Insights into the Conversion Mechanism. *Nano Lett.* **2012**, *12*, 6030-6037.