In Situ Hydrothermal Synthesis of LiFePO$_4$ Studied by Synchrotron X-ray Diffraction

Supporting information

Experimental

In situ XRD measurements were conducted at beamline X14A at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The x-ray beam was focused by a sagittal focusing-monochromator with a slit-limited beam size of 0.5 mm (vertical) x 1.0 mm (horizontal). The wavelength was tuned to 0.7748 Å. A Silicon Strip detector with 640 elements was mounted on the two-theta arm of a 6-circle Huber diffractometer and positioned ~1400 mm from the sample. The angular resolution of the detector was 0.005 degrees. The XRD patterns were taken by scanning the two-theta arm at 2 degrees per step. Each scan took about 4 minutes with a two-theta angular range of 8° to 27.4°.

The sample slurry was placed in the flame-sealed end of a quartz tube (~ 0.7 mm ID) and filled ~2mm of the tube. A small plug of quartz wool was inserted into the tube's end to keep the slurry in place. The quartz tube then was filled with deionized water, and connected to one end of a 1/16" Swagelok elbow at ambient pressure. More water was added to the elbow via its open end to minimize the amount of air trapped in the assembly. The open end was then sealed with a Swagelok cap. The reactor was uniformly heated using an air gun heater and the temperature was monitored with a K-type thermocouple attached to the exit of the air gun and manually controlled by a Variac ^{TM} autotransformer in a stepwise manner. Before the *in situ* XRD measurements were made, the temperature was calibrated by inserting a thermocouple place into the quartz tube at the sample position. Since there are no wire or gas lines attached to the closed reaction assembly, the sample was continuously rotated during the XRD measurements, which helps in reducing any preferred orientation effects and in assuring homogenization of the

reacting sample mixture. Rietveld refinements of the X-ray powder diffraction patterns were carried out using the GSAS/EXPGUI package. The in-situ hydrothermal data were refined over the range of 8° – 27.4° 2θ with a Chebyshev polynomial function, and 24 coefficients for the background. The final product, cooled to room temperature, was refined over the range of 8° – 40° 2θ with a Chebyshev polynomial function and 24 coefficients for the background. Lattice parameters were determined by TOPAS and Jana 2006; and most showed excellent agreement with those from the Rietveld refinement using the GSAS/EXPGUI package.

$LiFePO_4$ synthesis was performed using a procedure from an earlier publication.[1]

0.695g $FeSO_4 \cdot 7H_2O$ (98% Fisher), ~2.5ml 1M H_3PO_4 diluted from (85 wt.% solution Fisher), and 0.043 g L-ascorbic acid (99% Aldrich) were dissolved in 10 ml deionized water. 0.315 g $LiOH \cdot H_2O$ (98% Aldrich) was then slowly added into the mixture, while constantly stirring it. The molar ratio of the Li:Fe:P was 3:1:1. The pH value measured by PHTestr (Oaklon) was about 6.8. The resulting greenish slurry was immediately injected into the quartz capillary tube. The sample tube was then heated from room temperature to the desired temperature, or held at that temperature for a prescribed period.

Rietveld refinement Fitting Procedure

We performed full Rietveld refinement analyses, including atomic positions, cation distributions in the olivine structure, and isotropic atomic displacement using the GSAS/EXPGUI software. The initial mode of the crystal structure is adopted from Streltsov, V. A.; Belokoneva, E. L.; Tsirelson, V. G.; Hansen, N. K., Multipole Analysis of The Electron-Density in Triphylite, LiFePO4, Using X-Ray-Diffraction Data. Acta Crystallographica Section B-Structural Science 1993, 49, 147-153. The refinement was as follows: First, the background and scale factor parameter were determined. The scale factor was refined and 20 background coefficients were used for a Chebyshev polynomial function. Subsequent steps included the Refine Zero parameter, unit cell dimensions, and grain size parameters (X). After the initial refinement was stable (after several cycles), the other relevant parameters were released. First the atomic positions (coordinates) for the heavy atoms (Fe atom) were released and then slowly the light

atoms (oxygen atom) were released. In the following refinement, atomic displacement parameters (Uiso) were released slowly in reverse order of atomic number. For oxygen atoms, the Uiso were grouped together for better accuracy due to the low scattering factor for the oxygen atoms. Finally the site occupancy factors were refined together along with atomic position and the Uiso parameter.

Two crystallographic models are most likely for cation disorder in these samples, a lithium-iron mixing model ($Li_{1-y}Fe_y[Li_yFe_{1-y}]PO_4$) and an iron-rich model ($Li_{1-2y}Fe_yFePO_4$). Previous single crystal studies have shown that the iron-rich model shows the best structural solution for hydrothermally prepared lithium iron phosphate[3]. Similar results were obtained for hydrothermally prepared manganese phosphate[4]. We performed refinements using both models and found the best fits with the iron rich system consistent with ICP-OES results and this model (iron rich) was used for the refinements of site occupancy and to investigate the cation distribution. The Fe (M2) 4c site occupancy was restricted to unity. Several trial refinements were carried out with the shared lithium site (4a) occupancy initially set to different values (i.e 0.95, 0.9) to ensure the consistency of each refinement. The refinements consistently refined to a similar value, suggesting the results are reliable.

Table S1

Refined structural parameters for in-situ hydrothermal synthesis of $LiFePO_4$ at 155°C (without temperature soak) obtained from the Rietveld refinement. The numbers in parentheses are the estimated standard deviations.

Atom	x/a	y/b	z/c	Uiso	Occup.
Li1	0.0000	0.0000	0.0000	0.0313	0.949(4)
Fe1	0.28008(27)	0.25000	0.9723(9)	0.00974	1.00
Fe2	0.0000	0.0000	0.0000	0.0313	0.051(4)
P1	0.0942(6)	0.2500	0.4119(17)	0.01333	1.00
O1	0.1007(12)	0.2500	0.7410(25)	0.02299	1.00
O2	0.4444(19)	0.2500	0.2034(17)	0.02299	1.00
O3	0.1677(11)	0.0380(15)	0.2779(14)	0.02299	1.00

Space group : *Pnma* (No. 62) and $Z = 4$

$a = 10.3632(5)$ Å, $b = 6.0030(3)$ Å, $c = 4.7147(2)$ Å, cell volume = $293.30(4)$ Å^3

$\alpha = \beta = \gamma = 90°$ Rwp = 1.37% and Rp = 1.03%

Table S2
Refined structural parameters for in-situ hydrothermal synthesis of LiFePO$_4$ at 178°C (without temperature soak) is $a = 10.3515(3)$ Å, $b = 6.0119(2)$ Å, $c = 4.7060(1)$ Å, cell volume = $292.87(2)$ Å^3. Rwp=1.66% and Rp=1.32%.

Atom	x/a	y/b	z/c	Uiso	Occup.
Li1	0.0000	0.0000	0.0000	0.0363	0.992(3)
Fe1	0.28114(17)	0.25000	0.9721(5)	0.00994	1.00
Fe2	0.0000	0.0000	0.0000	0.0363	0.008(3)
P1	0.0936(4)	0.2500	0.4083(11)	0.01354	1.00
O1	0.0987(8)	0.2500	0.7350(16)	0.0235	1.00
O2	0.4404(11)	0.2500	0.2053(12)	0.0235	1.00
O3	0.1649(6)	0.0440(10)	0.2815(9)	0.0235	1.00

1. Chen, J. J.; Whittingham, M. S., *Electrochemistry Communications* **2006,** *8* (5), 855-858.
2. Chen, J.; Wang, S.; Whittingham, M. S., *Journal of Power Sources* **2007,** *174* (2), 442-448.
3. Chen, J. J.; Vacchio, M. J.; Wang, S. J.; Chernova, N.; Zavalij, P. Y.; Whittingham, M. S., *Solid State Ionics* **2008,** *178* (31-32), 1676-1693.
4. Fang, H. S.; Pan, Z. Y.; Li, L. P.; Yang, Y.; Yan, G. F.; Li, G. S.; Wei, S. Q., *Electrochemistry Communications* **2008,** *10* (7), 1071-1073.
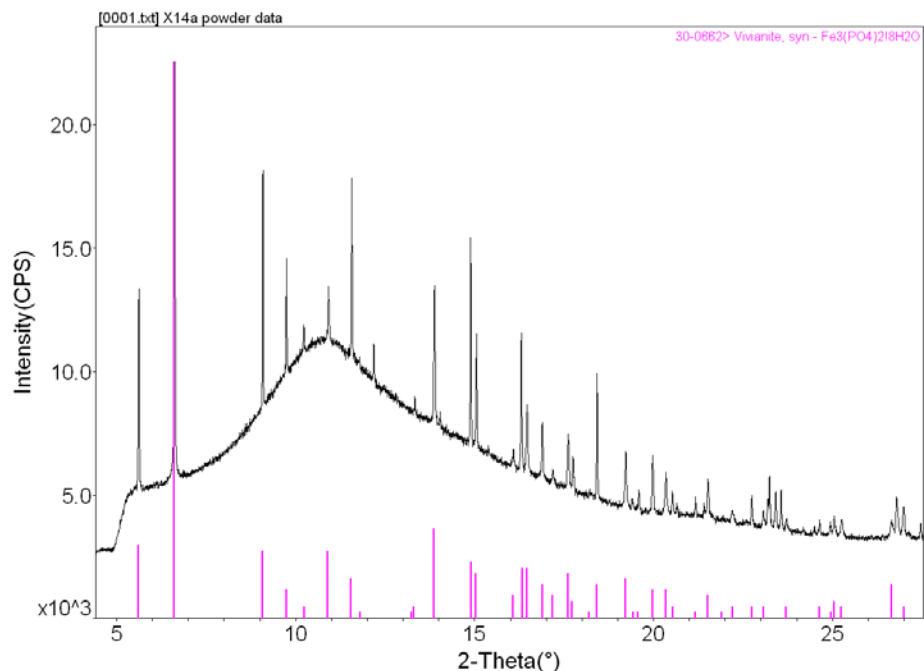
Figure S1. Synchrotron X-ray diffraction pattern of precursor $Fe_3(PO_4)_2 \cdot 8H_2O$ at room temperature.

Red: T = 105°C
Blue: T = 115°C

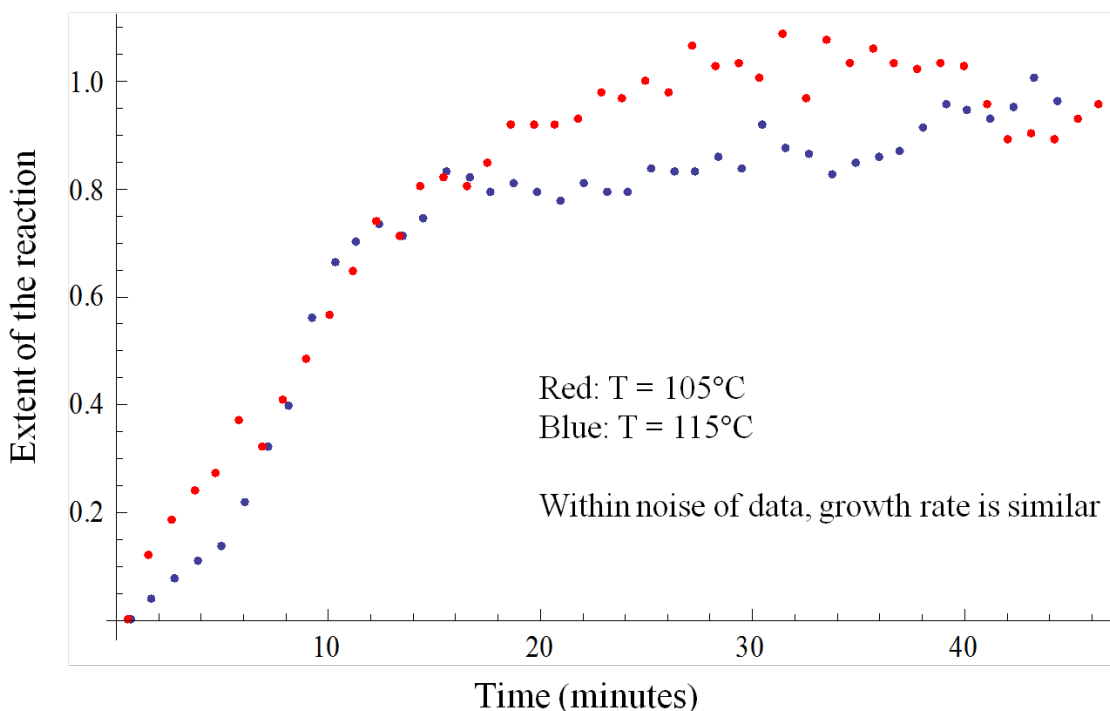Within noise of data, growth rate is similar

Figure S2. Comparison of crystallization curve for $LiFePO_4$ formed at 115°C and 105°C after correcting for small changes in the incubation time (time of first detection of crystalline product). The dots represent the integrated intensity of the (2 0 0) Bragg reflection.
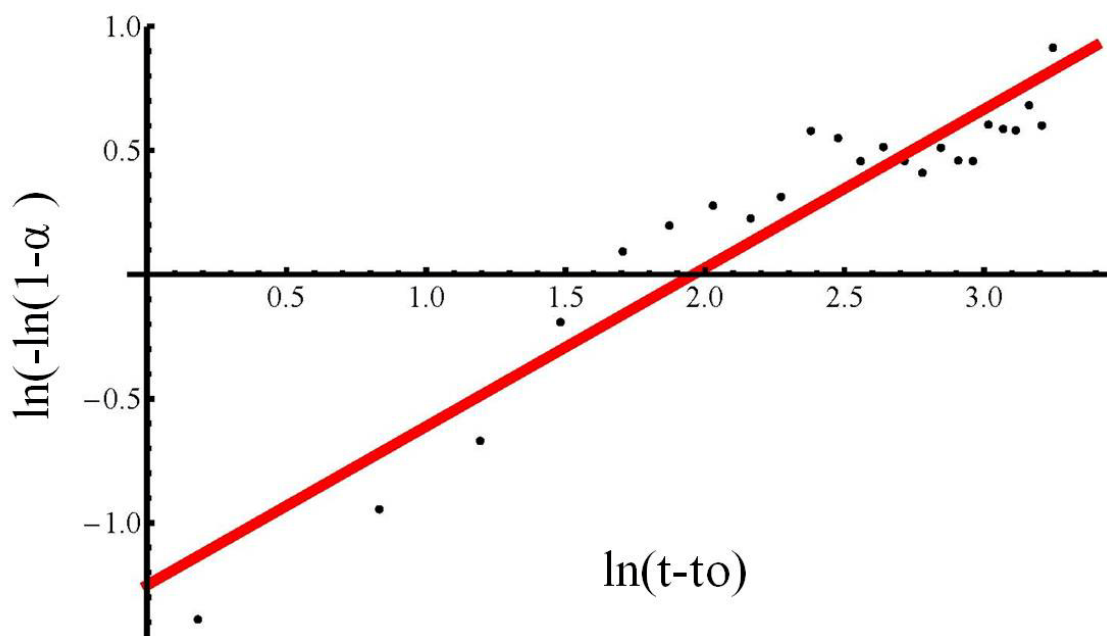
Figure S3. Sharp-Hancock plot for the formation of LiFePO$_4$ at 115°C
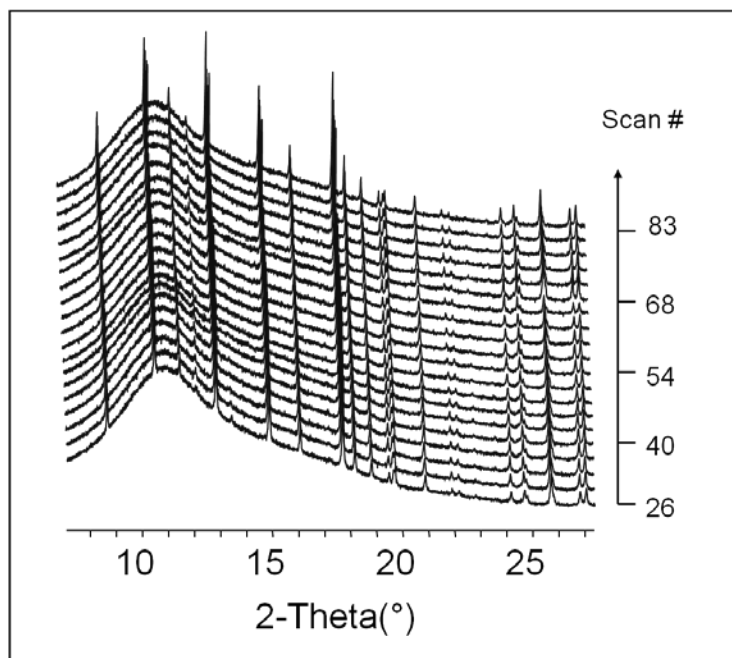
Figure S4. Time-resolved XRD patterns from the *in-situ* hydrothermal synthesis of LiFePO$_4$ heated from 160°C to 210°C.
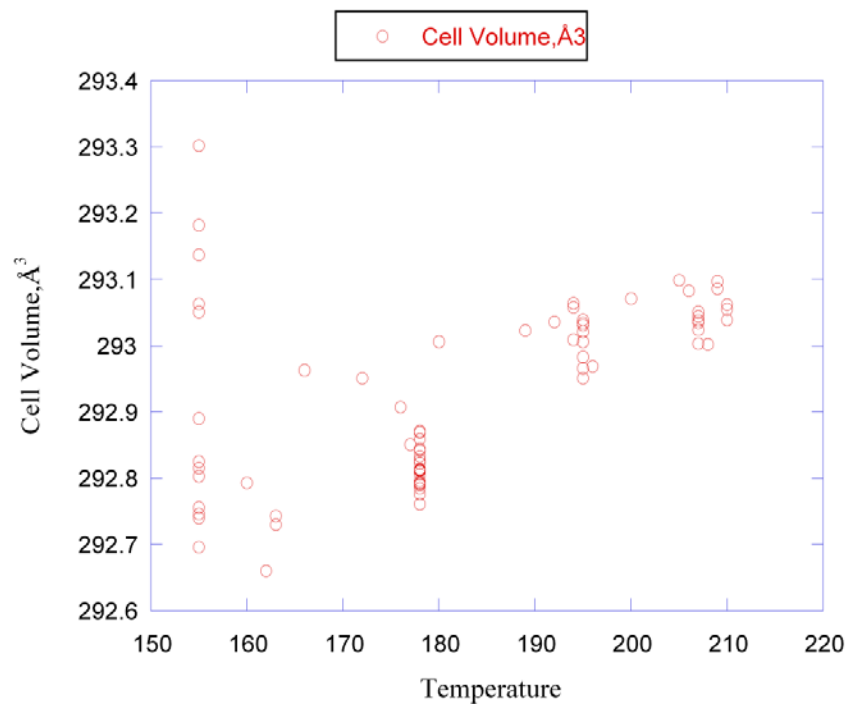
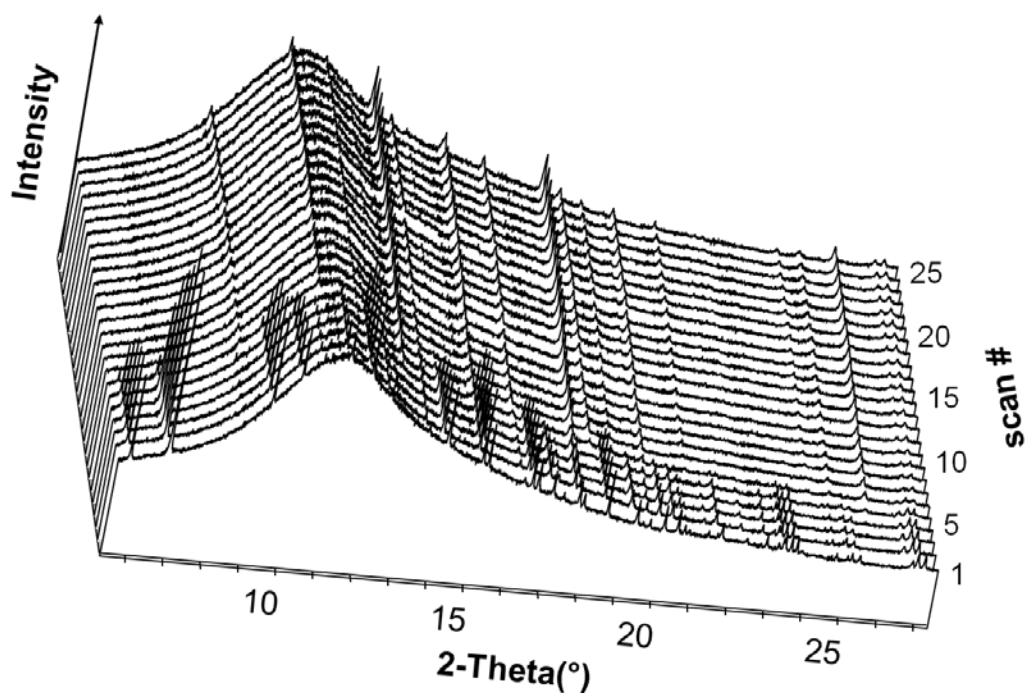**Figure S5.** The unit cell volume as a function of temperature from 155°C to 210°C.

Figure S6. Time-resolved XRD patterns from the *in-situ* hydrothermal synthesis of LiFePO$_4$ heated from room temperature 35°C to125°C and holding at 125°C for about 90 mins. XRD patterns were collected continuously with about 4 min/pattern x-ray wavelength λ=0.7748 Å, beamline X14A, NSLS, BNL).
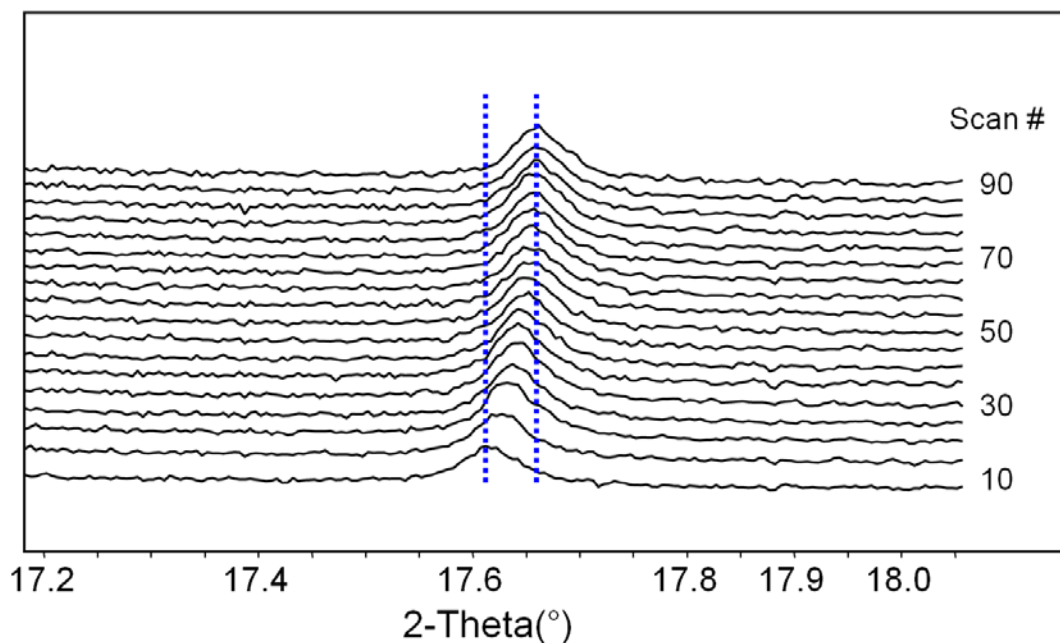
Figure S7. XRD patterns of *in-situ* hydrothermal synthesis of LiFePO$_4$ at 125°C and holding about 320 minutes, showing magnified (311) reflection at 2θ = 17.6.

Samples of the reaction product were collected at various stages of the reaction for *ex situ* electron microscopy characterization. Preliminary studies have shown interesting morphological evolution of the olivines (Figure S8). Vivianite, Fe$_3$(PO$_4$)$_2$•8H$_2$O, exhibits a heterogeneous mixture of cylindirical and prismatic (triangular or hexagonal) platelets. After transformation to LiFePO$_4$, thicker, diamond-shaped platelets appear to be common. It is interesting to note that the kinetics, determined from the crystallization curves, suggest 3D diffusion as the rate limiting step and yet the particles appear to have a platelet, or 2D morphology (Figure S8b). In this case the 3D diffusion that limits the reaction is occurring in the solution surrounding the particles. Since the particles are much smaller compared to the amount of solution around them the morphology of the particle does not play much of a role in determining growth kinetics.
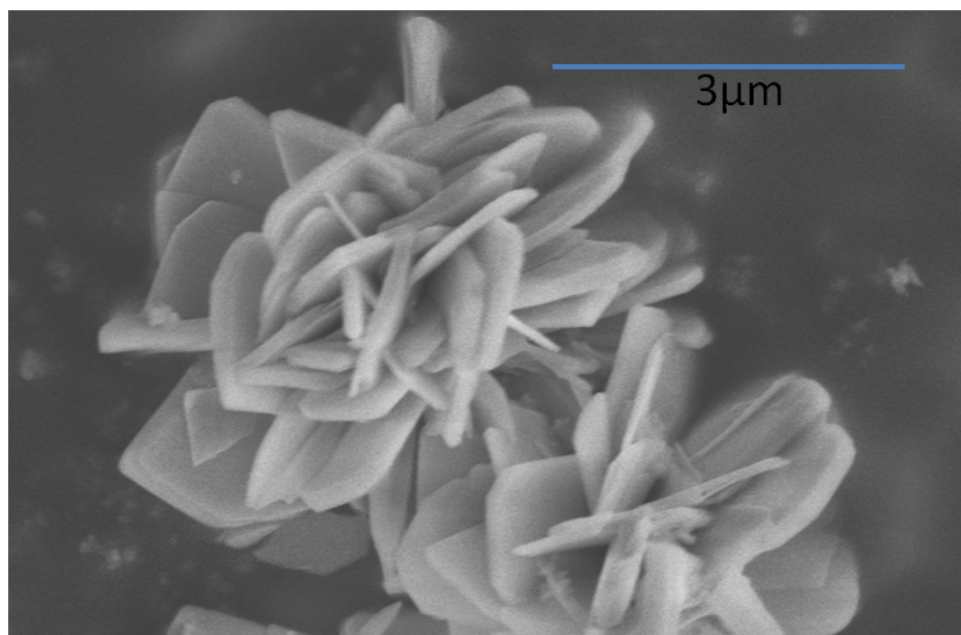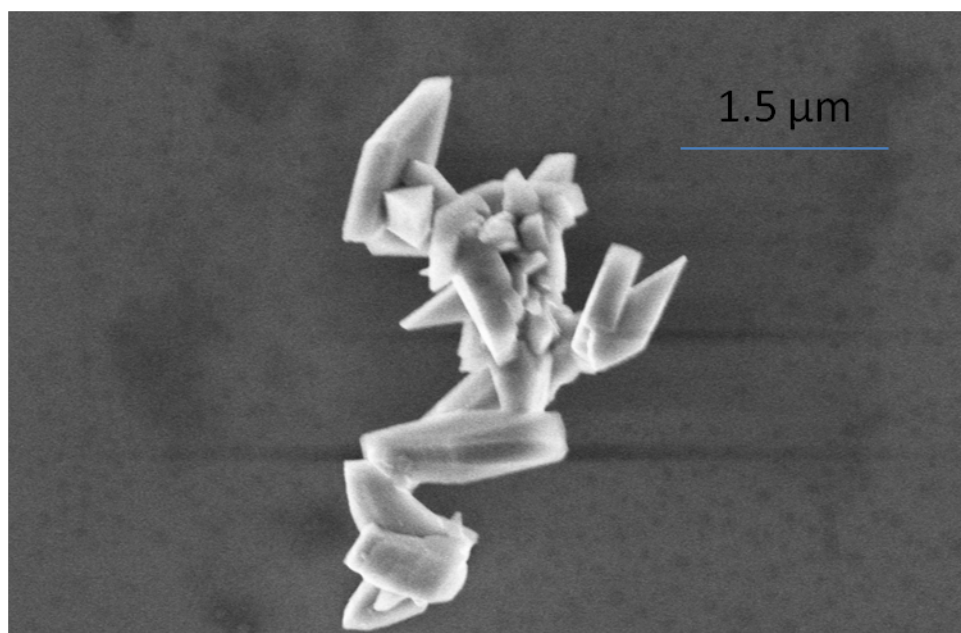
Figure S8(a). SEM images of precursor vivianite $Fe_3(PO_4)_2 \cdot 8H_2O$.

(b) SEM images of in situ hydrothermally synthesized $LiFePO_4$ at 125°C for 6 hours.