Electronic Supplementary Material (ESI) for RSC Advances
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Supporting Information

Experimental

Chemicals

Dopamine hydrochloride was purchased from Alfa-Aesar. Tris(hydroxymethyl)aminomethane (Tris) was purchased from Sigma-Aldrich. All chemicals were used as received without further purification.

Synthesis of LFP nanoparticles

The pristine $LiFePO_4$ powder was synthesized via solid-state reactions. Source materials including Li_2CO_3, $Fe_2C_2O_4$ and $NH_4H_2PO_4$ are stoichiometrically mixed together (mole ratio of Li: Fe: P=1.03:1:1). The mixture were milled using a planetary ball mill with ball-to-powder ratio of 4:1 (ball-diameter 10mm), rotating speed of about 200 rpm, and ball-milling time of 6 h. The product was then collected and subject to high temperature treatment at 700 ^{o}C under a H_2/Ar flow. The collected sample was then used as the pristine LFP sample with a very low carbon content at less than 0.1%.

Synthesis of thickness-controlled LFP@C composites

In a typical synthesis procedure, a suspension of LFP (126.78 mM) is prepared by dispersing LFP nanopowders in Tris-buffer (pH: ~ 8.5) with the help of ultrasonication. Subsequently, dopamine hydrochlorid was added into the suspension to reach a concentration of 5.27 mM. The mixture was stirred continuously for 24 h under room temperature, and the color of the mixture gradually turned from light grey to deep dark during the stirring period. The black precipitates (denoted as LFP@Dopa) were collected by centrifugation, washed three times with deionized water and once with alcohol, and then dried at 80 ºC in an electric oven for 5 h. The resulting sample was heated in a quartz tube to 500 ºC at a rate of 3 ºC/min in Ar/H_2 (95/5 in volume%) atmosphere and kept at this temperature for 4 h, and then further heated to 750 ºC with a heating rate of 5 ºC/min, and kept at this temperature for 15 h. The obtained composite was denoted as LFP@C1. The carbon content is determined to be 0.67 wt%.

LFP@C2 and LFP@C3 were obtained by changing the concentrations of the reactant as followes: 63.39 mM LFP and 10.54 mM dopamine for LFP@C2, and 38.03 mM LFP and 52.73

mM dopamine for LFP@C3. The rest of the reaction conditions were the same as for sample LFP@C1. The carbon contents for LFP@C2 and LFP@C3 are 3.53 and 8.92 wt% respectively.

For the synthesis of LFP@C4, two cycles of coating were adopted to achieve a thick coating: 105.46 mM dopamine was firstly used to coat 126.78 mM LFP. After the coating, the solid product was collected and then used for a second coating, in which 0.4 g of the obtained LFP@Dopa composites was taken and repeatedly mixed with another 42.19 mM dopamine under the same conditions as for LFP@C1. The carbon content is measured to be 13.72 wt%.

In order to compare the influence of coated-carbon and mixed-carbon on the performance of testing materials, a control experiment was performed. A certain amount of dopamine was added to Tris-buffer (pH: ~ 8.5) and the mixture was kept stirring for 24 h. The obtained dopamine polymer precipitates were collected and rinsed with water by centrifugation, and then dried at 80 ºC. Afterwards, 0.04g of the obtained polydopamine precipitates was mixed with 0.4g (50.71 mM) LFP totally under the same reaction conditions and heat treatments as for LFP@C1, 2, 3 and 4. This resulting sample was denoted as LFP-C, and the carbon content is 3.14 wt%.

Characterization

The size and morphology of the LFP and LFP@C samples were characterized using a JEOL 6701F scanning electron microscope (SEM) operated at 10 kV. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were carried out with a JEOL-2100F transmission electron microscope. X-ray diffraction (XRD) data were collected with a Shimadzu XRD-7000s diffractometer equipped with a Cu K α radiation (λ = 1.54056 Å) in the range (10~80°). Raman spectra were obtained with an NTegra spectra system (NT-MDT). Fourier-Transfer Infrared (FT-IR) spectra were recorded in the range 4000-400 cm^{-1} with Nicolet iN10 IR microscope (Thermo Fisher Scientific). The amount of carbon in the final products was determined by an LECO CS-344 carbon/sulfur analyzer.

Electrochemical evaluation

Electrochemical measurements were performed using CR2032 coin cells assembled in an argon-filled glove box with lithium metal as the counter and reference electrodes. Galvanostatic tests of the assembled cells were carried out using a Land CT2001A battery test system between 2.5 and 4.2 V. All the data are collected after being preconditioned for one cycle. The cathodes were prepared by mixing the active materials, super-P (SP), and poly(vinyl difluoride) (PVDF, Aldrich) at a weight ratio of 80:10:10, pasting on a pure Al foil (99.6%, Goodfellow) and cutting into circular electrodes of 0.64 cm^2 area. The weight for those active materials included in the electrodes are in the range from 1.4 to 2.0 mg. Specifically, for all the 6 samples tested, namely LFP, LFP@C1, LFP@C2, LFP@C3, LFP@C4 and LFP-C, their weight are 1.544, 1.656, 1.775, 1.944, 1.856, and 1.416 mg, respectively. Celgard polypropylene membrane was used as a separator. The electrolyte consisted of a solution of 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1, in wt %) obtained from Guotai-Huarong New Chemical Materials Co., Ltd. Electrochemical impedance spectra (EIS) were performed on an electrochemistry workstation (Princeton PARSTAT 2273).

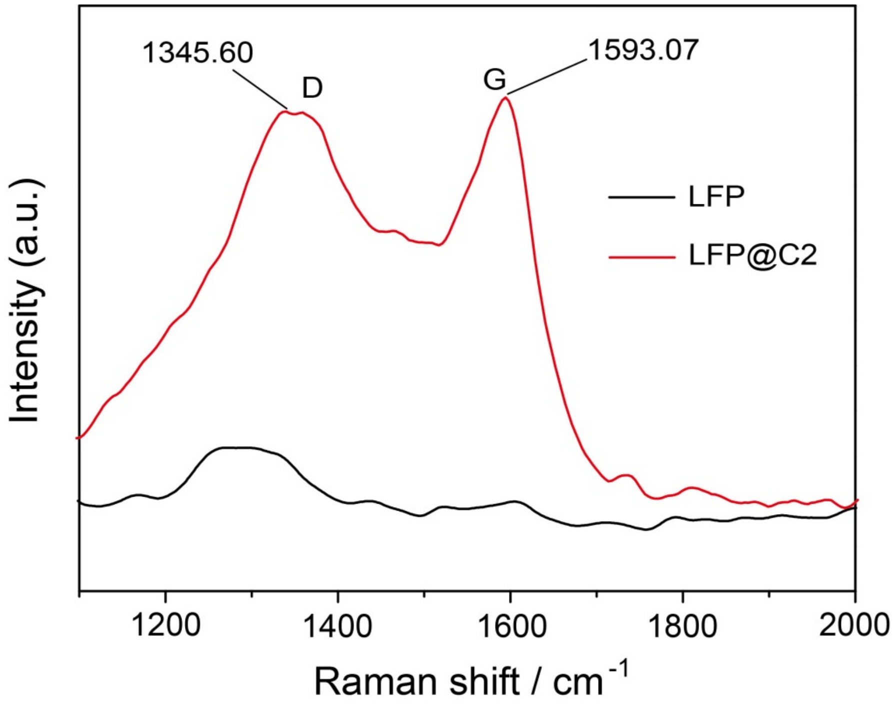

Fig. S1 A representative Raman spectra of carbon coated LFP sample with a thickness at 5 nm: the Peaks at 1593.07 cm^{-1} and 1345.60 cm^{-1} correspond to G and D bands, respectively.

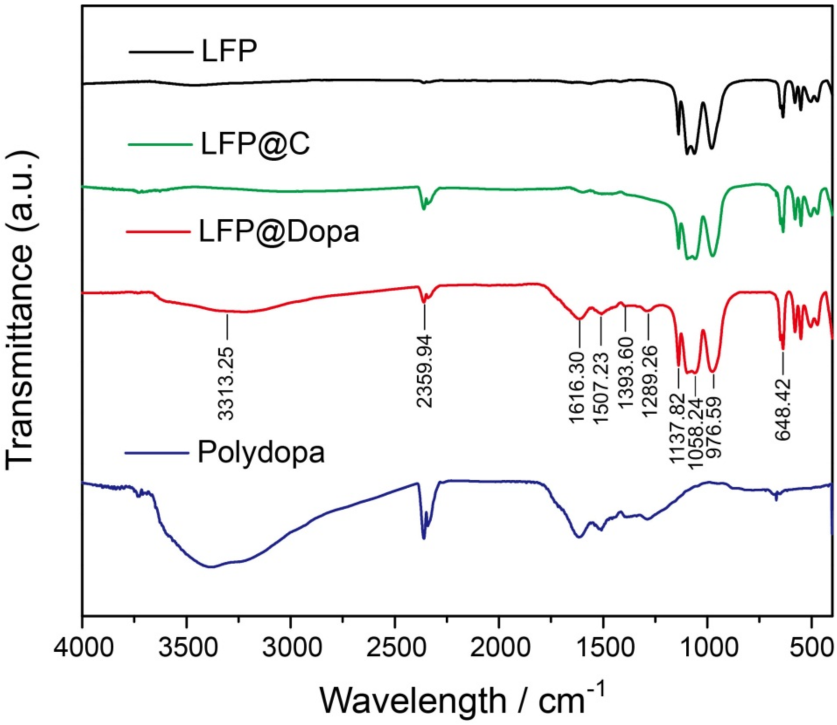

Fig. S2 IR spectra of LFP, LFP@C, LFP@Dopa and Polydopamine. Typically, the N-H and O-H stretching vibrations between 3600 and 3100 cm^{-1} [1], the N-H shearing vibration at 1507.23 cm^{-1} and the phenolic C–O–H bending and stretching vibration at 1393.60 and 1289.26 cm^{-1} [2] are fingerprint ones of polydopamine, confirming the existence of polydopamine in LFP@Dopa. These peaks cannot be found in the spectra of LFP@C, indicating the surface polydopomine species are transferred into conductive carbon by high temperature treatment.

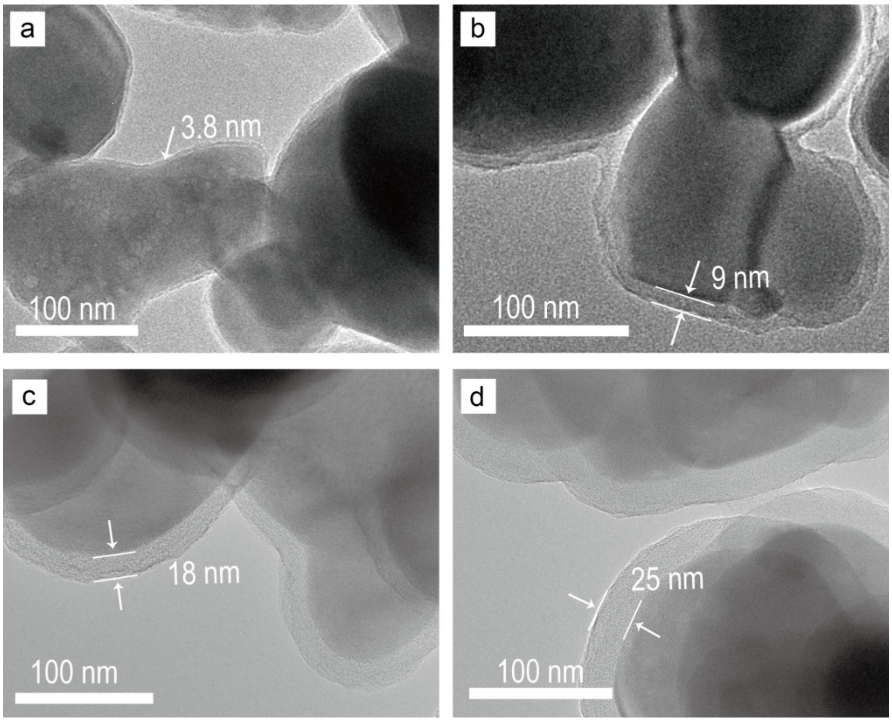

Fig. S3 TEM images of samples before calcination: (a) LFP@Dopa1, (b)LFP@Dopa2, (c)

LFP@Dopa3, and (d) LFP@Dopa4. The surface polydopamine layers are around 3.8 nm, 9 nm, 18 nm, and 25 nm in thickness, respectively.

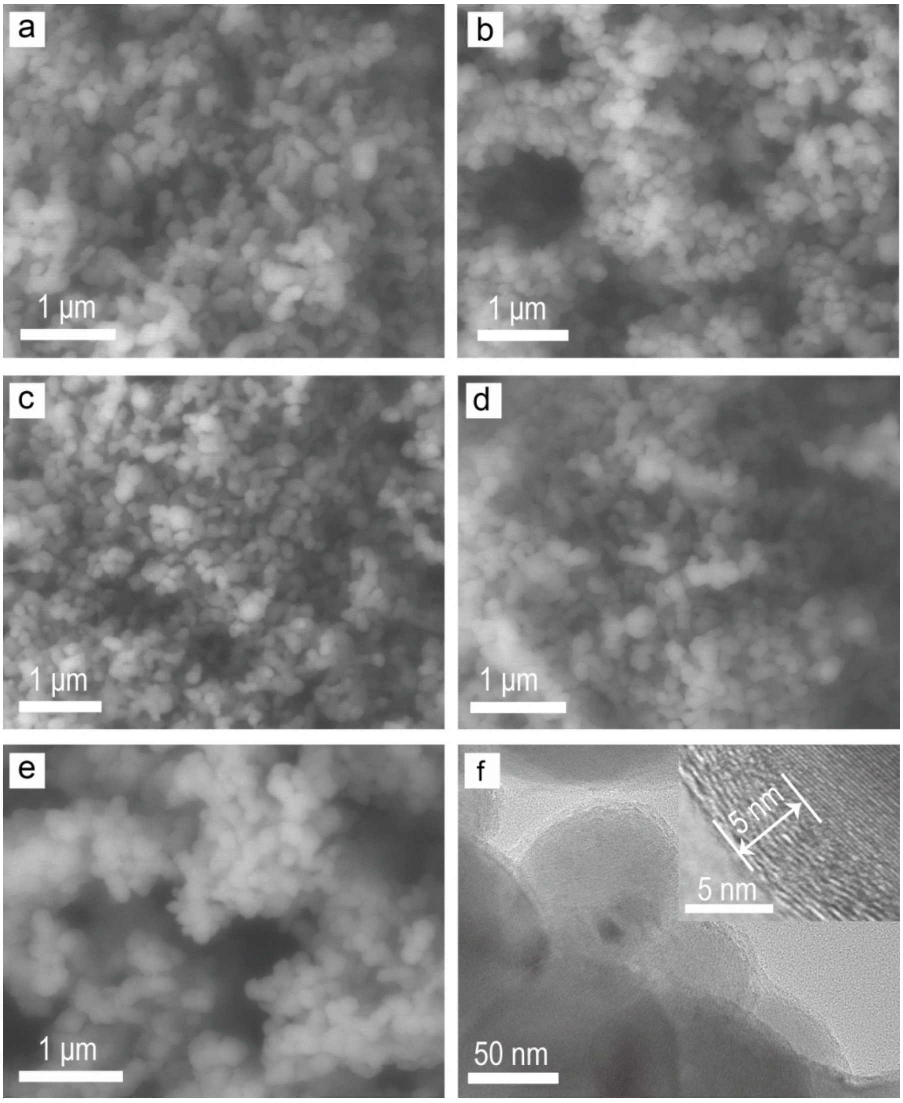

Fig. S4 (a) SEM images of LFP, (b-e) LFP@C1-4, showing that these powders are almost the same in shape; (f) TEM image of LFP@C2 after battery cycling. No detectable shedding of carbon layer and the thickness remains around 5 nm, indicating that the core-shell structured sample is pretty stable during cycling.

Reference

[1] J. Jiang, L. Zhu, X. Li, Y. Xu, B. Zhu, *J. Membrane Sci.,* **2010**, 364, 194.

[2] Z. Xi, Y. Xu, L. Zhu, Y. Wang, B. Zhu, *J. Membrane Sci,.***2009**, 327, 244.