## Carambola-shaped LiFePO<sub>4</sub>/C nanocomposites: directing synthesis and enhanced Li storage properties—Electronic Supplementary Information

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## **Experimental Section**

Preparation of n-LFP@C and c-LFP@C. All the reagents used in the experiment were of analytical grade purity and were used as received. LiOH•H<sub>2</sub>O, FeSO<sub>4</sub>•7H<sub>2</sub>O,  $(NH_3)_2HPO_4$  and L-ascorbic acid with the molar ratios of 2:1:1:1 (the molarity are 0.05, 0.025, 0.025 and 0.025 mol L<sup>-1</sup>, respectively) were dissolved in 100 mL ethylene glycol under magnetic stirring, respectively. At the same time, 0.1g CB were added into a 20mL Teflon-lined stainless steel autoclave, followed by the addition of the above solution (4 mL for each reactant). The sealed was heated at 160 °C with a heating rate of 5 °C min<sup>-1</sup> for 24 hours under magnetic stirring (150r min<sup>-1</sup>), and then cooled down to room temperature. The sample was denoted as c-LFP. For comparison, a normal LFP sample (denoted as n-LFP) was prepared using the same procedure free of LC. Asobtained mixture was separated at 150 °C, when LC was float on the top layer of the liquid phase (Table S2). A light green precipitate was finally collected and dried in an oven at 80 °C.

To prepare the n-LFP@C and the c-LFP@C composites, n-LFP and c-LFP were thoroughly ball milled with sucrose at a mass ratio of 9:1, then calcinated under argon at 700 °C for 4 h (heating rate: 3 °C min<sup>-1</sup>). The obtained products were denoted as n-LFP@C and c-LFP@C.

Structural characterization. Elemental analysis was conducted on an elementary analyzer (EA, Elementar Germany, Vario EL c) to obtain the carbon content in the composites. FESEM (FESEM, SU8020), TEM (JEM-2100F), and HRTEM (JEM-2100F) were employed to visualize the morphologies, sizes, and structures of the samples. Before carrying out TEM and HRTEM characterizations, samples were loaded onto a copper micro-grid covered with a porous carbon film. X-ray photoelectron spectroscopy (XPS) was carried out with a photoelectron spectrometer (Thermo American, ESCALAB250). The crystal structure of the as-prepared powders was characterized by XRD (Rigaku D/max-rB) with Cu-K $\alpha$  radiation. Nitrogen adsorption/desorption isotherms of the as-prepared samples were collected at 77.3 K with ASAP 2020 surface area pore size analyzer (Micromeritics American Inc).

Electrochemical measurements. Electrochemical measurements were performed with Swagelok-type cells assembled in an argon-filled glovebox. For preparing working electrodes, a mixture of active material, super-P acetylene black, and poly-(vinyl difluoride) at a weight ratio of 80:10:10 was pasted on an Al foil. The cathode had a diameter of 1 cm and an active material load of about 2 mg cm<sup>-2</sup>. Lithium foil was used as the anode. A carbonate electrolyte of 1 M LiPF<sub>6</sub> in ethylene carbonate / dimethyl carbonate (1:2 in v:v) was used to investigate the cycling and rate performances of the cathode. A glass fiber (GF/D) from Whatman was used as a separator. Galvanostatic charge-discharge tests were conducted on an Arbin BT-1 system at different rates of 0.1, 0.5, 1, 2, 5, 10 and 20 C with cut off voltages of 2.5–4.2 V (vs. Li/Li<sup>+</sup>). Electrochemical impedance measurement was carried out by applying alternating voltage in the frequency range of 0.1 to  $10^5$  Hz with amplitude of 5 mV on an Autolab PG302N.



Figure S1. XRD patterns of n-LFP, c-LFP, n-LFP@C and c-LFP@C particles.



Figure S2. Nitrogen adsorption and desorption isotherms of n-LFP@C and c-LFP@C.



Figure S3. XPS spectrum of n-LFP@C and c-LFP@C samples: (a) survey, (b) Fe 2p.



**Figure S4.** Cyclic voltammograms at a sweep rate of 0.1 mV s<sup>-1</sup> for c-LFP@C and n-LFP@C.



**Figure S4.** FESEM images of c-LFP@C after the ball-milling process. It is seen from the figures that, although some of the carambola-shaped c-LFP@C composites were broken, most of them (~400 nm in diameter and ~700 nm in length) still retained their morphologies after ball milling. Even for those broken carambolas, the c-LFP@C sheets still remained. As discussed in the manuscript, the favorable electrochemical performance of c-LFP@C is mainly attributed to the c-LFP@C sheets rather than the composite. Therefore, we believe the ball-milling process will not have a major influence on the battery performance of the composite.

## Table S1

Surface Area and Carbon Content Present in the LiFePO<sub>4</sub>/C Composite.

Sample	Carbon content (wt %)	Surface area ( $m^2 g^{-1}$ )
n-LFP@C	2.37	10.7
c-LFP@C	4.68	38.0

## Table S2

Elemental analysis of original LC and separate LC.

Sample	Carbon content (wt %)	Hydrogen content (wt %)
	Test (Cacld)	Test (Cacld)
original LC	83.14(83.21)	10.09(10.27)
separate LC	83.42(83.21)	10.38(10.27)