Electronic Supplementary Information (ESI)

**Novel Morphology-Controlled Synthesis of Homogeneous LiFePO$_4$ for Li-ion Batteries Using an Organic Phosphate Source**

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Experimental

In this work, all chemicals were used as purchased without further purification.

a. Synthesis of LFP hollow spheres and nanoplates

The samples of LFP were prepared by hydrothermal method in an autoclaved stainless steel reactor. The starting materials were FeSO$_4$·7H$_2$O, phosphate ester (TRITON XQS-20) and LiOH·H$_2$O; the molar ratio of the Li : Fe : P was 3 : 1 : 1; starting materials were separately dissolved in 20 mL distilled water; the concentration of LFP precursor solutions were 0.25 M in the final mixture.

Synthesis of LFP nanoplates

For the synthesis of LFP nanoplates, the mixing sequence was exchanged. In this case, the LiOH solution was added into a mixed solution of TRITON H-66 and FeSO$_4$·7H$_2$O, and the resultant mixture was hydrothermally treated at 180 °C for 18 h. The pH value of the solution was 7.3.

Synthesis of LFP hollow spheres

In a typical procedure, LiOH solution was added to TRITON H-66 solution. FeSO$_4$ solution was added to the mixed solution with constant stirring. The pH value of the solution was 7.1.

The autoclave was sealed and heated to 180 °C for 18 h. After being cooled to room temperature, the obtained precipitates were collected by centrifugation and washed several times with deionized water. Then the samples were dried at 80 °C.
To achieve the conductive carbon coating, the hydrothermal products were mixed with 20 wt.% of sucrose, and then carbonized at 650 °C for 5 h under Ar-H₂ (98:2) atmosphere with a heating rate of 5 °C/min.

b. Material Characterizations

The crystal structure of the resulting powder was analyzed by powder X-ray diffraction (XRD, Rigaku D/Max-2500/PC, Japan), using a Cu-Kα radiation source. The particle size and shape of the samples were examined by field emission scanning microscopy (FE-SEM, S-800, Hitachi, Japan). The chemical composition of the sample was analyzed by inductively coupled plasma (ICP) and energy-dispersive X-ray spectroscopy (EDS, S-800, Hitachi, Japan).

c. Electrochemical Measurements

A coin cell (CR2016) was used to determine the electrochemical performance of the obtained samples. A positive electrode was made by coating a slurry of the active material, Super P carbon black (MMM, Belgium), and a poly-(vinylidene fluoride) binder (Kurea, Japan) at a weight ratio of 8:1:1 onto an aluminum foil current collector. The electrolyte was a 1.0 M LiPF₆ solution in ethylene carbonate/ethyl methyl carbonate (1/1 vol %, Cheil Ind., Korea). Li metal was used as a negative electrode. Galvanostatic charge and discharge tests of the cell were carried out at constant current–constant voltage (CC-CV) mode, and the performed between 2.0 and 4.3 V at room temperature.
Figure S1 TEM images of LFP (a) the hollow sphere and (b) shell of the hollow sphere.
Figure S2 TGA curves of the carbon-coated LFP nanoplates and hollow spheres.
**Figure S3** SEM images of the samples synthesized by adjusting synthesis parameters: a) Quadruple the concentrations of the reactants; b) 120 °C. The other synthesis parameters are kept unchanged with those for the synthesis of the LFP hollow spheres.