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Supporting Information for

Accurate surface control of core-shell structured $LiMn_{0.5}Fe_{0.5}PO_4$@C for improved battery performance

Zi-Xiang Chi [a], Wei Zhang [a], Xu-Sheng Wang [b], Fu-Quan Chen [b], Ji-Tao Chen [b], An-Min Cao* [a], Li-Jun Wan* [a]

E-mail address: anmin_cao@iccas.ac.cn, wanlijun@iccas.ac.cn

[a] *Key Laboratory of Molecular Nanostructure and Nanotechnology and Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences (CAS), Beijing 100190, PR China*

[b] *College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, PR China*

Experimental Section

Chemicals

Resorcinol was purchased from Beijing Yili Fine Chemicals Co., Ltd. Formaldehyde solution (37%) was purchased from Beijing Modern Oriental Fine Chemistry Co., Ltd. Ammonia solution (25 %) was purchased from Beijing Chemical Works. Metal salts $MnSO_4 \cdot H_2O$ and $FeSO_4 \cdot 7H_2O$ were purchased from Xilong chemical Co., Ltd. All chemicals were used as received without further purification.

Synthesis of LMFP nanoparticles

Pristine $LiFe_{0.5}Mn_{0.5}PO_4$ nanoparticles were synthesized by the modified solvothermal method. [10, 32] H_3PO_4 (10 ml, 3M) was mixed with tetraethylene glycol (TEG) (150 ml) in a

500 ml beaker. Then LiOH (2 M) aqueous solution was slowly added into the above mixture to adjust the pH to 8.6 under vigorous stirring, and a milk white suspension was formed through the neutralization reaction. Subsequently, 20ml aqueous solution containing $MnSO_4$ (15 mmol) and $FeSO_4$ (15mmol) was introduced into the mixture under stirring, resulting in a grey-green suspension. After stirring for about 20 min under room temperature, the mixture was transferred into an autoclave which was sealed and heated to 250 ^oC, and maintained at the same temperature for 12 h. Afterwards, the autoclave was cooled down to room temperature. The grey-green product was collected via centrifugation and washed with H_2O for two times and then ethanol once. The final product was dried at 80 ^oC for 6 h. The collected precipitates was characterized by inductively coupled plasma (ICP) analysis for chemical composition, from which the chemical composition is determined to be $LiMn_{0.5}Fe_{0.5}PO_4$.The collected powder was then used as the pristine LMFP sample with a very low carbon content of 0.13 %.

Synthesis of thickness-controlled LMFP@C composites

The thickness of the carbon coating layer on LFMP nanoparticles can be controlled by varying the initial concentrations of the starting materials LFMP and resorcinol monomer. In a typical synthesis procedure, a suspension of LMFP was prepared by dispersing LMFP nanoparticles (183.65 mM) in a mixed solvent of H_2O and ethanol (H_2O:EtOH=2:1, v/v) with the help of ultrasonication, followed by the addition of resorcinol monomer reach the concentration of 6.055 mM. Subsequently, a small amount of ammonia ($NH_3 \cdot H_2O$, 25% wt%) was added into the mixture to adjust the pH value in the range of 9-10. Finally, a certain amount of formaldehyde solution (37% wt% in H_2O) was added to make sure the mole ratio between resorcinol and formaldehyde fixed at 1:1.4. The mixture was stirred continuously for about 20 h under room temperature, and the color of the mixture gradually turned from grey-green to deep brown during the stirring period. The brown precipitates (denoted as LMFP@RF) 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 400 ºC at a rate of 3 ºC/min in Ar/H_2 (95/5 in volume%) atmosphere and kept at this temperature for 2 h, and then further heated to 700 ºC with a heating rate of 5 ºC/min, and kept at this temperature for 15 h. The obtained composite was denoted as LMFP@C1. The carbon content was determined to be 1.81 wt%.

LMFP@C2, LMFP@C3 and LMFP@C4 were obtained by changing the initial concentrations of the reactant as followes: 113.02 mM LMFP and 6.05mM resorcinol for LMFP@C2, 70.63 mM LMFP and 10.09 mM resorcinol for LMFP@C3, and 84.76 mM LMFP and 40.36 mM resorcinol for LMFP@C4. The rest of the reaction conditions were the same as for sample LMFP@C1. The carbon contents for LMFP@C2, LMFP@C3 and LMFP@C4 are 2.52, 5.15 and 13.50 wt% respectively.

LMFP@C samples with the coating thickness of 2, 5, 8 and 10 nm were prepared by slightly changing the initial concentrations of reactants according to those used for LMFP@C1-C3 respectively. For LMFP@C sample with 2 nm nanoshell, the only change is that the concentration of LMFP was decreased from 183.65 mM for LMFP@C1 to 169.52 mM while the amount of resorcinol was kept unchanged. For 5 nm carbon-coated sample, it only needed to change the concentration of resorcinol from 10.09 mM for LMFP@C3 to 8.07 mM. For LMFP@C samples with the coating thickness 8 and 10 nm, the concentrations of the resorcinol used for them were increased from 10.09 mM for LMFP@C3 to 15.13 mM and 22.20 mM respectively. The other experiment conditions are exactly the same as those for synthesis of LMFP@C1-C3.

The LMPF@C samples with coating thickness of 2.5, 4, 7 and 12 nm were prepared by controlling the reaction time during the RF polymerization period in the synthesis of LMFP@C4. The reaction time was fixed to 1.5 h, 3 h, 6 h and 12 h respectively, then the produced LFMP@RF samples were subjected to the same graphitization procedure as for LMFP@C4, and the resulting LMFP@C with 2.5, 4, 7 and 12 nm coating layers were obtained.

A control experiment was performed in order to compare the influence of coated-carbon and mixed-carbon on the performance of testing materials. A certain amount of resorcinol monomer and formaldehyde was added to a mixed solvent of H_2O and ethanol (H_2O:EtOH=2:1, v/v) with the pH value adjusted by ammonia to 9-10, and the mixture was kept stirring for 24 h. The obtained red RF polymeric resin precipitates were collected and rinsed with water by centrifugation, and then dried at 80 ºC. Afterwards, 0.03g of the obtained RF precipitates was mixed with 0.5g (70.63 mM) LMFP totally under the same reaction conditions and heat treatments as for LMFP@C1, 2, 3, and 4. This resulting sample was denoted as LMFP-C, and the carbon content is 2.91 wt%.

Transition metal dissolution

The metal dissolution measurement was carried out according to a modified method. [33, 34] Typically, 200 mg of the olivine compound was stored in a closed vial containing 2 mL electrolyte solution under Ar atmosphere, and then the mixtures were moisture-contaminated by 100 ppm H_2O. The solution was removed after 14 days of storage at 55 °C, and then was put on a heating plate to evaporate the organic electrolyte. A small amount of HNO_3 was added to the residue to dissolve the metal ion. Then the mixture was filtrated to remove the insolubles, diluted to a certain volume by distilled water, and finally analyzed by ICP (Model: ICPE-9000, Shimadzu Corporation) for the presence of metal.

Characterization

The size and morphology of the LFMP and LFMP@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). Differential scanning calorimetry (DSC) analysis was performed on a Mettler-Toledo DSC1 STAR^{e} system. The conductivity tests were performed on a Four-Point Probe test equiptment (Model: RST-8, Guangzhou 4-Probe tech Co., Ltd.). The chemical composition of the synthesized $LiMn_{0.5}Fe_{0.5}PO_4$ active materials was determined using inductively coupled plasma (Model: ICPE-9000, Shimadzu Corporation) analysis and the amount of carbon contents 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. Charge and discharge measurements for the cells were carried out on a Land CT2001A battery test system. For LMFP@C cathode materials, all cells were cycled in a constant current mode at a 1/10C-rate to 4.5 V, and discharged to 2.5 V at a specific rate (1C=170 mAh/g). 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. 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).

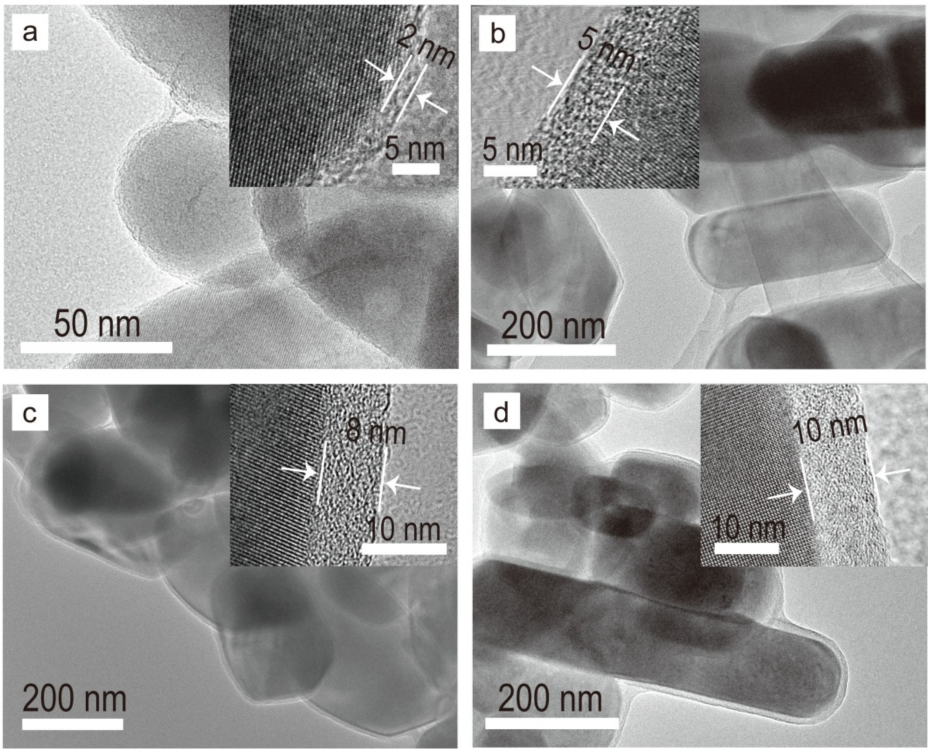

Figure S1. TEM images of LMFP@C samples with controlled thickness of 2, 5, 8 and 10 nm.

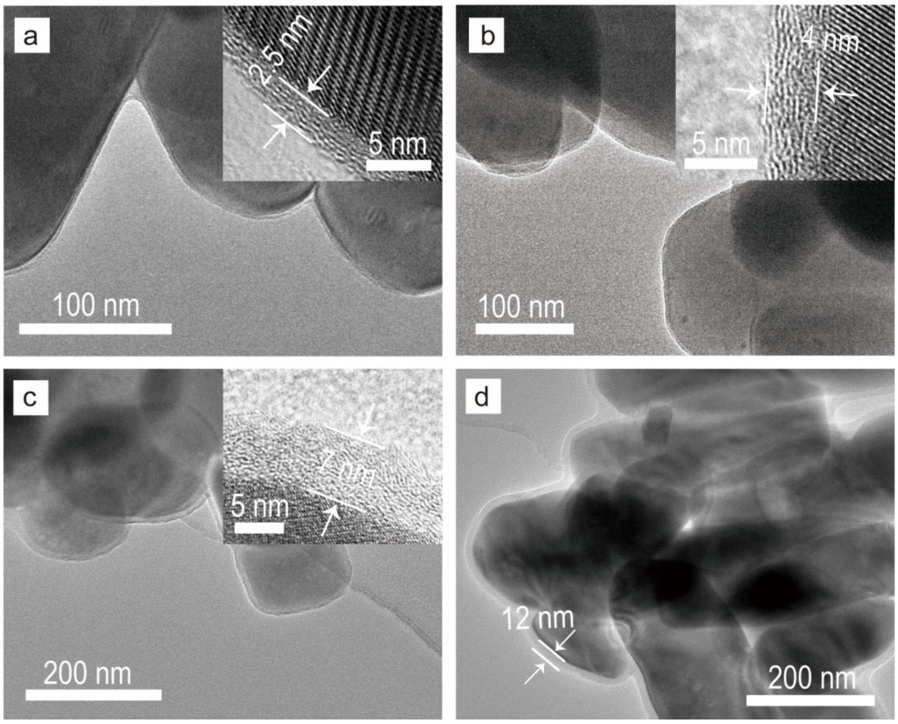

Figure S2. LMFP@C samples with coating thickness of 2.5, 4, 7 and 12 nm, prepared by controlling the reaction time for 1.5 h, 3 h, 6 h and 12 h respectively in the synthesis of LMFP@C4.

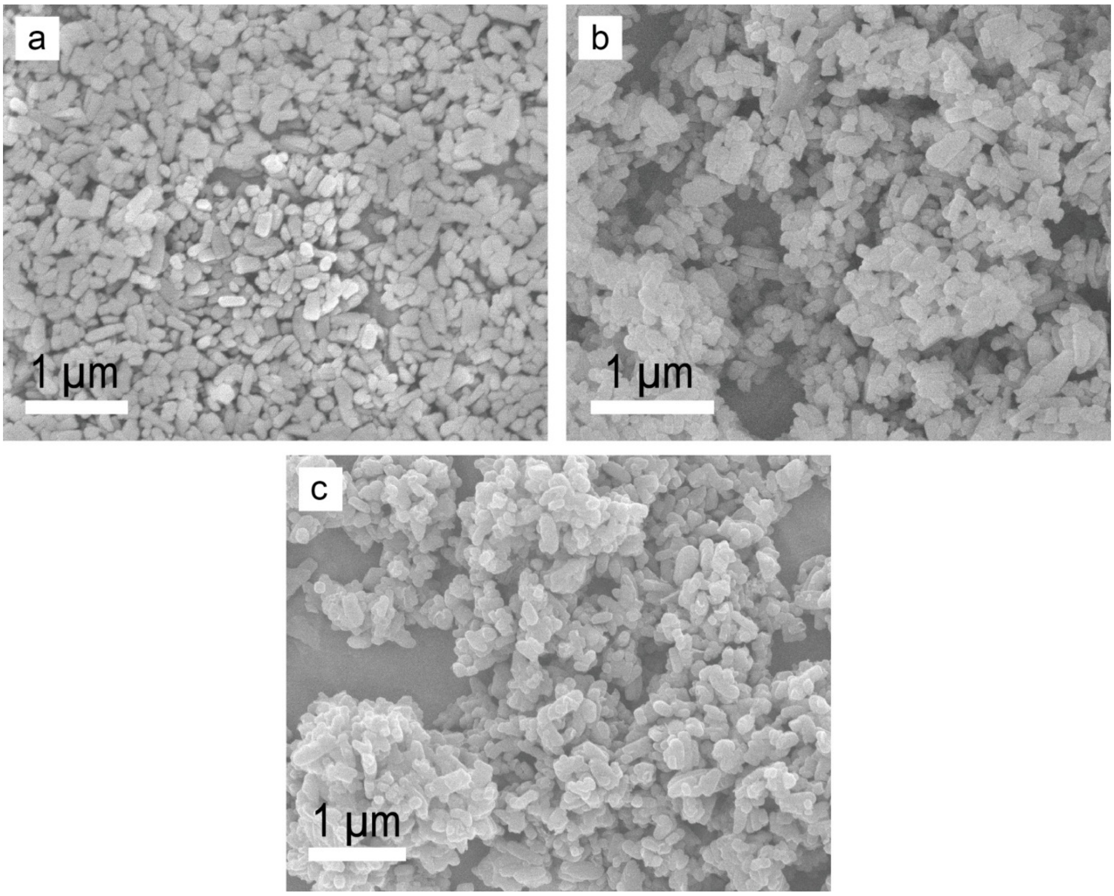

Figure S3. SEM images of the hydrothermally synthesized LMFP (a), LMFP@RF (b) and LMFP@C (c).

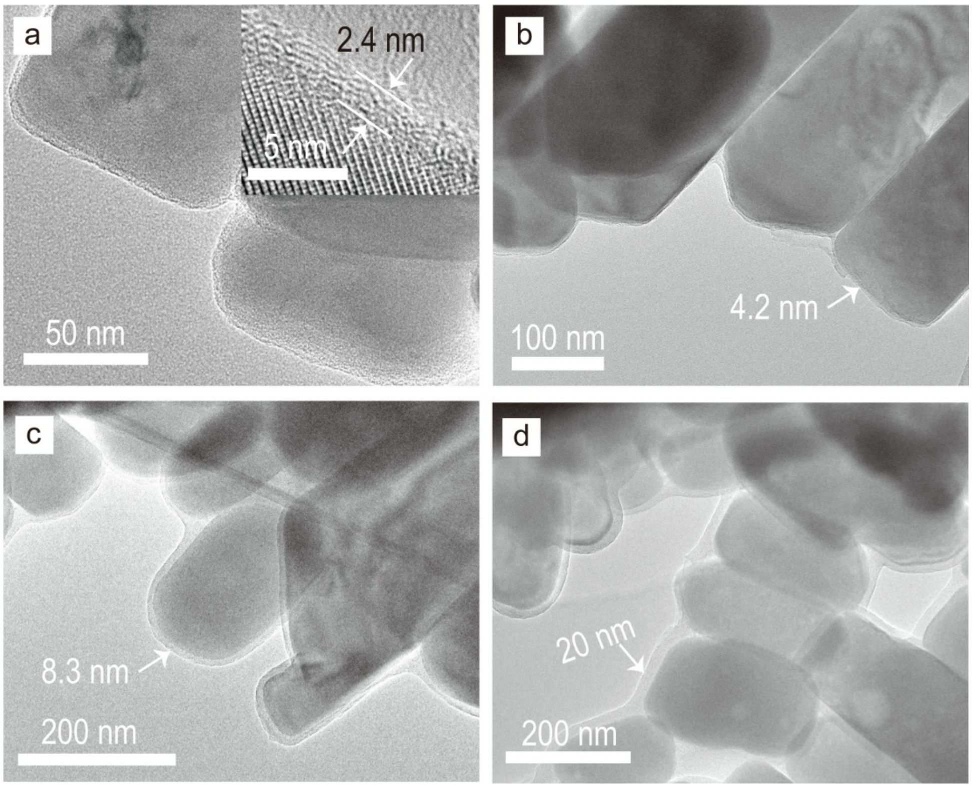

Figure S4. TEM images of samples before calcination: (a) LMFP@RF1, (b)LMFP@RF2, (c) LMFP@RF3, and (d) LMFP@RF4. The surface RF layers are around 2.4 nm, 4.2 nm, 8.3 nm, and 20 nm in thickness, respectively.

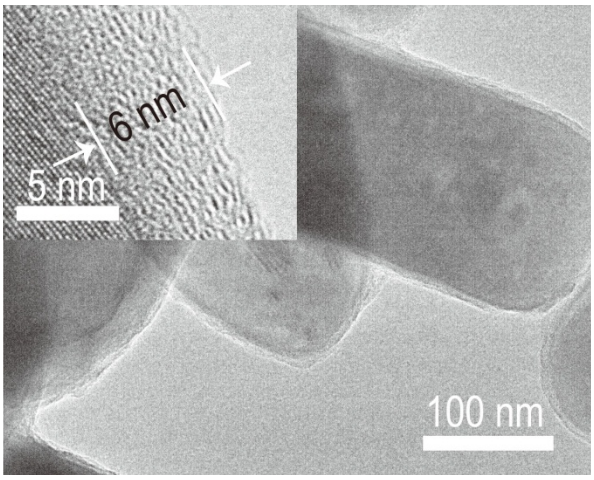

Figure S5. TEM image of LMFP@C3 after battery cycling. No shedding of carbon layer is detectable and the thickness remains around 6 nm for LFMP@C3, indicating the core-shell structured samples are pretty stable during cycling.

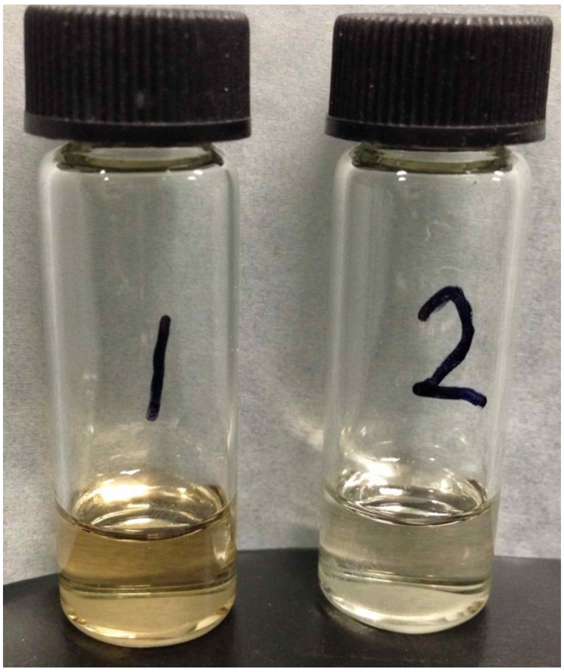

Figure S6. Color contrast between the electrolytes removed from pristine LMFP and LMFP@C2 after a period of high-temperature storage. The color of pristine LMFP (labeled as number 1) is much deeper than that of LMFP@C2 (labeled as number 2), indicating that the amount of Fe dissolution is more than that of pristine LMFP.

Table S1 Chemical composition of the synthesized LMFP, LMFP@RF2 and LMFP@C2 determined by inductively coupled plasma (ICP) analysis on Mn and Fe, showing the composition of Mn and Fe is not changed during RF coating process and the high temperature treatment.

	Pristine LMFP	LMFP@RF2	LMFP@C2
Fe (ppm)	8.87	6.49	8.68
Mn (ppm)	8.80	6.37	8.63
Mn:Fe	1.009:1	1.036:1	1.011:1

Table S2 Conductivity test of LMPF and LMFP@C2.

Sample	Electrical conductivity (S/cm)
Pristine LMFP	N/A
LMFP@C2	6.54×10^{-2}