

Electronic Supplementary Information

Carbon-coated Fe₃O₄ microspheres with a porous multideck-cage structure for highly reversible lithium storage

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Experimental Section

Synthesis of $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ microspheres. In a typical procedure, 1 g of PVP (MW~ 58K), 0.5 mmol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 0.3 mmol of trisodium citrate, and 0.5 mmol of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ were successively added in 40 mL of distilled water under magnetic stirring to form a clear solution. Subsequently, the resulting mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave, which was sealed and maintained at 180 °C for 10 h. After naturally cooling down to room temperature, the as-prepared precipitate in green color was collected and washed with distilled water and ethanol for several times respectively, then dried under vacuum at 60 °C for 6 h.

Synthesis of $\text{FePO}_4/\text{Fe}_2\text{O}_3$ composite microspheres. In a typical procedure, the as-prepared $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ microspheres were loaded into a quartz crucible and placed at the center of a tube furnace. First, the quartz tube was purged with a pure NH_3 flow at a constant rate of 20 sccm for 20 min to remove oxygen and moisture. Then, the system was calcined at 600 °C for 2 h with a heating rate of 5 °C min⁻¹ under the same NH_3 flow rate. After cooling down to room temperature, the product was calcined in air at 700 °C for 2h.

Synthesis of Fe_2O_3 -PMCMs and $\text{Fe}_3\text{O}_4@\text{C}$ -PMCMs. In a typical procedure, 30 mg of $\text{FePO}_4/\text{Fe}_2\text{O}_3$ composite microspheres was dispersed in 10 mL of EG with the assistance of sonication for 10 min, and then 2 mL of H_3PO_4 dissolved in 5 mL of EG solution was added drop by drop to the above solution under stirring for 1 h at 35 °C. Finally, the as-prepared Fe_2O_3 -PMCMs were collected and washed with ethanol for several times by centrifugation, then dried in an oven at 60 °C for 6 h.

For synthesis of $\text{Fe}_3\text{O}_4@\text{C}$ -PMCMs, 0.05 g of the synthesized Fe_2O_3 -PMCMs was dispersed in 30 mL of aqueous glucose solution (with 0.5 g of glucose) by ultrasonication. Then, the resulting suspension was transferred to a 50 mL of Teflon-lined autoclave, which was then heated in an

air-flow electric oven at 170 °C for 8 h. The product was harvested by centrifugation and washed with distilled water and ethanol for at least five times, and dried at 60 °C. Finally, the above product was annealed at 500 °C for 4 h with heating rate of 1 °C min⁻¹ under N₂ atmosphere to obtain Fe₃O₄@C-PMCMs.

Materials Characterization. Powder X-ray diffraction (XRD) measurements of the samples were performed with a Philips PW3040/60 X-ray diffractometer using Cu-K α radiation at a scanning rate of 0.06 ° s⁻¹. Field-emission scanning electron microscopy (FESEM) was performed with a Hitachi S-4800 scanning electron microanalyzer with an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were conducted at 200 kV with a JEM-2100F field emission TEM. N₂ adsorption-desorption isotherms were obtained using a Micrometrics ASAP 2020. Thermogravimetric analysis (TGA) of the products was performed on a Netzsch STA 449 C thermal analyzer.

Electrochemical Measurements. The electrochemical tests were carried out in two-electrode Swagelok cells. The working electrode consists of 70 wt% of active material, 20 wt% of conductive carbon black (Super-P-Li), and 10 wt% of polymer binder (polyvinylidene fluoride, PVDF). The typical loading mass of the active materials is ~ 1 mg cm⁻². The electrolyte is 1M LiPF₆ in a mixture of ethylene carbonate and diethyl carbonate (1:1 by weight). Lithium disc was used as both the counter and reference electrode. Cell assembly was carried out in an Ar-filled glovebox with moisture and oxygen concentrations below 1.0 ppm. The charge-discharge tests were performed on a NEWARE battery tester. Cyclic voltammograms (CVs) were obtained with a CHI-660D electrochemical workstation.

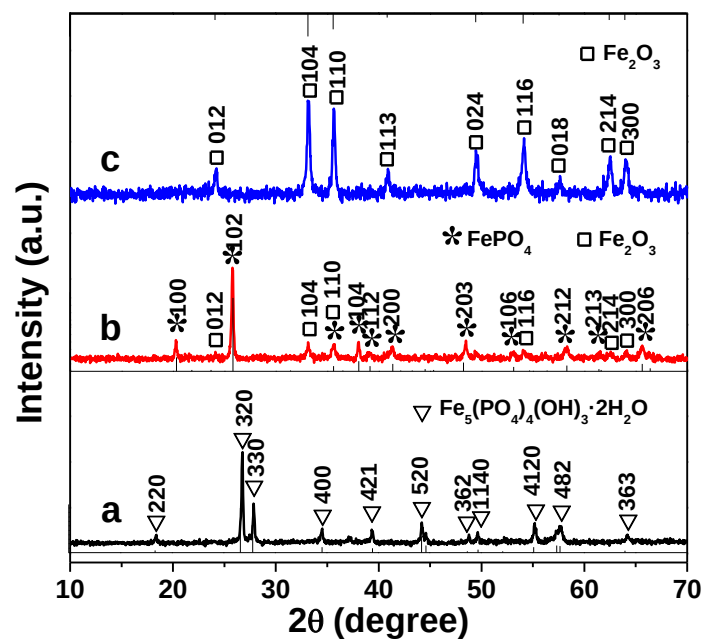


Fig. S1 XRD patterns of (a) the as-prepared $\text{Fe}_5(\text{PO}_4)_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ microspheres, (b) $\text{FePO}_4/\text{Fe}_2\text{O}_3$ composite microspheres, and (c) Fe_2O_3 -PMCMs.

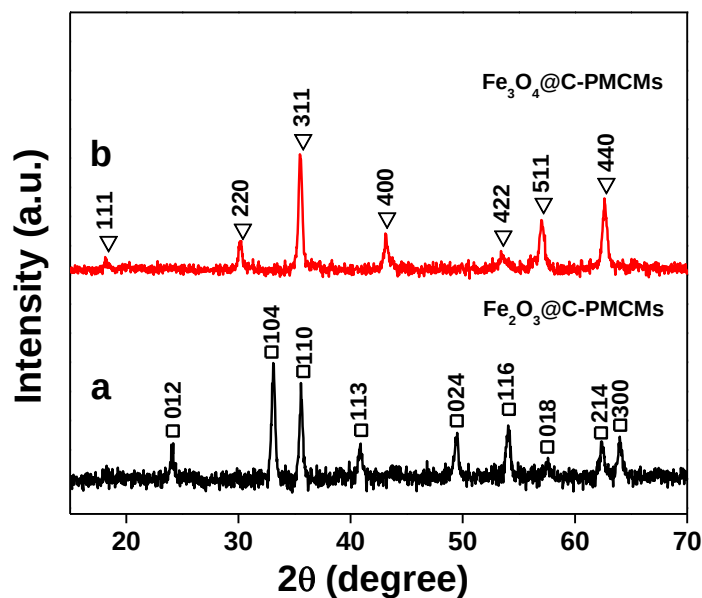


Fig. S2 XRD patterns of the as-prepared products obtained before and after being annealed in N_2 : (a) $\text{Fe}_2\text{O}_3@\text{C-PMCMs}$, and (b) $\text{Fe}_3\text{O}_4@\text{C-PMCMs}$.

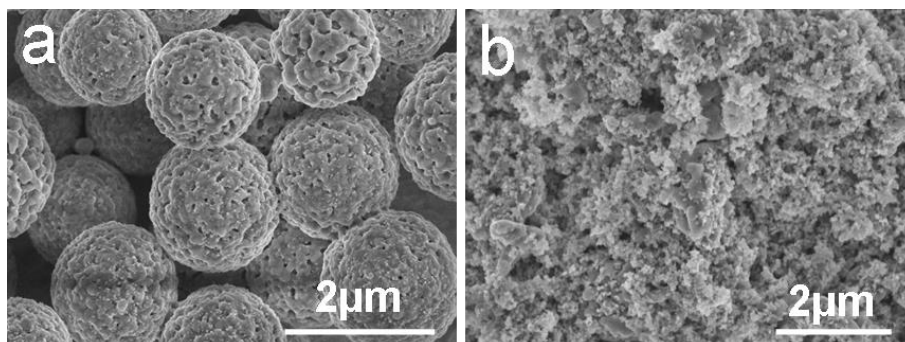


Fig. S3 FESEM images of (a) the as-obtained $\text{FePO}_4/\text{Fe}_2\text{O}_3$ composite microspheres obtained after annealing only in air, and (b) $\alpha\text{-Fe}_2\text{O}_3$ obtained after etched by H_3PO_4 in EG.

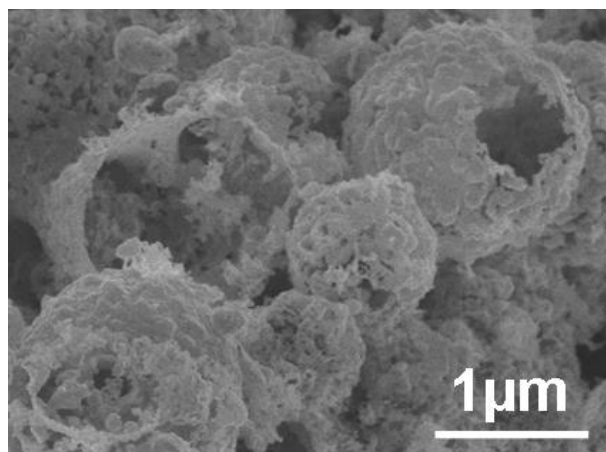


Fig. S4 FESEM image of the product obtained after etching by H_3PO_4 in H_2O .

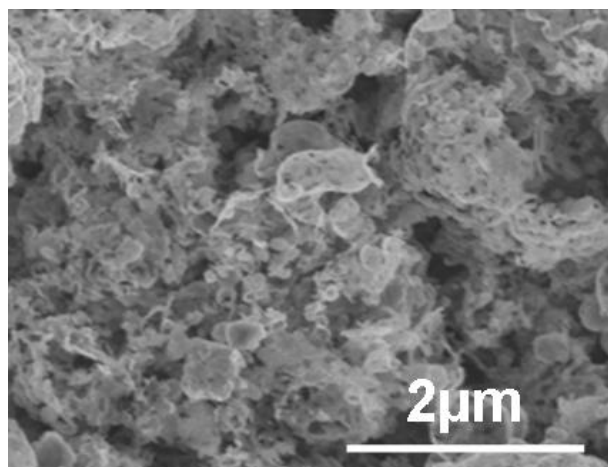


Fig. S5 FESEM image of the product obtained after etching by HCl in EG.

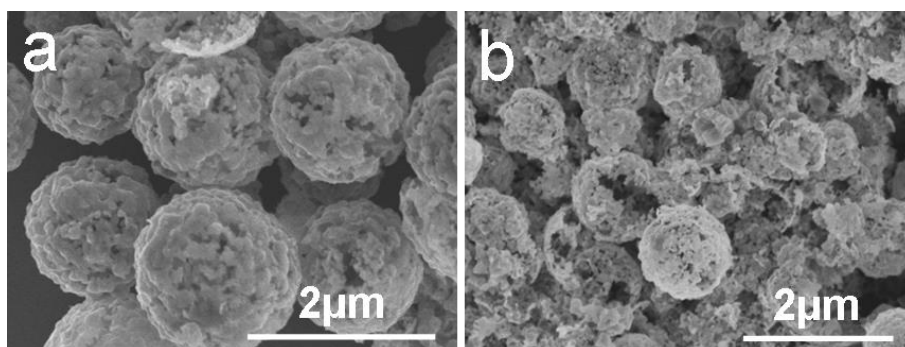


Fig. S6 FESEM images of the product obtained after etching with different amounts of H_3PO_4 in EG:

(a) 1 mL of H_3PO_4 , and (b) 3 mL of H_3PO_4 .

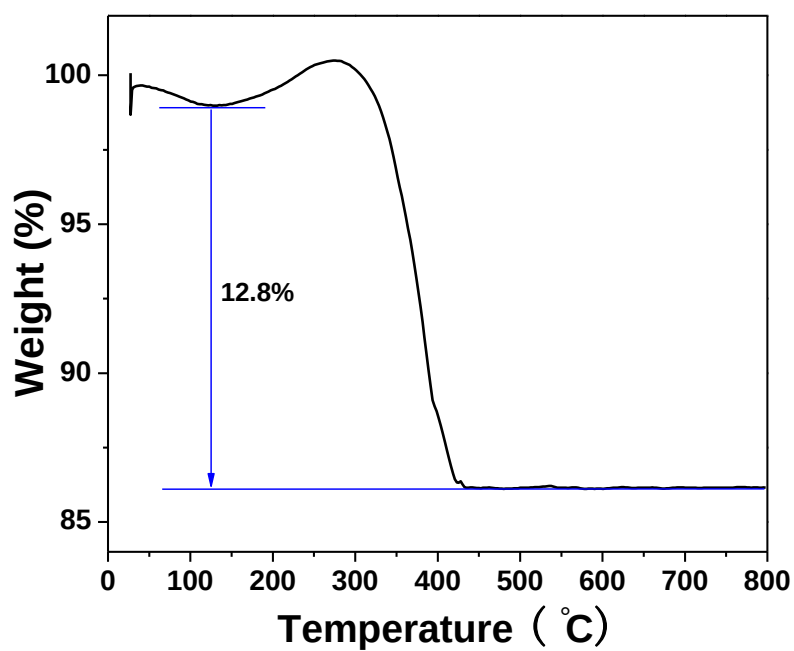


Fig. S7 TGA curve of $\text{Fe}_3\text{O}_4\text{@C-PMCMs}$ in air between 30 and 800 °C with a heating rate of 10 °C min^{-1} .

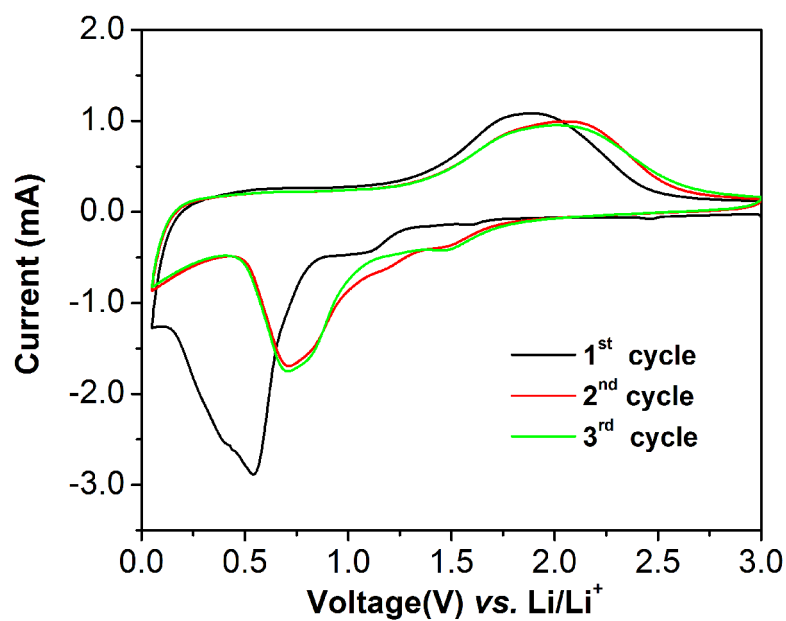


Fig. S8 CV curves of $\text{Fe}_3\text{O}_4\text{@C-PMCMs}$ showing the 1st, 2nd and 3rd cycles between 0.05 and 3.0 V at a scan rate of 0.5 mV s^{-1} .