Electronic Supplementary Information (ESI) for

Hydrothermally synthesized $LiFePO_4$ crystals with enhanced electrochemical properties: simultaneous suppression of crystal growth along [010] and antisite defect formation

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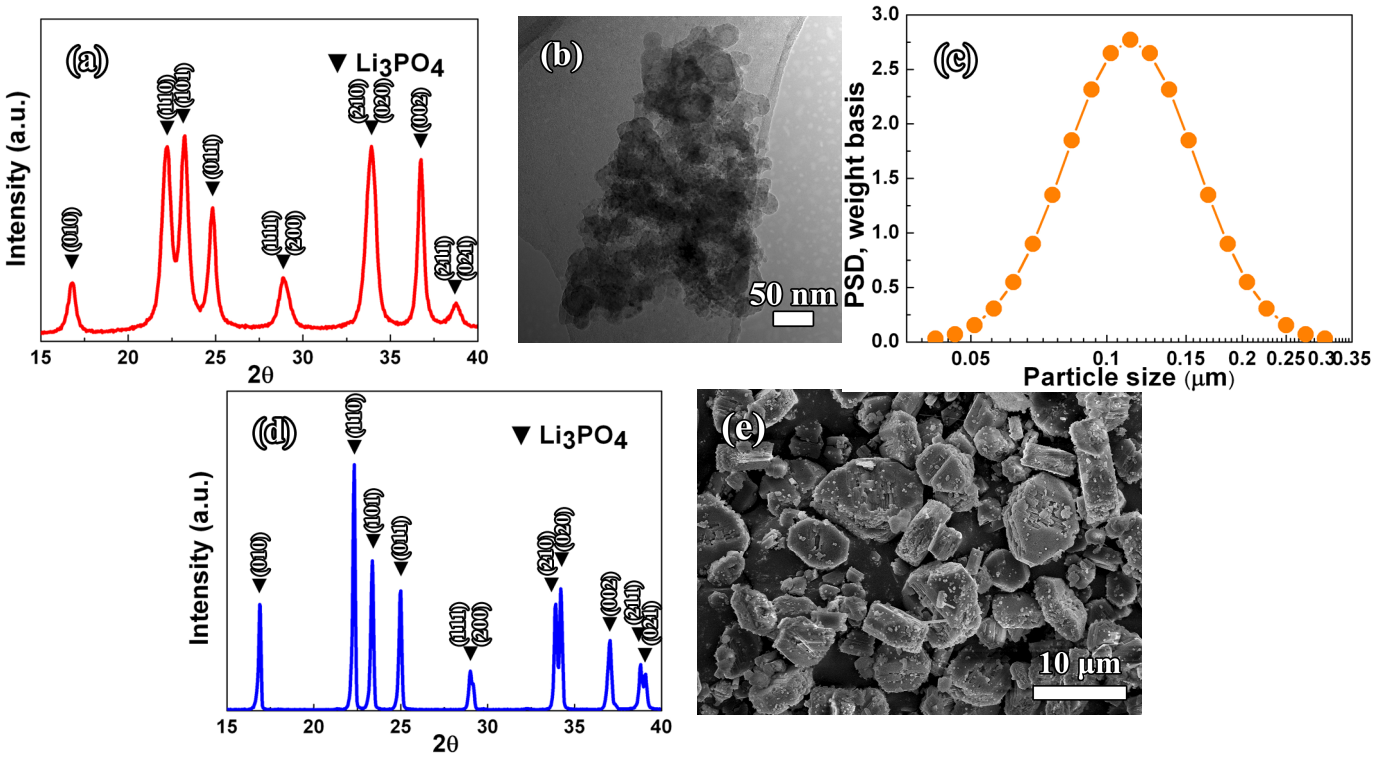


Fig. S1. Characterization of nanosized Li_3PO_4 obtained by slow addition of H_3PO_4 into LiOH solution. (a) XRD pattern and (b) TEM image of Li_3PO_4 before hydrothermal treatment, showing that the formed Li_3PO_4 consists of shapeless nano-particles. (c) PSD profile, illustrating smaller particle size and good particle size homogeneity. (d) XRD pattern and (e) SEM image of Li_3PO_4 particles after hydrothermal treatment at 180 °C for 3 h.

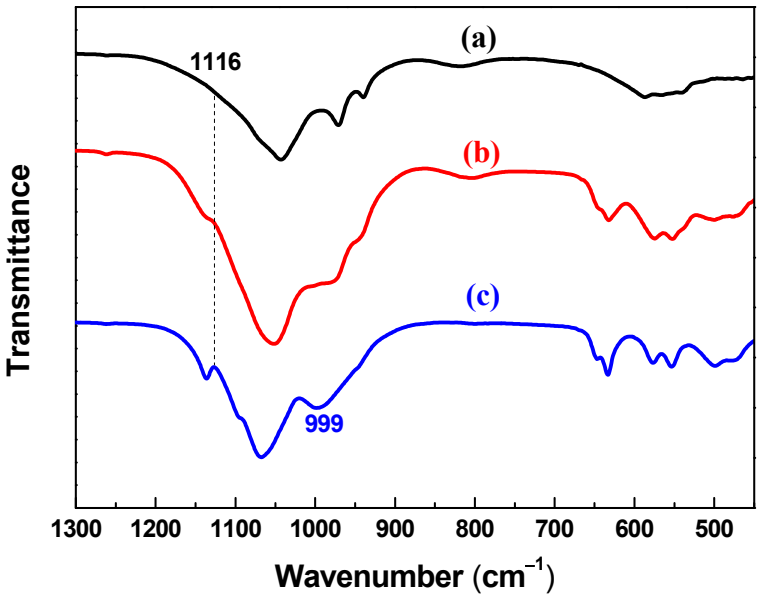


Fig. S2. FTIR spectra of the NP hydrothermally treated up to (a) 135, (b) 140 and (c) 145 °C without holding time, showing the absence of complex composites like tetraphosphate in the NP.

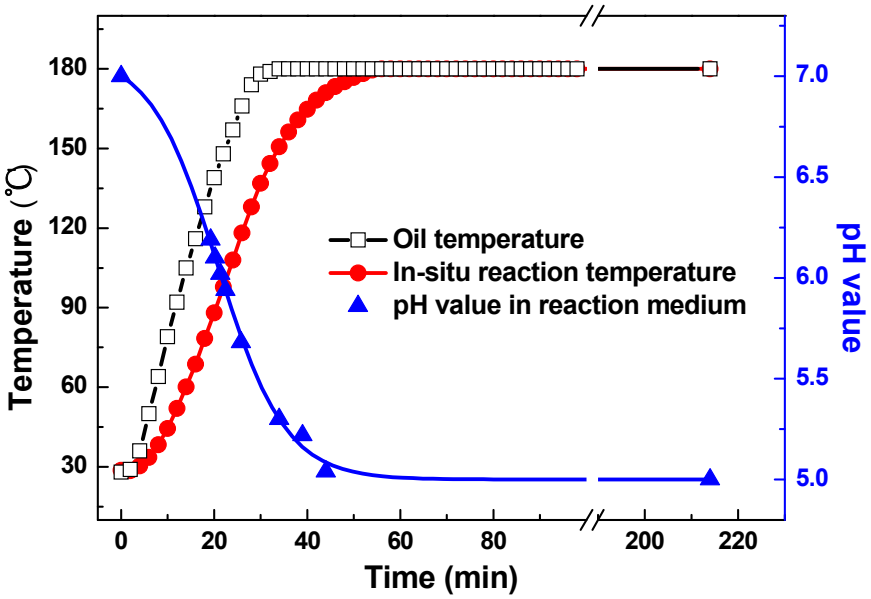


Fig. S3. Evolution of pH values in supernatant. The pH drop is mainly contributed to the decomposition of ascorbic acid and increased amount of Li_2SO_4 as the reaction proceeded.

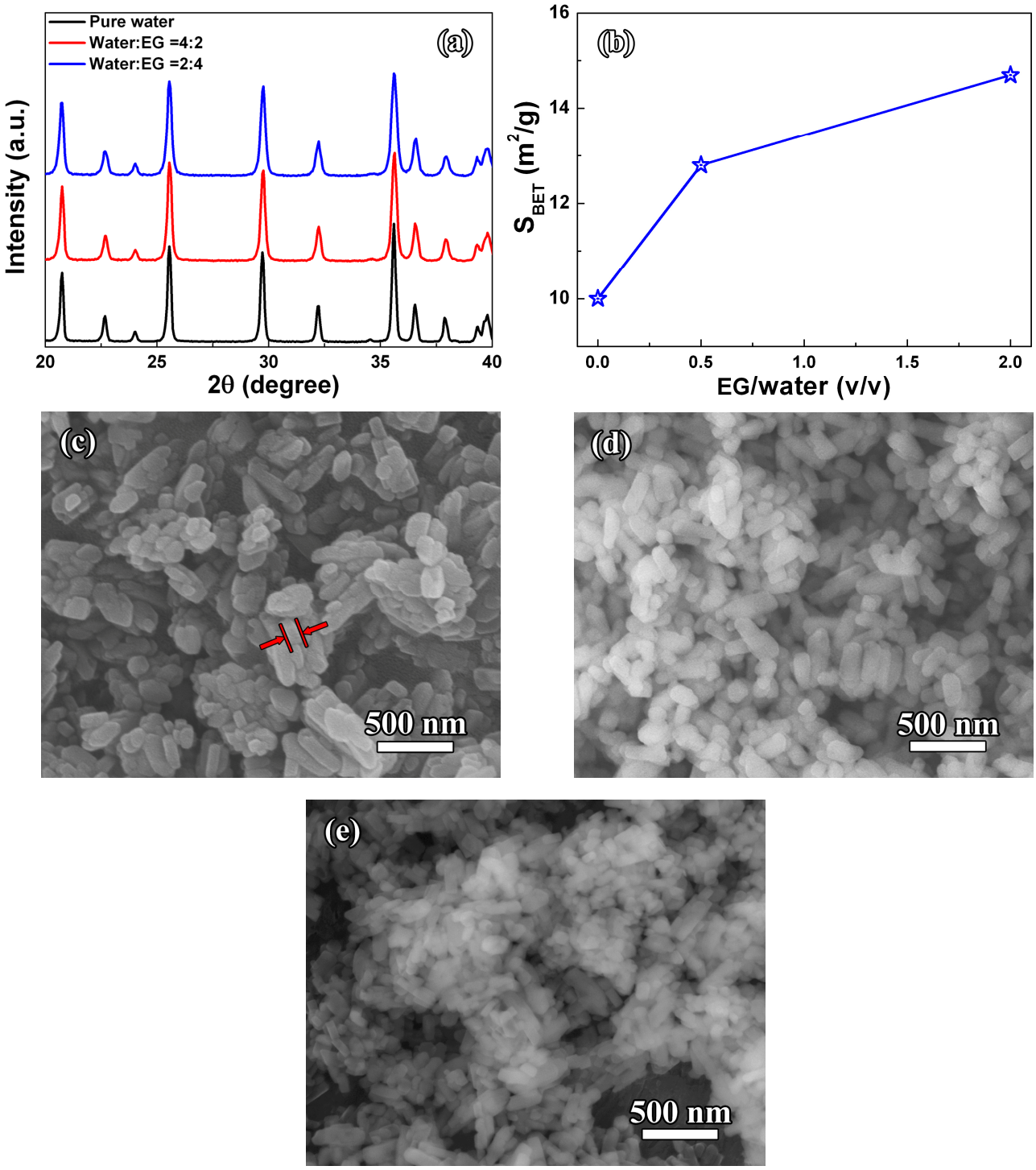


Fig. S4. (a) XRD patterns of $LiFePO_4$ powders synthesized hydrothermally without EG and with indicated EG contents. (b) dependence of S_{BET} on EG contents. SEM images of $LiFePO_4$ powders synthesized (c) in pure water, (d) with water:EG=4:2, and (e) water:EG=2:4 .

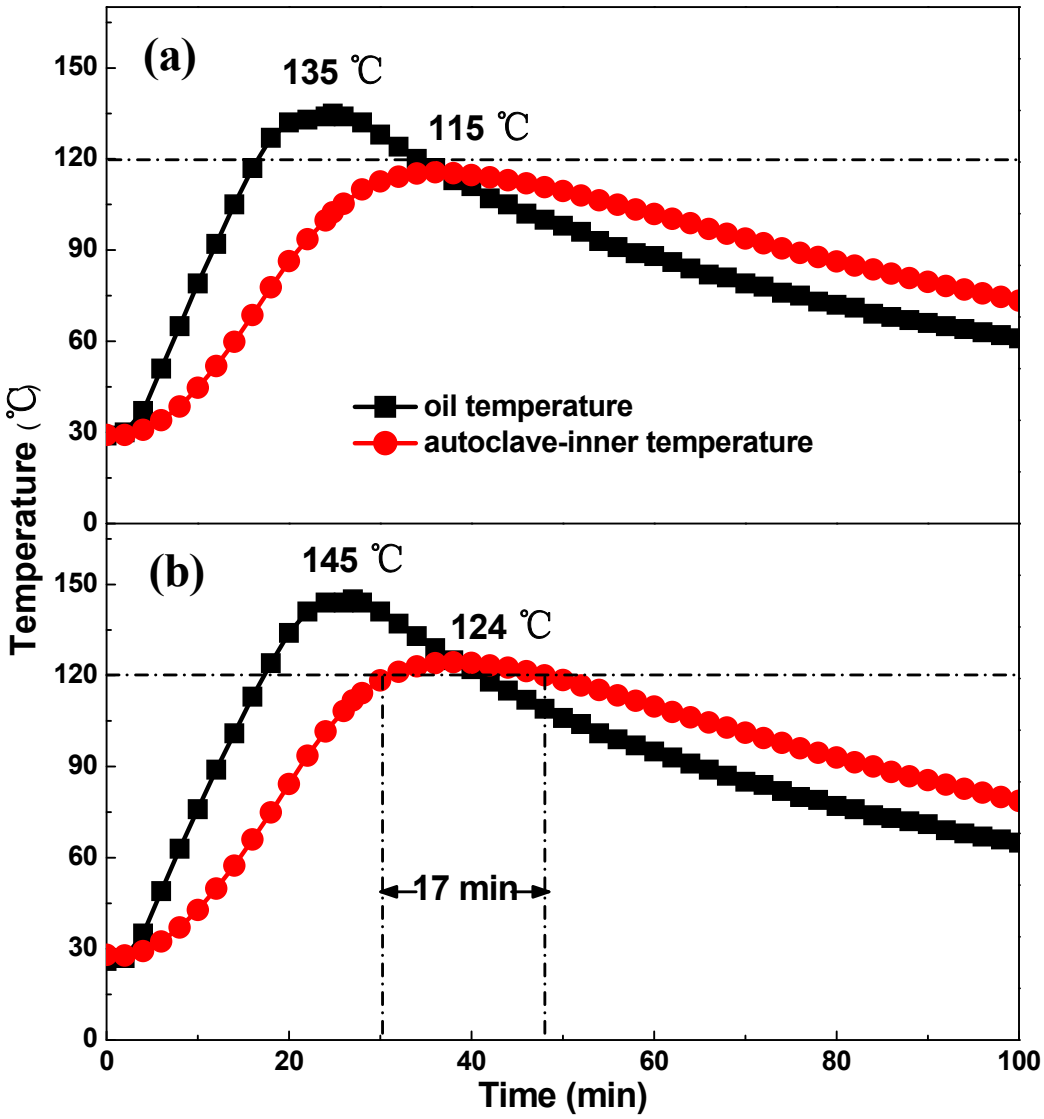


Fig. S5. Comparisons of *in-situ* reaction and oil temperatures against time. Hydrothermally treated up to (a) 135, and (b) 145 °C without holding time. In combination of *in-situ* temperature and XRD phase analysis (Fig. 1a), an ultrafast formation rate for $LiFePO_4$ hydrothermally synthesized by using NP, is identified.

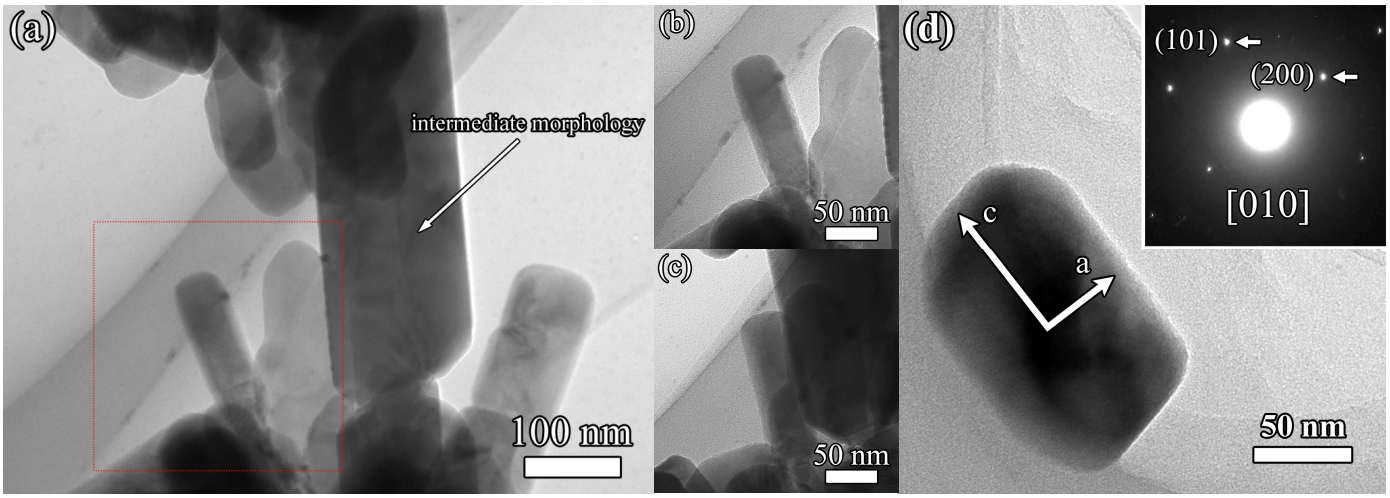


Fig. S6. TEM images. (a) $LiFePO_4$ crystals synthesized hydrothermally by using NP at 180 °C for 3 h. (b) morphology of the boxed region in (a) before tilting and (c) after tilting 27°, demonstrating typical rod morphology. (d) TEM image of rod-like particle with corresponding crystal growth orientation. Inset shows corresponding SAED pattern with incident beam along the [010] direction.

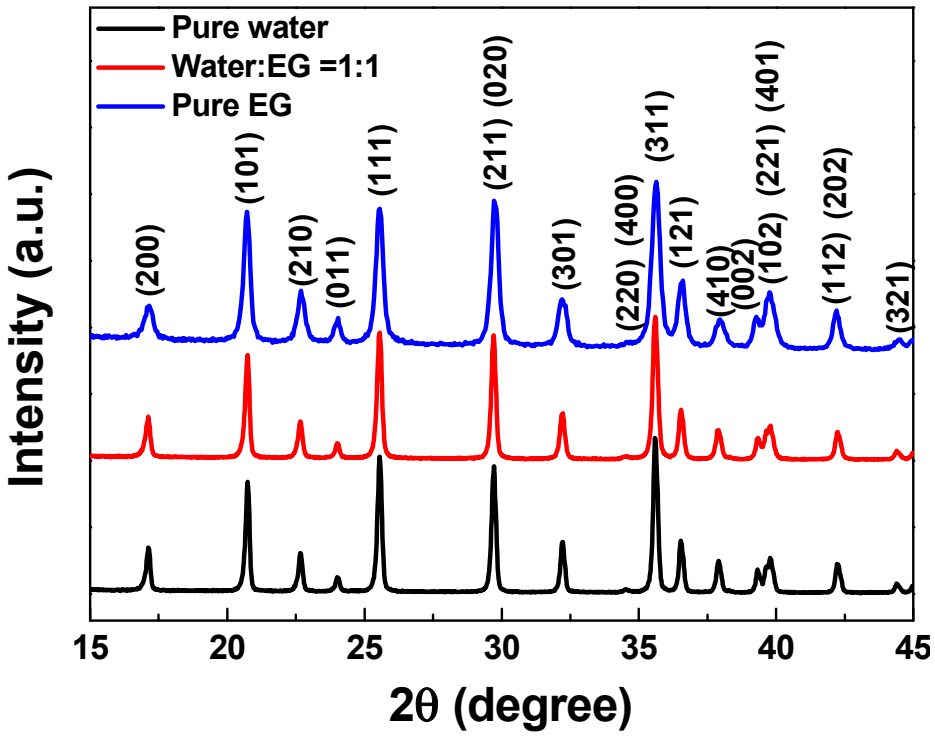


Fig. S7. Powder XRD patterns of $LiFePO_4$ prepared in different volume ratios of water to EG.

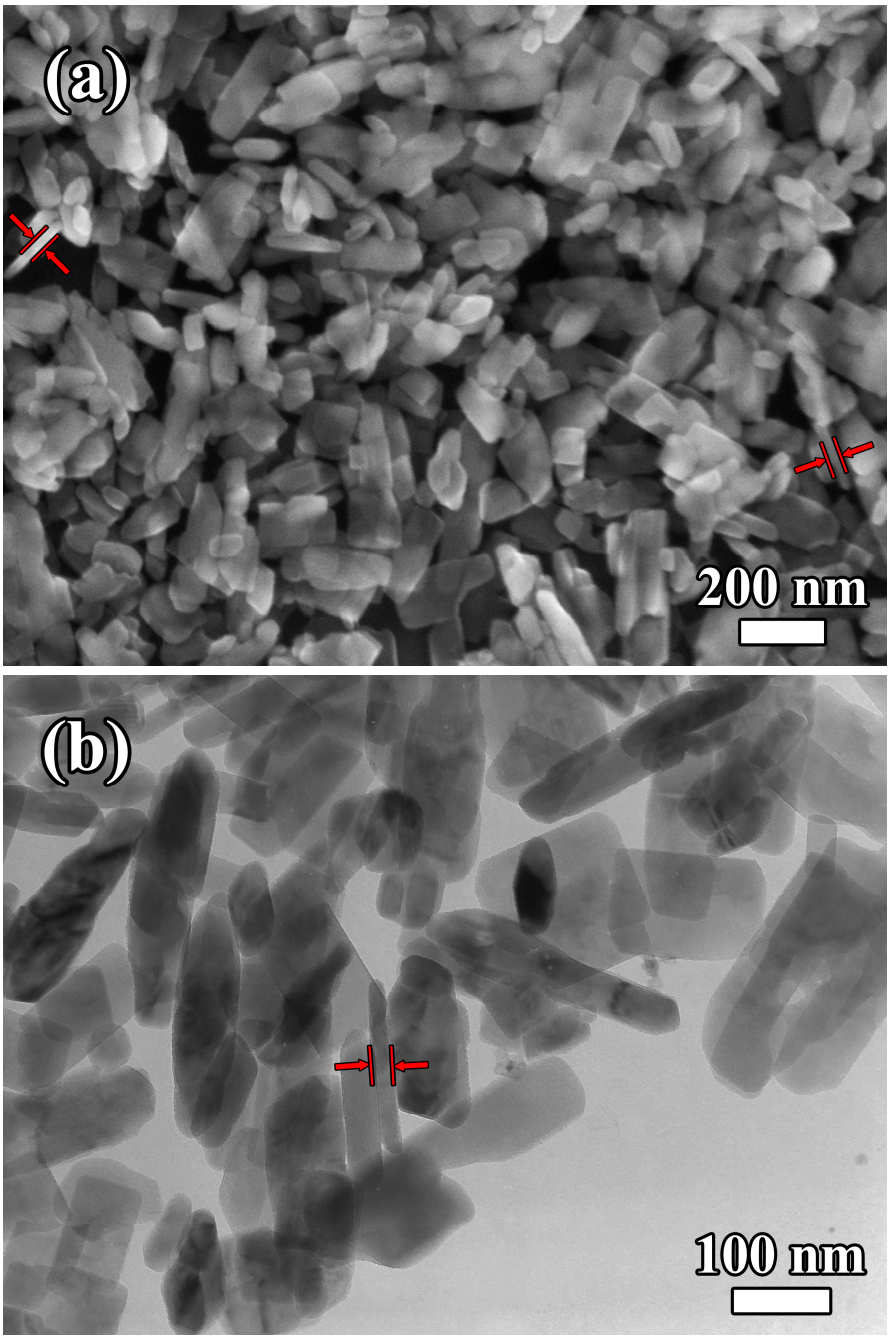


Fig. S8. Typical (a) SEM and (b) TEM images of $LiFePO_4$ particles synthesized hydrothermally in water/EG (1:1; v/v) system show a few vertical $LiFePO_4$ particles. In comparison with non-EG-mediated sample with thickness of ~80 nm along [010] crystallographic direction as displayed in Fig. S4c, it shows thinner thickness of ~38 nm and higher S_{BET} value of 17.0 m^2 g^{-1}.

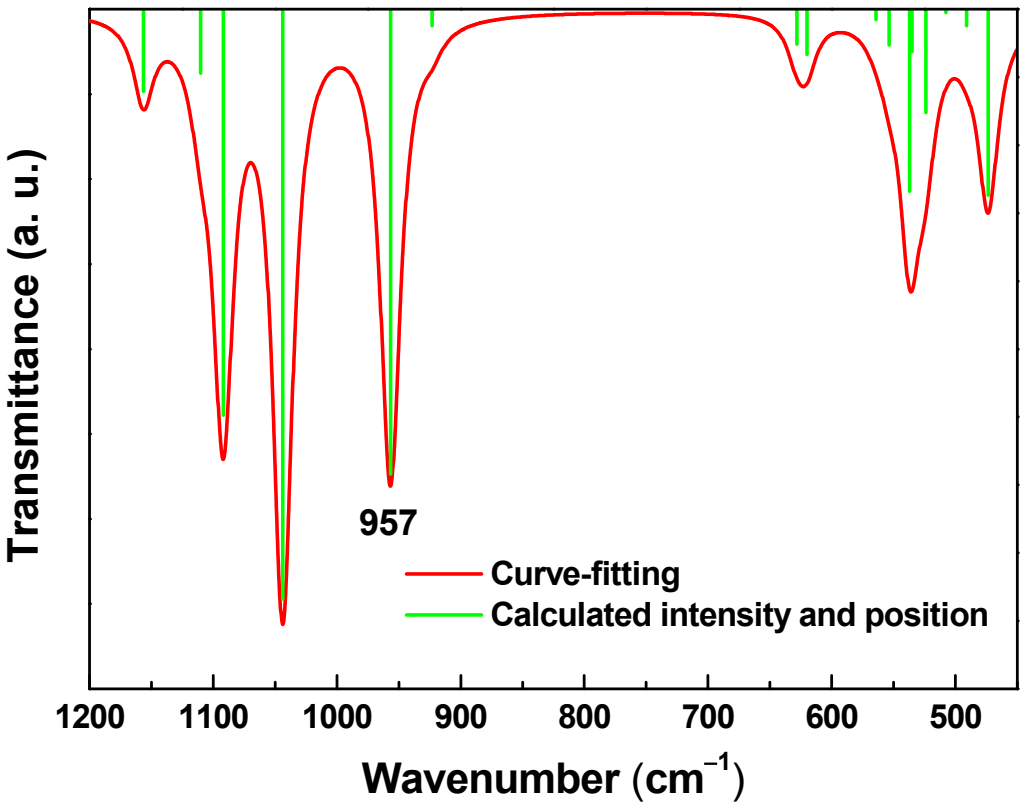


Fig. S9. Calculated FTIR spectrum of defect-free $LiFePO_4$ using computational simulation technology. The IR vibration modes were obtained from first-principles electronic structure methods based on density functional perturbation theory (DFPT) [1] by using the CASTEP code [2]. The Hellmann-Feynman forces constant matrix was calculated by coupling a standard density functional theory (DFT) with linear response phonon model. The IR intensities were given by the change in electric dipole moment of the system with respect to the atomic motion under excitation of a phonon mode. In the present calculations, the electron-ion interactions were represented by the norm-conserving potentials generated using the kinetic energy optimization scheme developed by Lin *et al.* [3], and Lee [4]. The electronic exchange correlation energy was treated as the generalized gradient approximation (GGA PBE) [5]. The plane wave basis set cut off was 990 eV. The special k-point sampling integration was used over the Brillouin zone by using the Monkhorst-Pack method with 3×4×5 mesh [6].

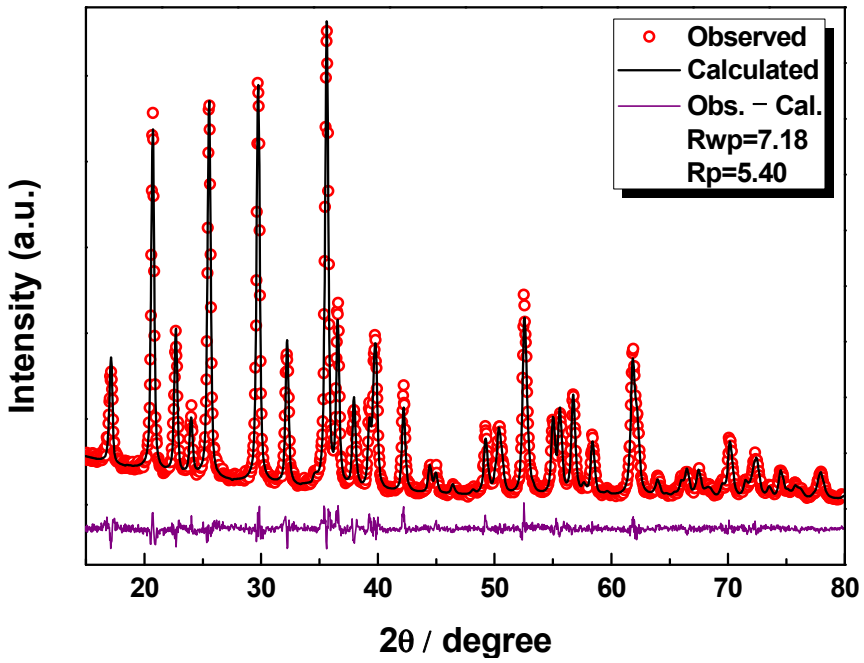


Fig. S10. Rietveld refinement of sample synthesized at 180 °C for 3 h in pure EG reaction system. The result indicates a phase-pure $LiFePO_4$. The observed intensity data are shown by red rings, and the black solid line overlying them is the intensity calculated using RIETAN-2000 software. Differences between observed and calculated intensities are plotted by purple solid line. The Rietveld analysis show that lattice constants of olivine structure are a=10.3005±0.0016 Å; b=5.9895±0.0009 Å; c=4.695±0.0007 Å; V=289.6±0.0738 $Å^3$, respectively. The model considers [010] preferred-orientation as a result of the very thin crystal thickness along [010] crystallographic direction.

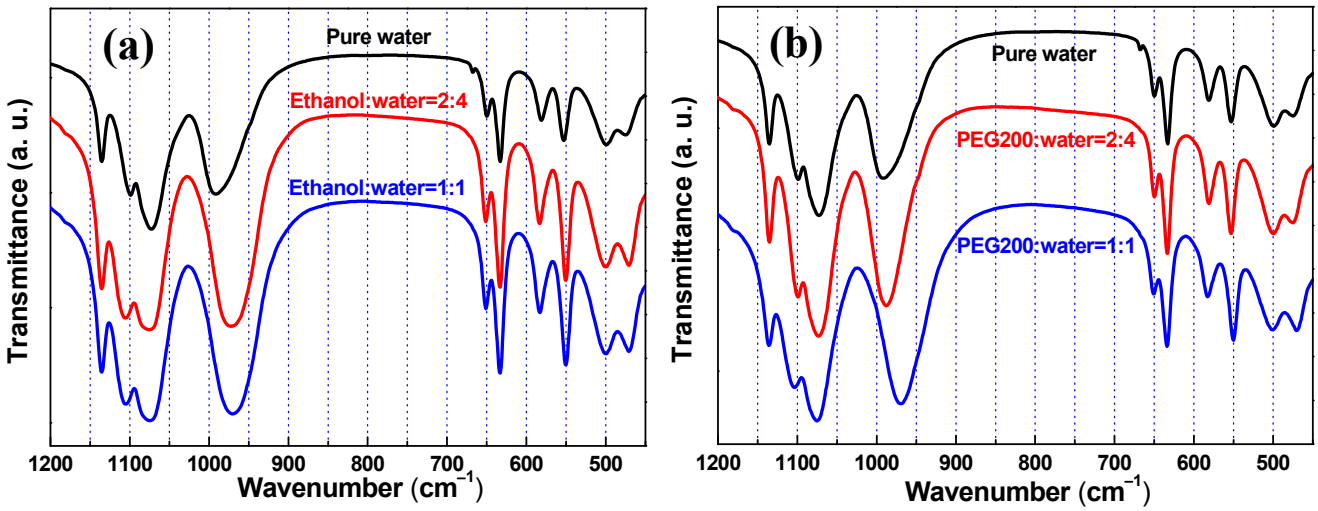
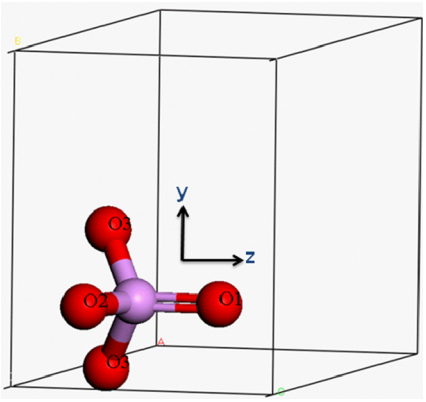


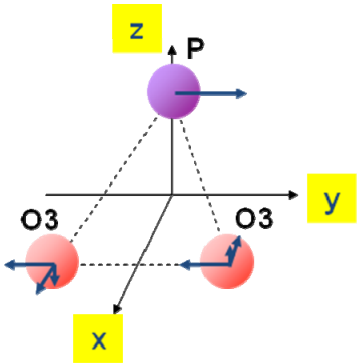
Fig. S11. FTIR spectra of $LiFePO_4$ prepared by introducing various amounts of (a) ethanol (b) polyethylene-glycol(200) (PEG200).

Table S1. Calculated atomic vibrations and force constants in phosphate group along different direction while a few Li sites were occupied by divalent Fe ions.

Atom	P	O1	O2	O3	O3
Δx	0	0	0	0.126	-0.126
Δy	0.315	-0.006	-0.003	-0.223	-0.223
Δz	0	0	0	-0.095	0.095



	x	y	z
Perfect crystal	51.2	45.5	64.0
$Fe_{Li}^{\bullet}$ antisite defects	48.0	53.0	64.5



Compared with almost unvibrated O1 and O2, the calculated results suggest that the obvious vibrations of atom P and O3 along different direction occur when the $Fe_{Li}^{\bullet}$ antisite defects form. Therefore, we further calculate the force constants of P and O3 along different directions. The force constants were calculated by the finite displacement method. When given a small nonequivalent displacement on an atom along the specific direction, the atomic Hellmann-Feynman forces was obtained by VASP [7, 8], which is a density functional theory (DFT) total energy calculation code. The employed 1×2×2 supercell contains 112 atoms. A 2×2×3 *k*-point mesh and 550 eV energy cutoff were used when calculating the Hellmann-Feynman forces in the supercell. The electron-ion interactions were represented by the projector augmented wave (PAW) method [9]. The electronic exchange-correlation energy was treated as the generalized gradient approximation (GGA PBE) [5]. Considering y direction is dominating vibration direction, we believe that the force constants of phosphate group increase when the $Fe_{Li}^{\bullet}$ antisite defects form.

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