

Electronic Supplementary Information

Hollow microspherical LiFePO_4/C synthesized from a novel multidentate phosphonate complexing agent

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Experimental Section

Material preparation

First, EDTMP and lithium hydroxide (LiOH) were dissolved in 80 °C de-ion water. The pH value of the solution was adjusted and maintained between 8 and 9 by addition of ammonia solution. Then, iron (II) acetate (Fe(AC)₂) solution was slowly dripped into the previous mixed Li-EDTMP solution through a burette. Dark green transparent sol was obtained with rigid stirring. The designed element molar ratio of Li: Fe: P in the sol was 1: 1: 1, therefore molar ratio of the starting materials of LiOH, EDTMP and Fe(AC)₂ was 4:1:4. The sol was dried via two approaches as shown in Scheme. 1c in the main article. As for a conventional sol-gel route, the sol was kept at 80 °C with pH 8-9 with rigid stirring until a brown viscous gel was formed. The gel was then thoroughly dried in an 80 °C oven. As for the sol-gel-spray-drying route, the sol was rapidly sprayed and dried at 240 °C using a centrifuge spray-dryer (Shanghai Yacheng YC-015). The precursors were finally calcinated at 700 °C for 6 h in flowing purified argon to obtain the LiFePO₄/C products.

Characterization

Powder X-ray diffraction (XRD, Shimadzu XRD-6000, Cu-*K*α radiation) was used to determine the crystal structure with a scan rate of 0.5 degree min⁻¹ and a step-width of 0.02 degree. Micromorphologies of the synthesized LiFePO₄/C composites were observed using field emission scanning electron microscope (FE-SEM, Hitachi S-4300) and transmission electron microscope (TEM, JEM-3010F). Carbon contents in LiFePO₄/C composites were determined by thermo gravimetric

analysis (TGA) using Shimadzu DTG-60H.

Electrochemical tests

The working electrode comprised of the LiFePO₄/C composites, carbon black (Super PTM) and polyvinylidene fluoride (PVDF, 99%, Sigma-Aldrich) in a ratio of 80:15:5 by weight. Active material loading densities were controlled in the range of 4-5 mg cm⁻². Two electrode SwagelokTM type half cells were assembled in an argon glove box. One Celgard 2500TM separator was sandwiched between the working electrode and a 0.59 mm thick metallic lithium foil. The electrolyte consists of 1 M LiPF₆ in ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC) (DC: EC: DMC, 1:1:1, vol.) solutions. Galvanostatic charge-discharge cycling tests were carried out between 2.2 V and 4.3V using Maccor 4304 or Neware Battery Test Station BTS-5V1A. Discharge rate capability was test with a charge current of 0.1C and discharge currents from 0.1C to 30C, where 1C was defined to be 160 mA g⁻¹.

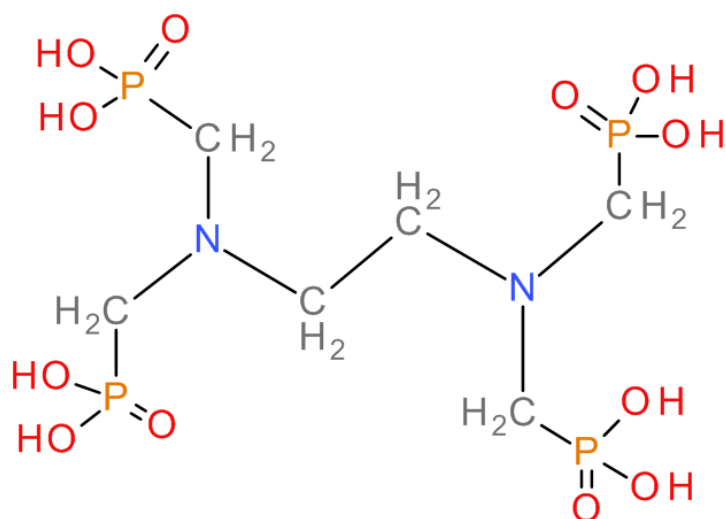


Fig. S1 Schematic of EDTMP molecular formula

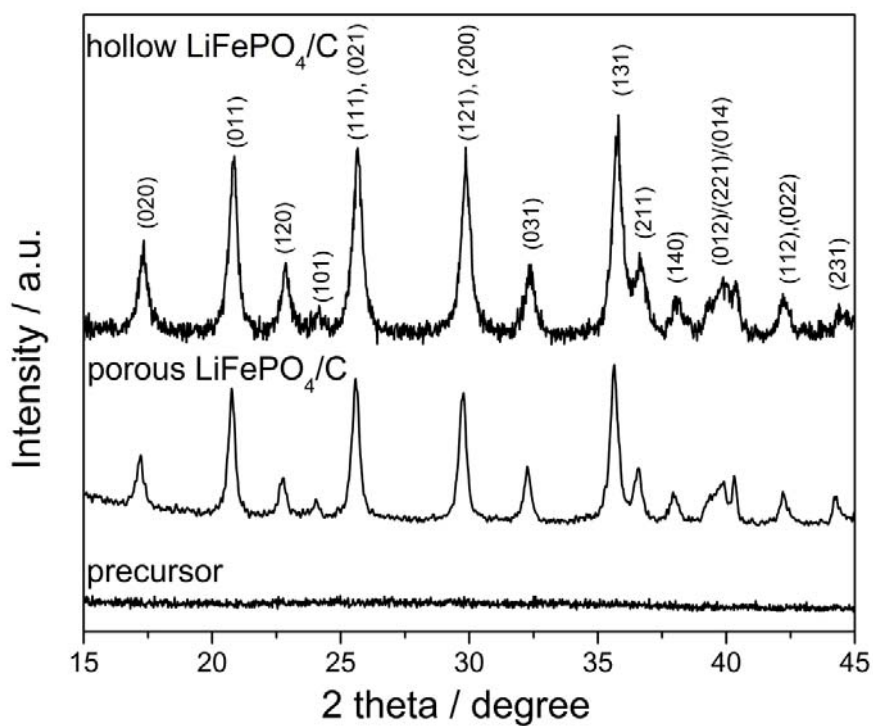


Fig. S2 XRD patterns of porous and hollow LiFePO_4 as well as precursors

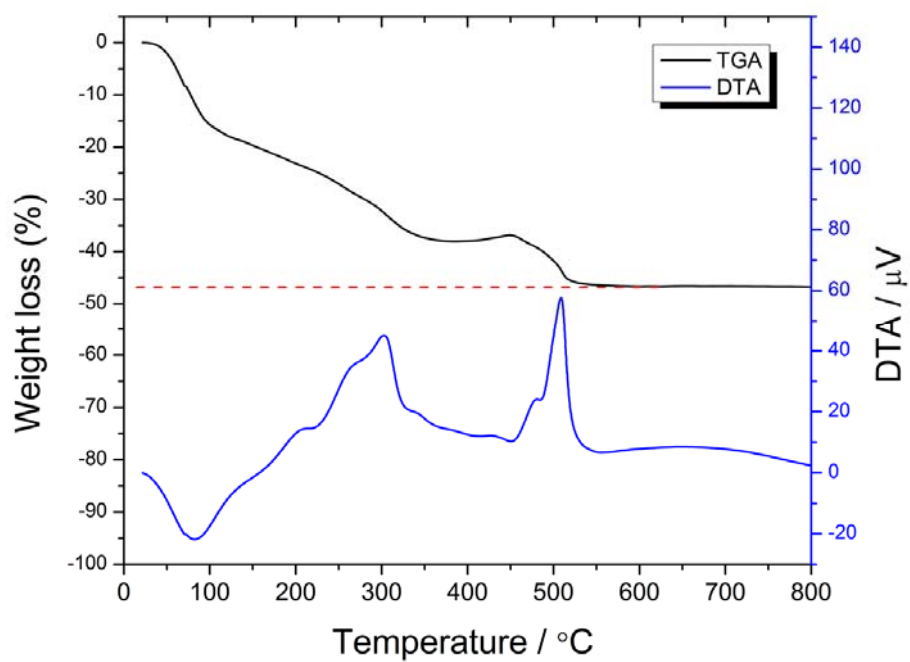


Fig. S3 TGA and DTA curves of the spray-dried precursor

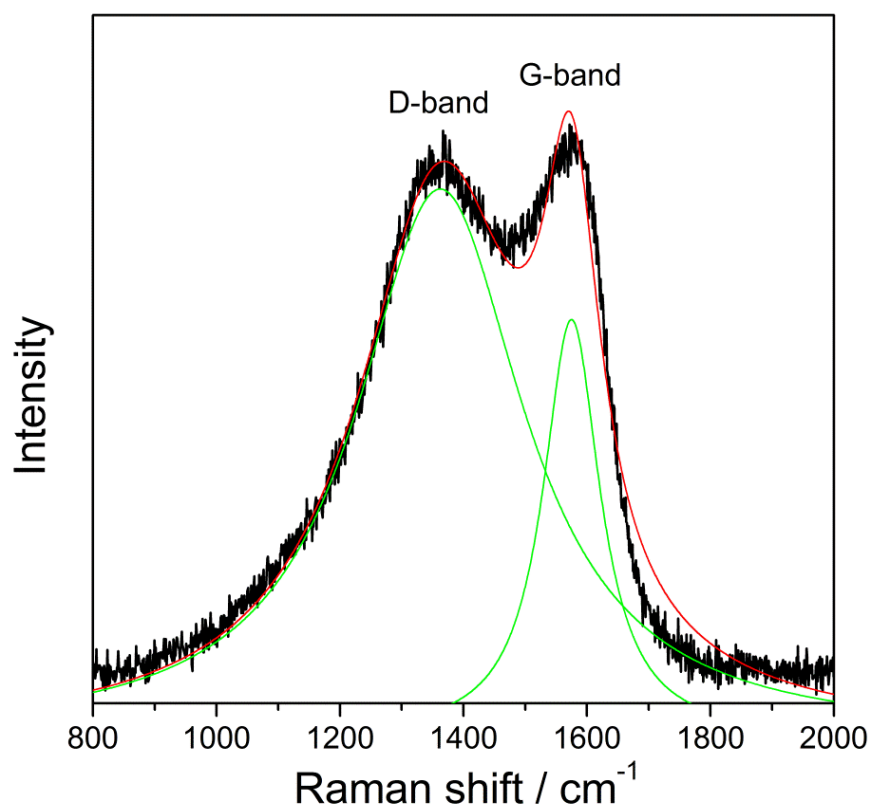


Fig. S4 Raman spectrum of the hollow LiFePO₄/C

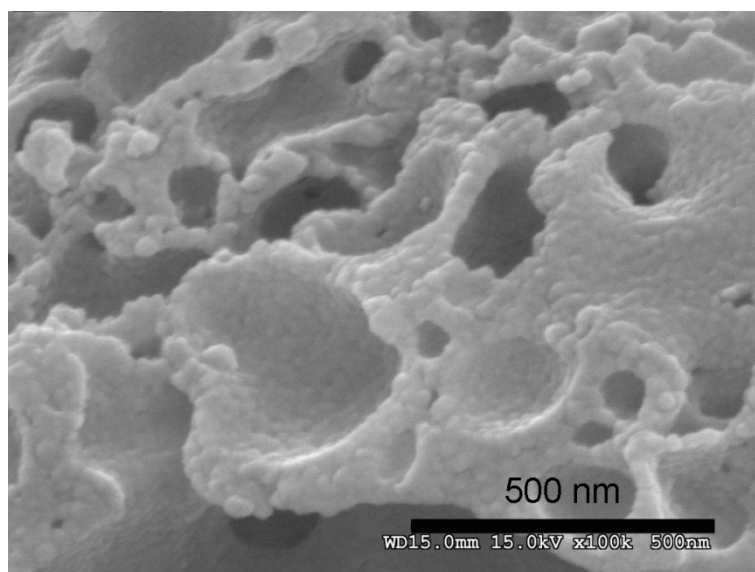


Fig. S5 SEM image of the porous LiFePO₄/C

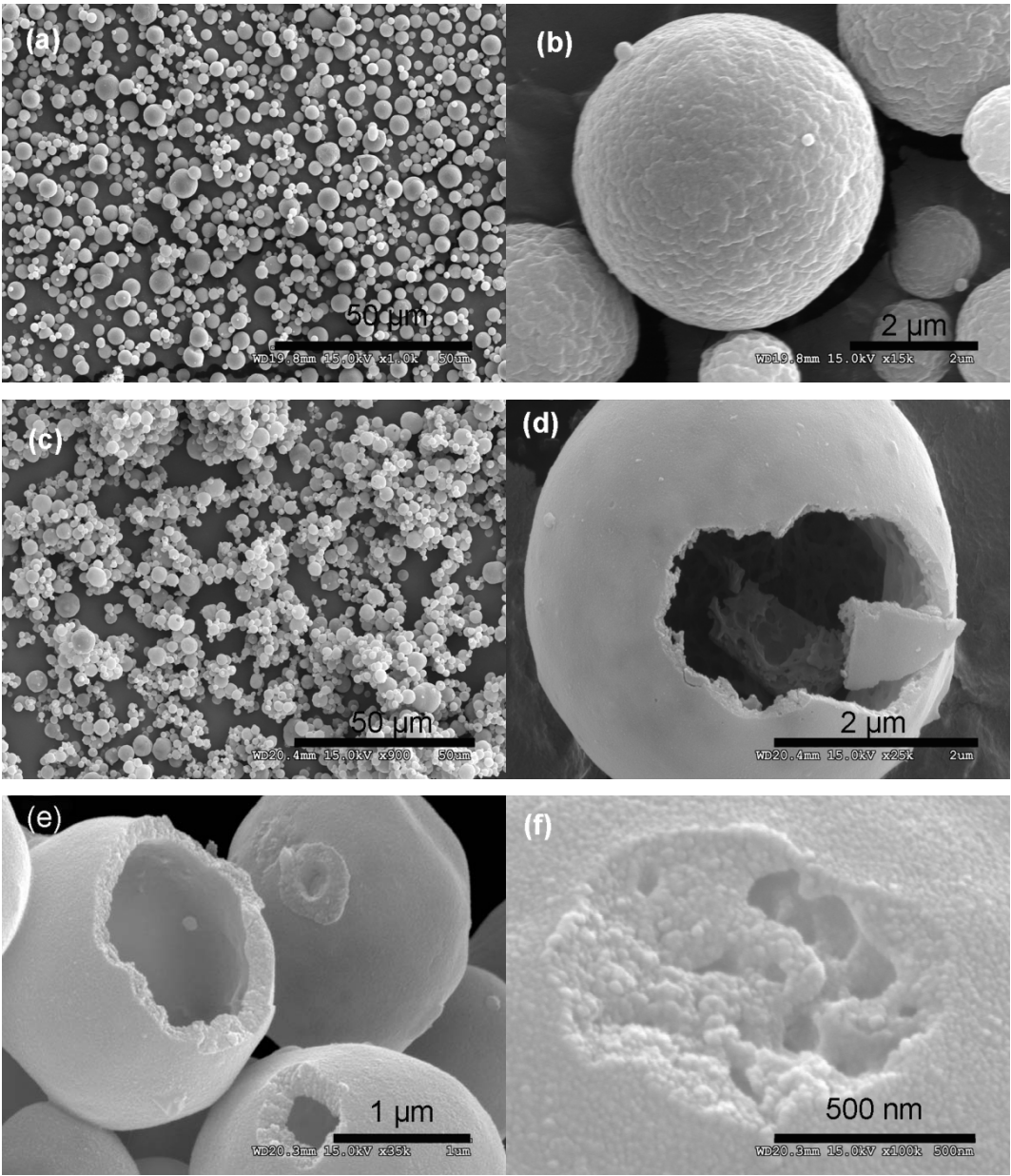


Fig. S6 Supplementary SEM images of (a, b) precursor to hollow LiFePO₄/C, (c, d, e, f) hollow LiFePO₄/C

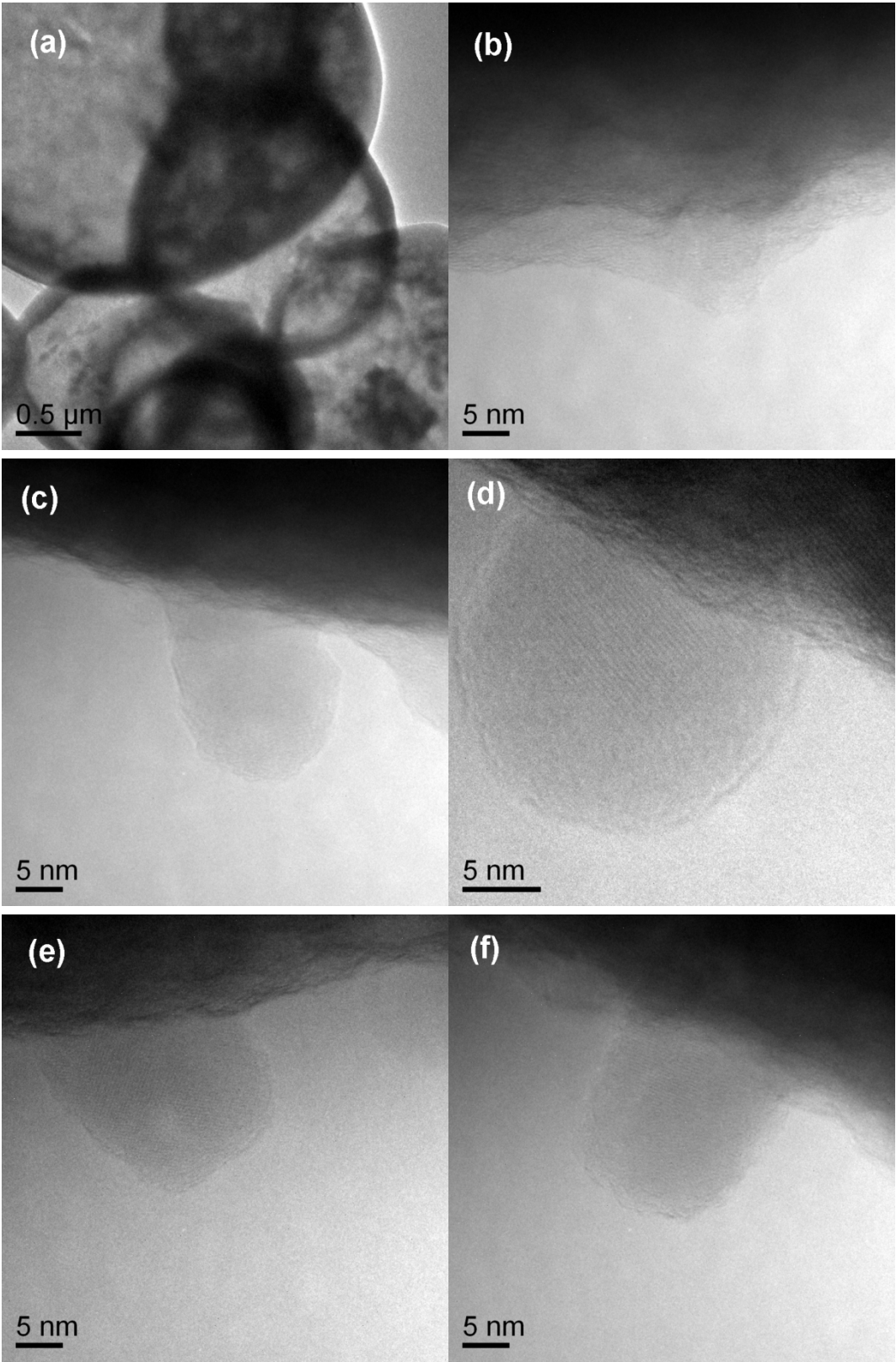


Fig. S7 Supplementary TEM images of hollow LiFePO_4/C

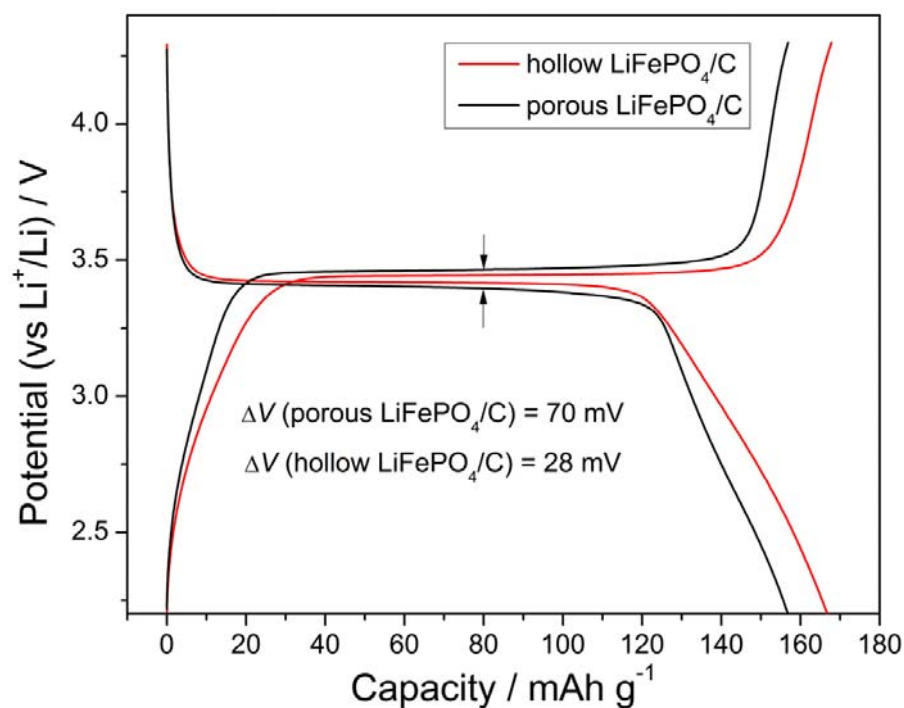


Fig. S8 Charge-discharge curves of the LiFePO_4/C composites at 0.1C

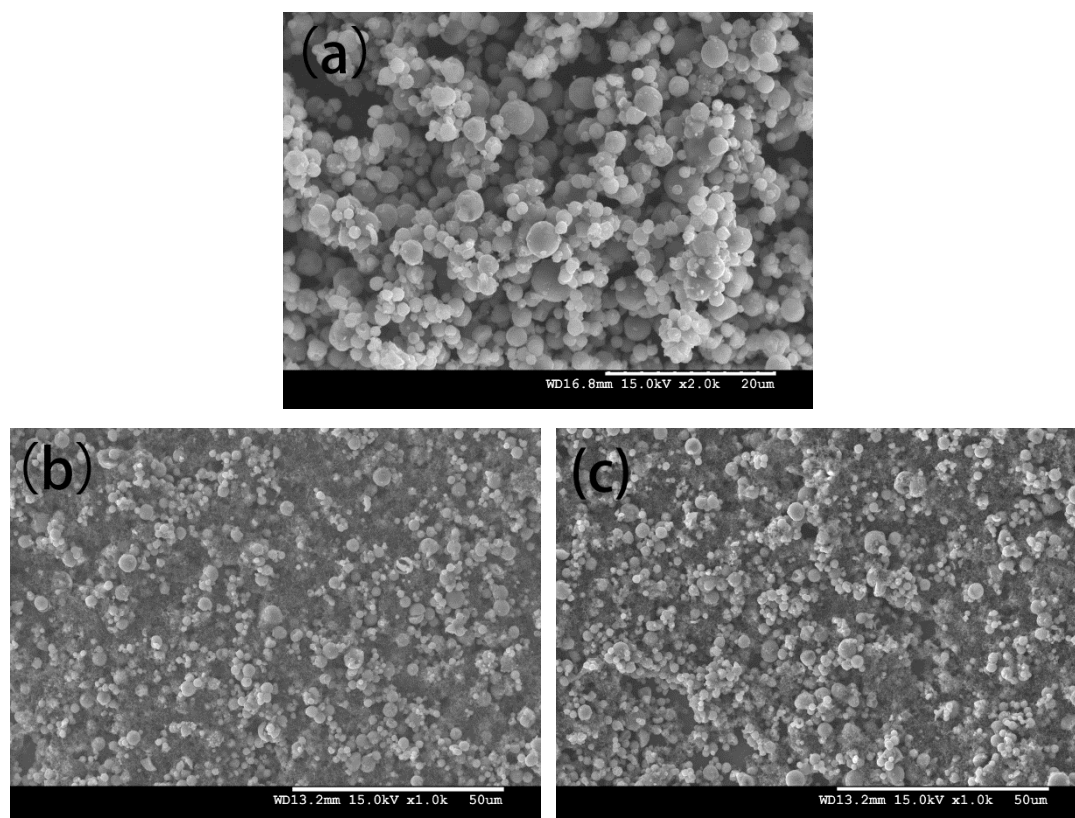


Fig. S9 SEM images of (a) LiFePO₄/C hollow microspheres after mild grinding, (b) as-prepared hollow LiFePO₄/C electrode, and (c) hollow LiFePO₄/C electrode after 50 cycles at 1C (washed by ethanol to remove possible side products of electrolyte degradation)