Supplementary Material (ESI) for Chemical Communications

Supporting Information

A Hollow Sphere Secondary Structure of $LiFePO_4$ Nanoparticles

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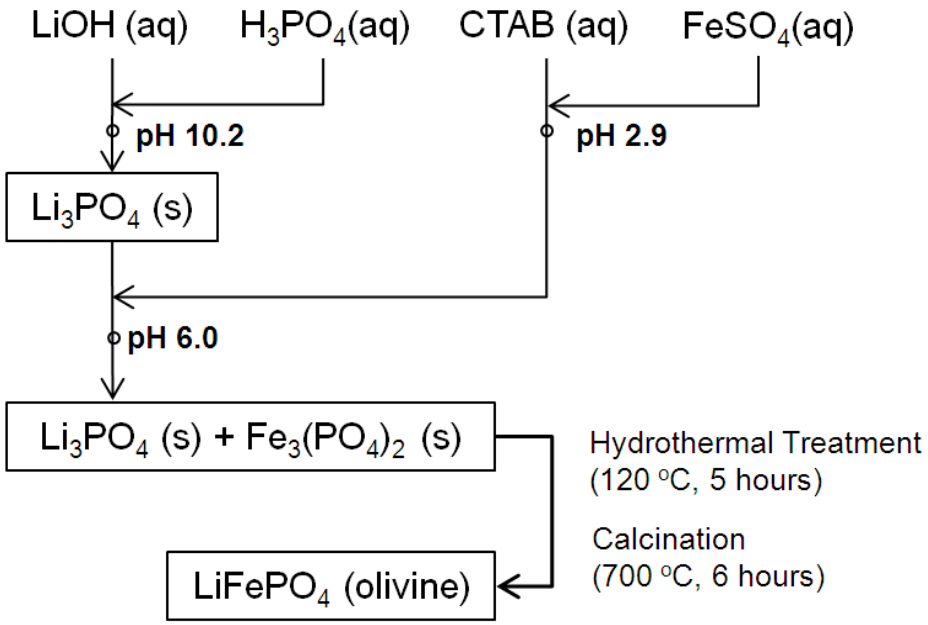
Experimental

Preparaton. Hollow-sphere-secondary-structured $LiFePO_4$ was prepared by precipitating Li_3PO_4 and $Fe_3(PO_4)_2$ sequentially with CTAB (cetyltrimethylammonium bromide) and heating the mixture at 120 ^oC for 5 hours hydrothermally and then at 700 ^oC for 6 hours in an inert atmosphere (Scheme S1). The first intermediate precipitate (Li_3PO_4) was prepared by adding phosphoric acid to an aqueous solution of LiOH. An aqueous mixture of $FeSO_4$ and CTAB (cetyltrimethylammonium bromide) was added to the first solution containg the Li_3PO_4 precipitate. The measured pH of each solution was indicated in Scheme S1 (pH was not adjusted). The resultant concentration is 1.2 M LiOH, 0.4 M $FeSO_4$, 0.4M H_3PO_4 and of 0.16 M CTAB.

Cell Test. The 2016R-type coin half cell configuration were used with 1.15M $LiPF_6$ in 3:7 v/v ethylene carbonate/ dimethyl carbonate (EC/DMC) as electrolyte for charge and discharge tests. Lithium foil was used as anode. Cathode was constructed by mixing active materials, polyvinylidene fluoride (PVdF) as a binder and Super P carbon black as a conduction enhancer at a weight ratio of 8:1:1 in a NMP solvent. The mixed slurry was cast onto Al foil by a doctor blade coater (loading density of active material = 3 mg cm^{-2}); heated at 130 °C for 20 minutes to evaporate its solvent; and then pressed by using a roll press. Two different $LiFePO_4$ were used as active materials: the hollow-sphere-secondary-structured $LiFePO_4$ prepared from the sequential precipitation mentioned above as well as the commercially available one (non-hollow, ~ 200 nm) made by solid state reaction as a

reference for comparison. Carbon content was estimated at ~ 2 wt. % for both $LiFePO_4$ by elemental analysis based on combustion method.



Scheme S1 Preparation of olivine phase $LiFePO_4$ via sequential precipitation in presence of a carbon precursor (CTAB). 1.2 M LiOH, 0.4 M $FeSO_4$ and 0.4M H_3PO_4 were used in the presence of 0.16 M CTAB (Cetyltrimethylammonium bromide, $CH_3(CH_2)_{15}N(Br)(CH_3)_3$). The measured (not adjusted) value of pH of each solution was indicated.

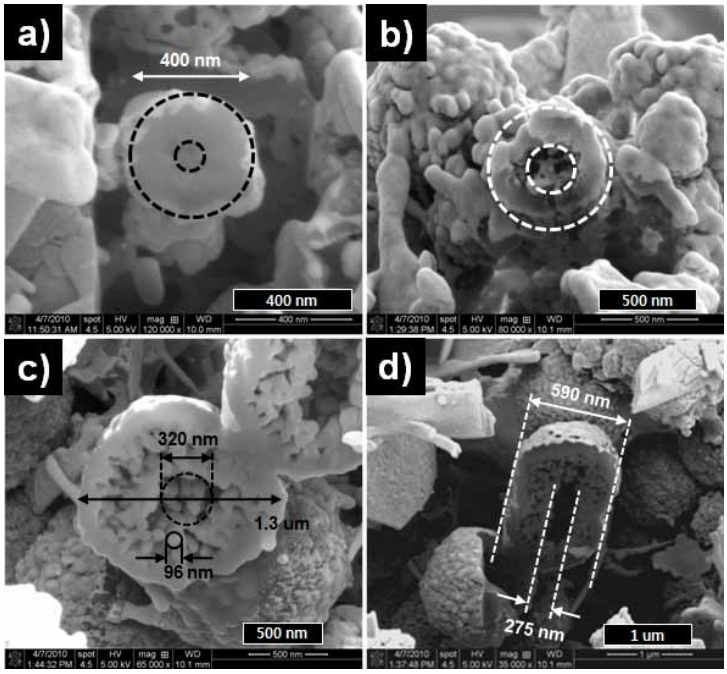
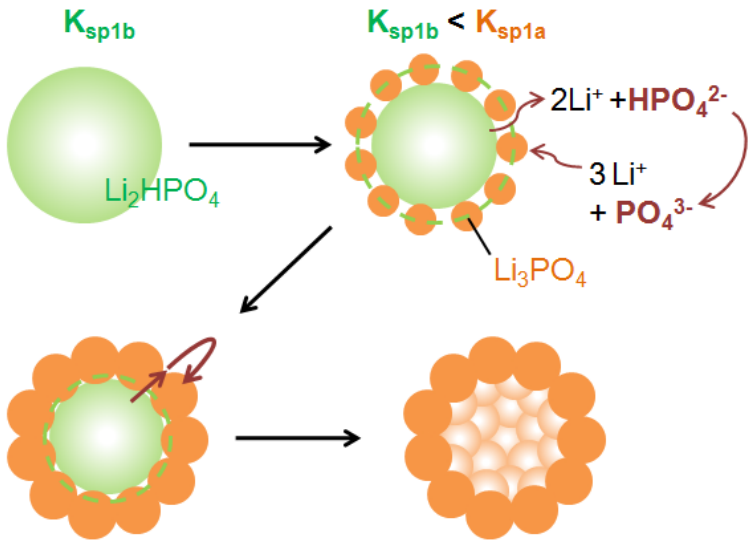


Fig. S1 Scanning electron microscopic images of cross-section of hollow $LiFePO_4$. The cross-sectioned samples were prepared by focused ion beam (FIB). The sample was partly melt due to the high energy of FIB during the sample preparation. It was difficult to obtain clear images of one layer hollow sphere that is dominantly populated (a and b) because whole volume of thin shell was melt down. A rare population of secondary particles has a structure of multi-layer hollow sphere (c and d).



Scheme S2 Formation of a hollow sphere secondary structure of Li_3PO_4 particles. The second precipitate Li_3PO_4 is formed on the first precipitate Li_2HPO_4, sacrificing the first one in presence of Li^+.

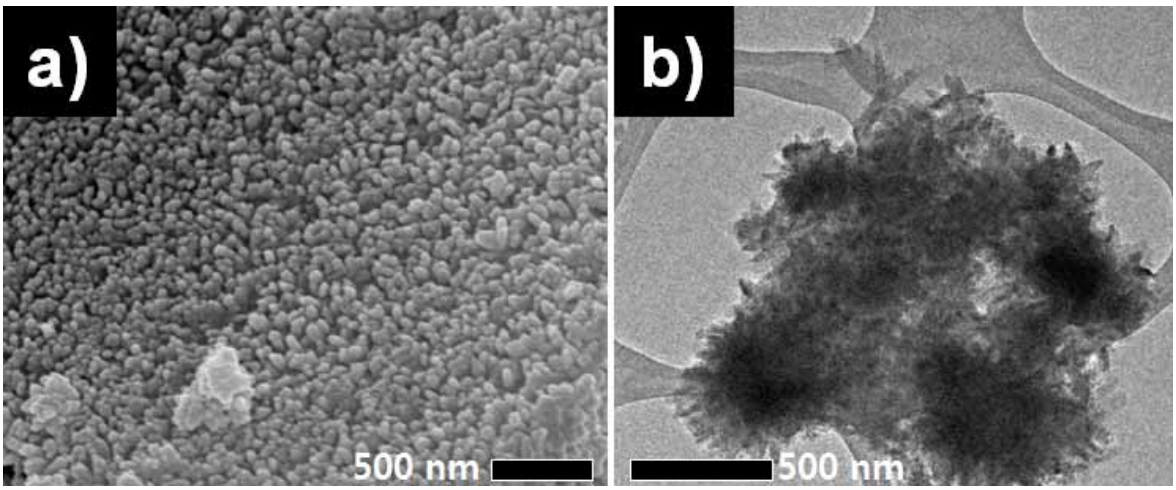


Fig. S2 Electron microscopic photos of non-hollow Li_3PO_4 obtained from high pH synthesis adjusted by NH_4OH. Only primary particles with ~50 nm dimension are observed without a secondary structure of defined geometry.

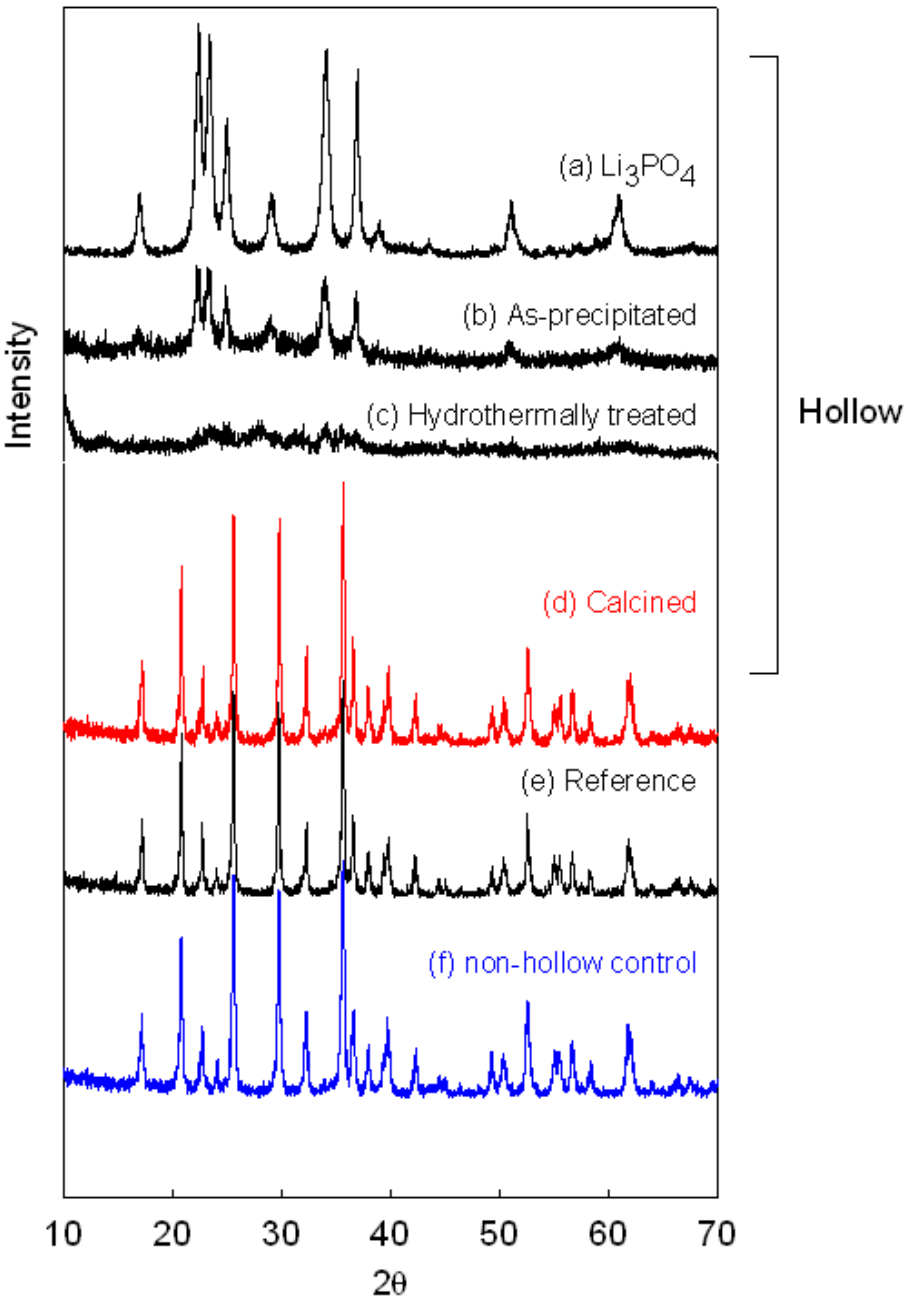


Fig. S3 X-ray diffraction (XRD) patterns of the intermediate precipitates (a and b) and the thermally treated ones (c and d) obtained through the each step of the sequential precipitation. The olivine phase $LiFePO_4$ was obtained after calcination. Also, XRD patterns of the reference (e) and non-hollow control (f) are shown for comparison.

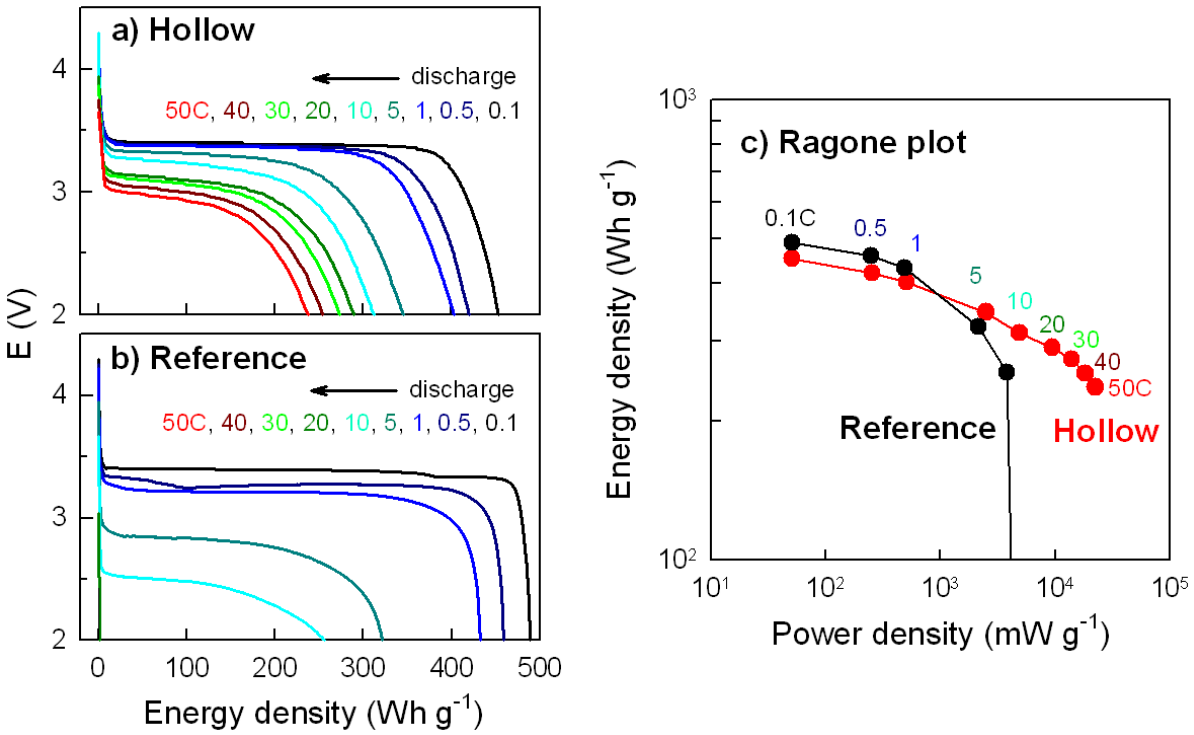


Fig. S4 (a and b) Potential profiles of half coin cells of hollow-sphere-secondary-structured (a) and non-hollow reference (b) $LiFePO_4$. This figure is exactly the same one as Figure 3a and 3b except of abscissa. Energy density is used in these plots instead of capacity (Q). From 10C, the hollow-sphere-secondary-structured $LiFePO_4$ passed the non-hollow reference $LiFePO_4$ ahead in terms of energy density. (c) Ragone plot. Only the mass of active cathode materials was considered for calculation of power and energy densities.