

supporting information

Fe₇Se₈@C Core-Shell Nanoparticles Encapsulated within Three-Dimensional Graphene Composite as High-Performance Flexible Anode for Lithium-Ion Battery

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Experiment Methods

Graphene oxide (GO) Synthesis and Purification: GO was synthesized by oxidation of natural graphite powder (325 mesh, Aladdin, 99.95% metal basis) according to the modified Hummers' method. All the other items are purchased at Sinopharm Chemical Reagent Co.,Ltd.

Preparation of 3DG/Prussian blue(PB) Composite: The GO/PB composite was synthesized by two-step centrifugation method. Typically, 0.1 mL of 0.5 mol L⁻¹ potassium ferrocyanide (K₄Fe(CN)₆) was dissolved into 1 mL of 2 mg mL⁻¹ graphene oxide suspension in centrifugal tube. Then, the dispersion was centrifuged at 10000 rpm for 15 minutes. 1 mL deionized water was added after the supernatant was removed. 0.1 mL of 0.5 mol L⁻¹ ferric chloride (FeCl₃·6H₂O) was added into the solution. After the solution was stirred uniformly, the mixture was centrifuged at 10000 rpm for 15 minutes. The GO/PB composite was obtained by removing the supernatant. Herein, excessive metal ions were necessary for the successful combination of GO and the rapidly formed PB nanoparticles and decreasing the dosage of Fe³⁺ will lead to the appearance of large amount PB nanoparticles that are not deposited on GO. To obtain the 3DG/PB composite, 0.1 mL of 88 mg mL⁻¹ vitamin C (VC) was firstly added into GO/PB composite, and the solution volume was subsequently increased to 2 mL by adding deionized water. Finally, the 0.5 mL mixture was added into 5 mL bottle, and sealed into 95 °C oven for two hours. Soaking in the deionized water to remove other ions for three times, the 3DG/PB composite was obtained by freeze-drying overnight.

Preparation of 3DG/Fe₇Se₈@C Composite: The 3DG/Fe₇Se₈@C was synthesized by one-pot method used 3DG/PB as precursor. Typically, the 3DG/PB composite was mixed with Se powder, then annealed at 600 °C for 2 hours in Ar/H₂. Finally, the 3DG/Fe₇Se₈@C can be used as electrode materials without binders. In the control experiment, we obtained the PB powder as the way of synthesis of the above 3DG/PB. The FeSe_x@C powder obtained by one-step annealing of Prussian blue powder at the same condition. To get the FeSe_x@C electrode, the FeSe_x@C powder with poly (vinylidene fluoride) (PVDF) binder and conductive carbon black (8:1:1, weight ratio) was coated on Cu foil and dried in a vacuum oven for 12 hours.

Characterizations: SEM measurements were measured on a Zeiss Ultra-55 field emission scanning electron microscope(FESEM). TEM studies were conducted on a FEI Tecnai G2 20 TWIN electron microscope at an operating voltage of 200 kV. XRD analysis was performed on a Rigaku D/Max 2500 X-ray diffractometer with Cu-Kα

radiation ($\lambda = 1.54 \text{ \AA}$) at a generator voltage of 40 kV and a generator current of 20 mA with a scanning speed of 5° min^{-1} from 10° to 70° . Thermogravimetric analysis (TGA) was tested with a Mettler Toledo TGA with a heating rate of 20° C/min under 20 mL/min of flowing air.

Electrochemical Characterization: Electrochemical experiments were carried out by using 2016 coin-type cells. The working electrodes are free-standing, binder-free, the metallic lithium foil was used as the counter electrode. 1M LiPF_6 in (EC: DMC = 1:1 by volume ratio) was used as the electrolyte, the Cellgard 2400 was used as the separator. For LIB fabrication, the cells were assembled in an argon-filled glove box with the concentrations of moisture and oxygen below 0.1 ppm. The galvanostatic charge–discharge experiments were tested using a land battery testing system in the voltage window from 0.01 to 3.00 V at different current rates. The cyclic voltammetry (CV) were conducted at a scan rate of 0.5 mV/s in the voltage range of 0.01 to 3.00 V (vs Li^+/Li) by CHI760D electrochemical workstation (CHI instrument).

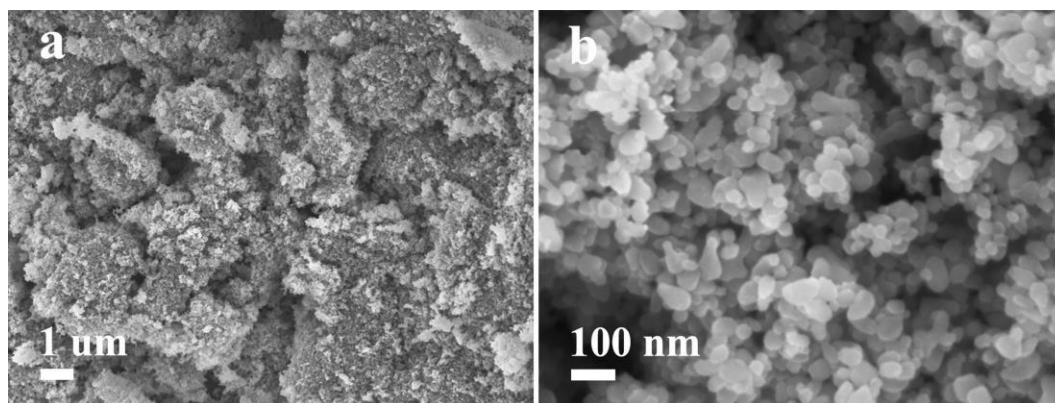


Fig. S1 SEM images of pure PB nanoparticles.

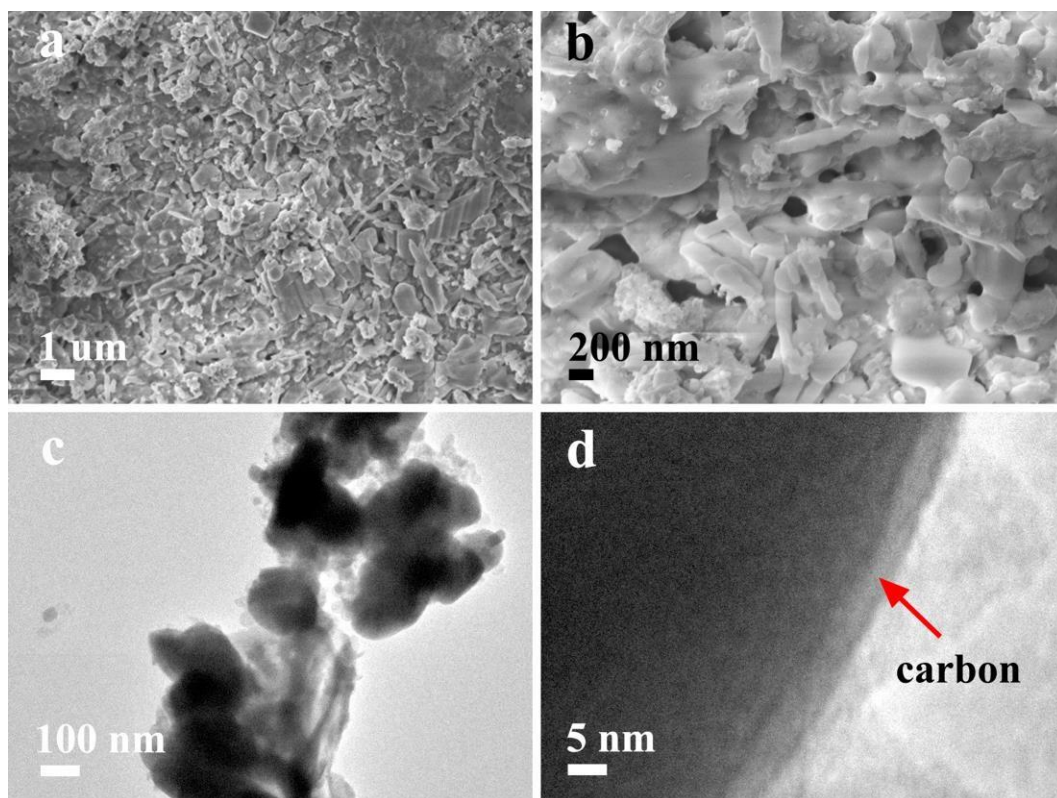


Fig. S2 SEM (a, b) and TEM (c, d) images of FeSe_x@C.

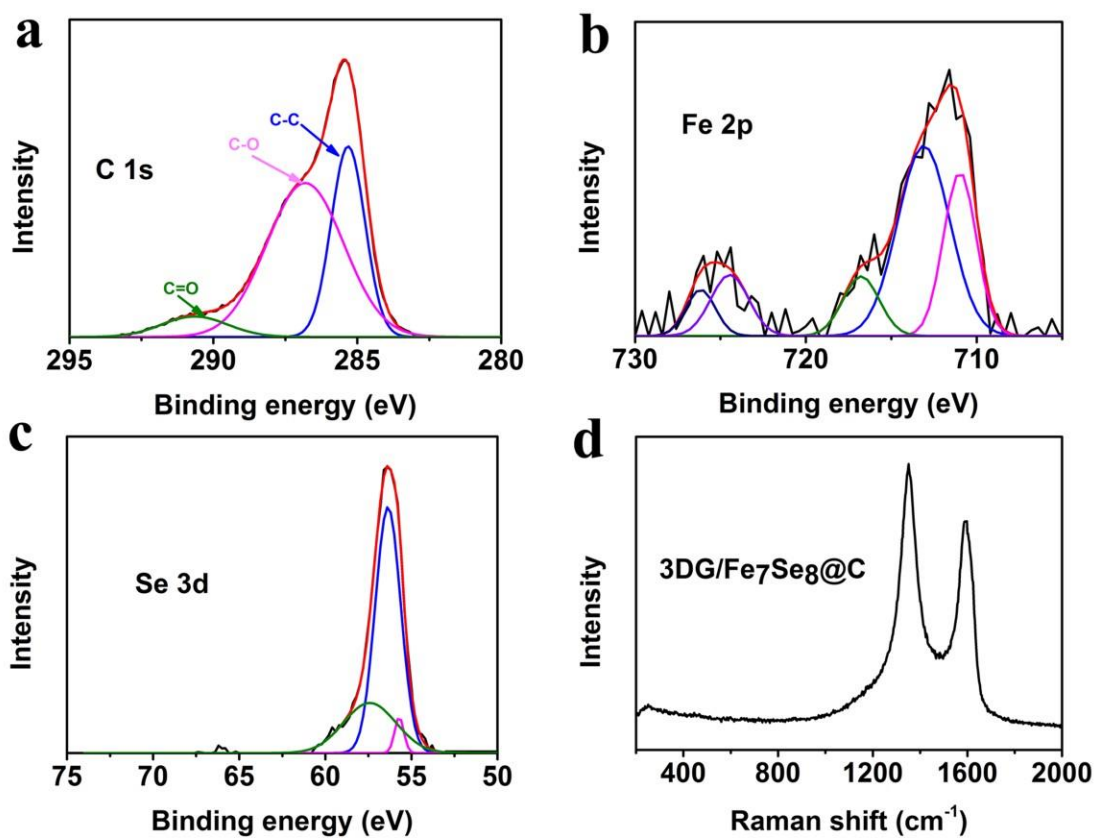


Fig. S3 The xps spectra of 3DG/Fe₇Se₈@C nanostructures. (a) C 1s, (b) Fe 2p and (c) Se 3d. (d) Raman shift image of 3DG/Fe₇Se₈@C composite.

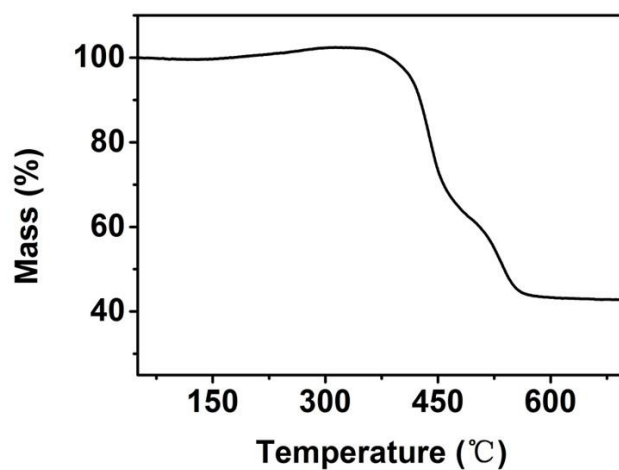


Fig. S4 TGA curves of 3DG/Fe₇Se₈@C composite heated in air flow from room temperature to 700 °C.

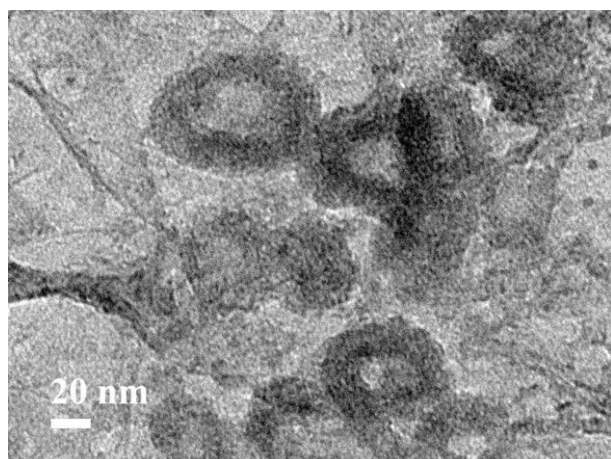


Fig. S5 TEM image of 3DG/Fe₇Se₈@C after cycling 250 cycles.

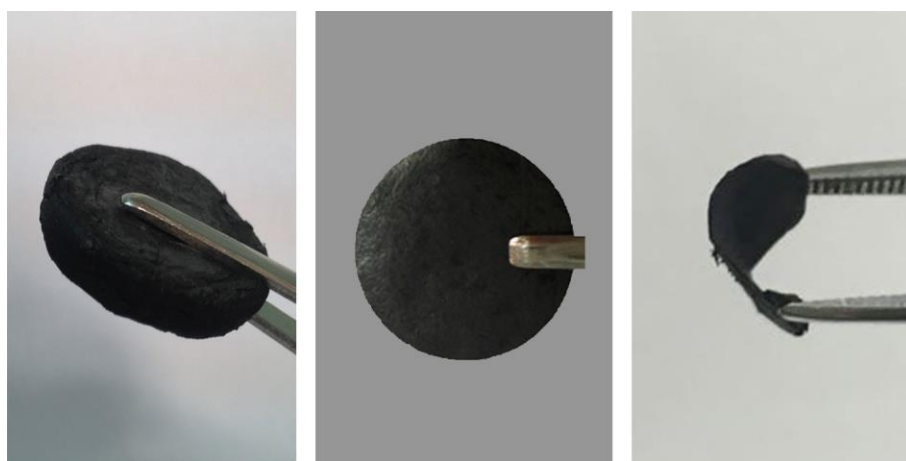


Fig. S6 The images of 3DG/Fe₇Se₈@C aerogel, 3DG/Fe₇Se₈@C aerogel after compressing, and curved aerogel through compressing from left to right, respectively.

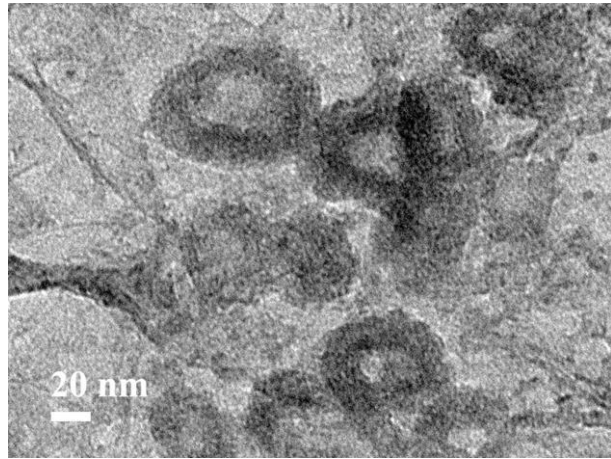


Fig. S7 The Nyquist plot of 3DG/Fe₇Se₈@C and FeSe_x@C before cycling.

Table S1 The electrochemical performance comparison of Fe-based anode material in LIBs.

Materials	Ratio of active materials	Current density (mA g ⁻¹)	Capacity (mAh g ⁻¹) / after cycles	High current density (mA g ⁻¹)	Capacity (mAh g ⁻¹) / after cycles	The range of voltage (V)	Ref.
FeP@C	80%	200	720 / 100	500	610 / 400	0.005~3	<i>J. Mater. Chem. A</i> , 2016, DOI: 10.1039/C6TA04521A
			576 (by electrode)		488 (by electrode)		
α -FeSe	90%	0.04	340 / 40	N.A.	N.A.	1.2~2.5	<i>Electrochem. Commun.</i> , 2014, 38 , 124-127
			306 (by electrode)		N.A. (by electrode)		
Fe ₇ S ₈ @C	90%	100	695 / 50	1000	241 / 5	1.2~2.5	<i>RSC Adv.</i> , 2015, 5 , 14828-14831
			625.5 (by electrode)		216 (by electrode)		
Fe ₂ O ₃ /3DGN	100%	200	864 / 50 (by electrode)	1000	785 / 10 (by electrode)	0.01~3	<i>Angew. Chem. Int. Ed.</i> 2014, 53 , 1404
3DG/Fe ₇ Se ₈ @C	100%	100	884.1 / 120 (by electrode)	1000	815.2 / 250 (by electrode)	0.01~3	This work