Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information for

Controllable synthesis of $LiFePO_4$ in different polymorphs and study of reaction mechanism

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S1. Calculation method about reaction kinetics and dynamics.

According to basic chemical kinetics and dynamics equations:

$$k = \frac{\Delta c}{t} \tag{1}$$

$$\Delta G = \Delta H - T\Delta S \tag{2}$$

and function from Transition state theory:

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G}{RT}} \tag{3}$$

where Boltzmann constant k_B=1.38 $\times 10^{-23}$ J/K, Planck constant h=6.626 $\times 10^{-34} J \cdot s$, Gas constant R=8.314 $J/(mol \cdot K)$. To calculate the specific values, reaction rate k of P1.8 for really long time was calculated to be $5.4 \times 10^{-7}\ g/s$, which would lead to value of $\Delta G \gg 0$ on the assumption that the reaction happened from bLFP straight to aLFP, meaning that reaction would not happen spontaneously, which in contrast with the fact that the reaction happened for fact. The conflict of theory and fact illustrates the assumption of phase change directly from bLFP to aLFP was incorrect, leading to conclusion that the reaction was indirect and phase change went through dissolution-recrystallization process.

Table S1. XRD Refinement Results of aLFP and bLFP.

parameter	a/Å	b/Å	c/Å	V/Å^3	Average size/nm	GOF	Rexp	Rwp	Rp
Synthesized aLFP	10.310	5.990	4.702	290.4	58.7	1.19	1.66	1.96	1.50
Synthesized bLFP	5.531	8.260	6.195	283.0	27.7	1.28	1.07	1.37	1.04

Table S2. Detailed analyse of XRD for samples with different reaction time in P1.8.

Reaction time	aLFP (%)	bLFP (%)	GOF	Rexp	Rwp	Rp
8 h	1.12	98.88	1.48	0.75	1.11	0.82
3 d	18.39	81.61	1.21	1.08	1.31	1.02
7 d	30.81	69.19	1.19	1.05	1.25	0.97
12 d	60.11	39.89	1.15	1.07	1.23	0.95
21 d	81.51	18.49	1.16	1.05	1.22	0.95

Table S3. Lattice parameters of 4 kinds of crystal.

Lattice properties	Space group	a/Å	b/Å	c/Å
Li_3PO_4	Pnma (Orthorhombic)	10.490	6.120	4.972
aLFP	Pnma (Orthorhombic)	10.310	5.990	4.702
$Fe_7H_4(PO_4)_6$	P1 (Triclinic)	6.675	8.108	9.583
bLFP	Cmcm (Orthorhombic)	5.531	8.260	6.195

Table S4. Detailed analyse of XRD for samples with different water content in P1.8.

Water Content (%)	aLFP (%)	bLFP (%)	Rwp
0	0	100	1.25
2	15.02	84.98	1.27
4	37.55	62.45	1.35
6	94.62	5.38	1.36
8	100	0	1.30

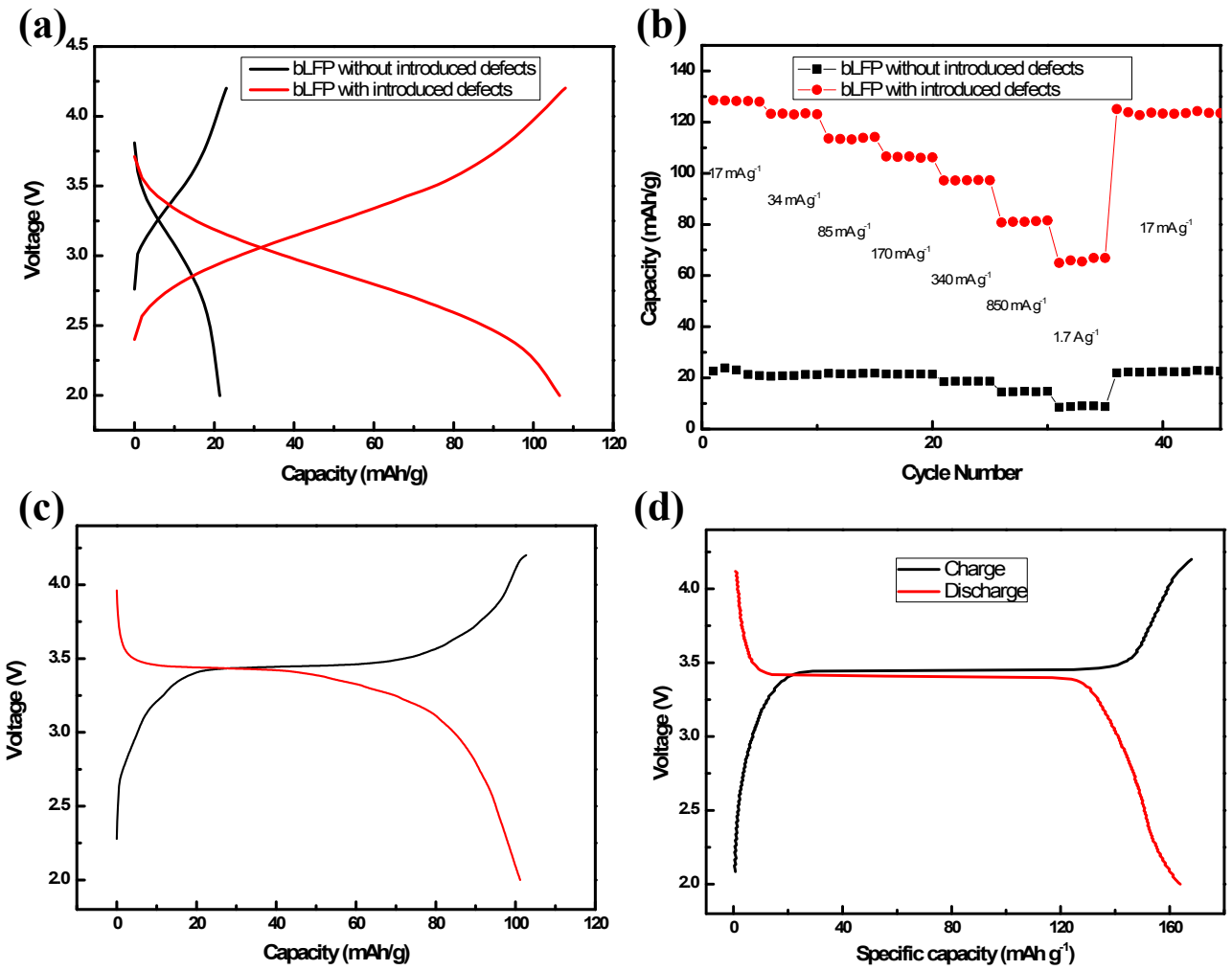

Figure S1. (**a**) Voltage-Capacity profile and (**b**) rate performance for bLFP with and without defects introduced, with Voltage-Capacity profile of (**c**) non-carbon coated aLFP (produced by annealing of bLFP) and (**d**) carbon-coated aLFP (produced by annealing of bLFP with carbon coating).

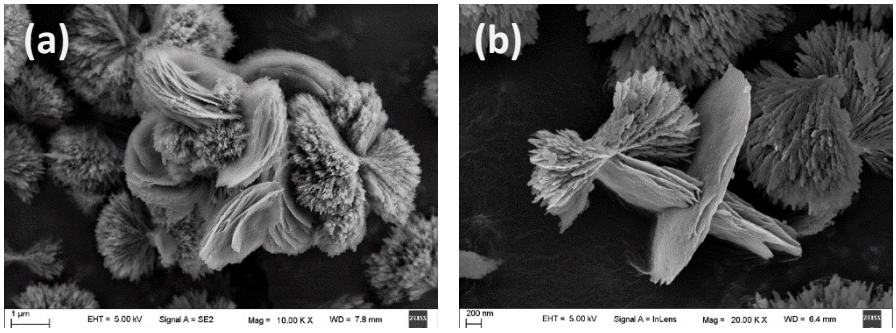

Figure S2. Certain intermediate products showing combination of aLFP and bLFP with staggering morphology, illustrating dissolution-recrystalization mechanism of bLFP formation.

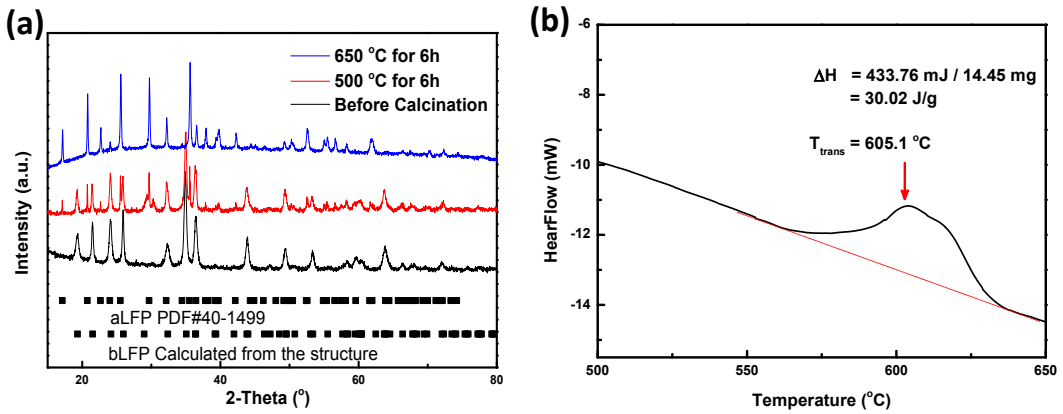

Figure S3. After heating, bLFP could phase-change to aLFP. **(a)** XRD results before/after calcination and **(b)** DSC result shows a heat absorption peak around 600 °C, representing phase change temperature of bLFP.

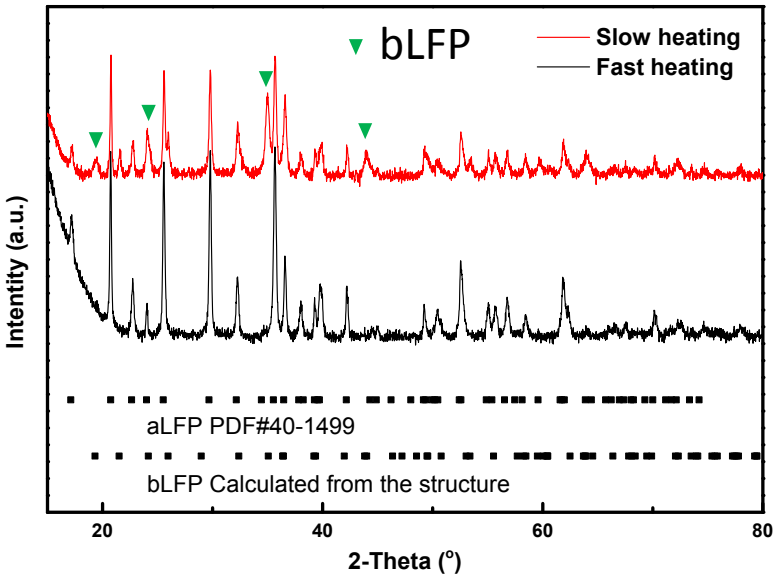

Figure S4. Same P1.5 reactions with different reaction time.

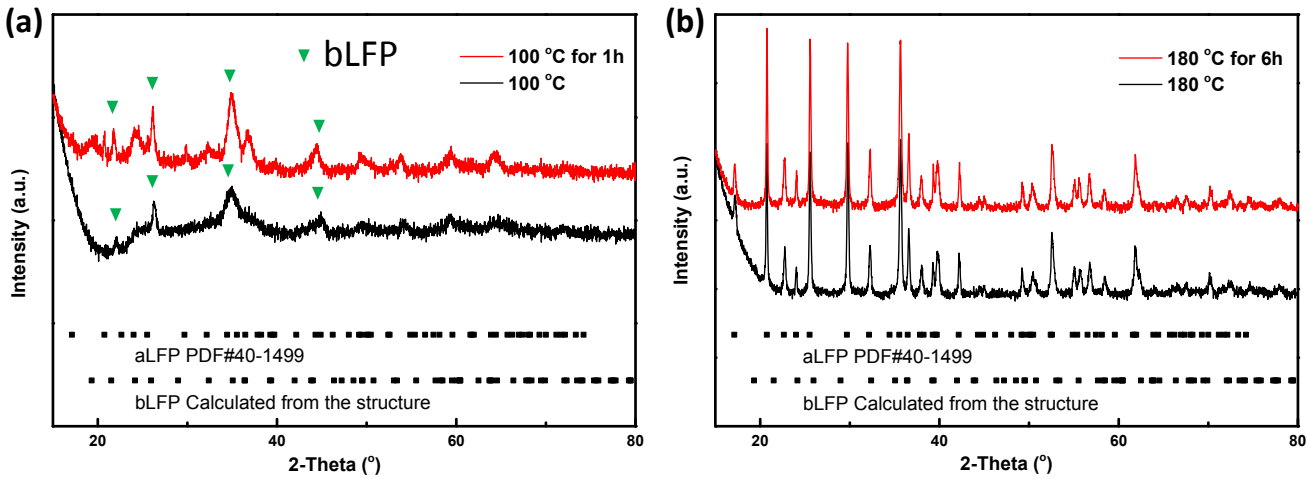

Figure S5. P1.5 reaction holds **(a)** 100 °C for 1h and **(b)** 180 °C for 6h.

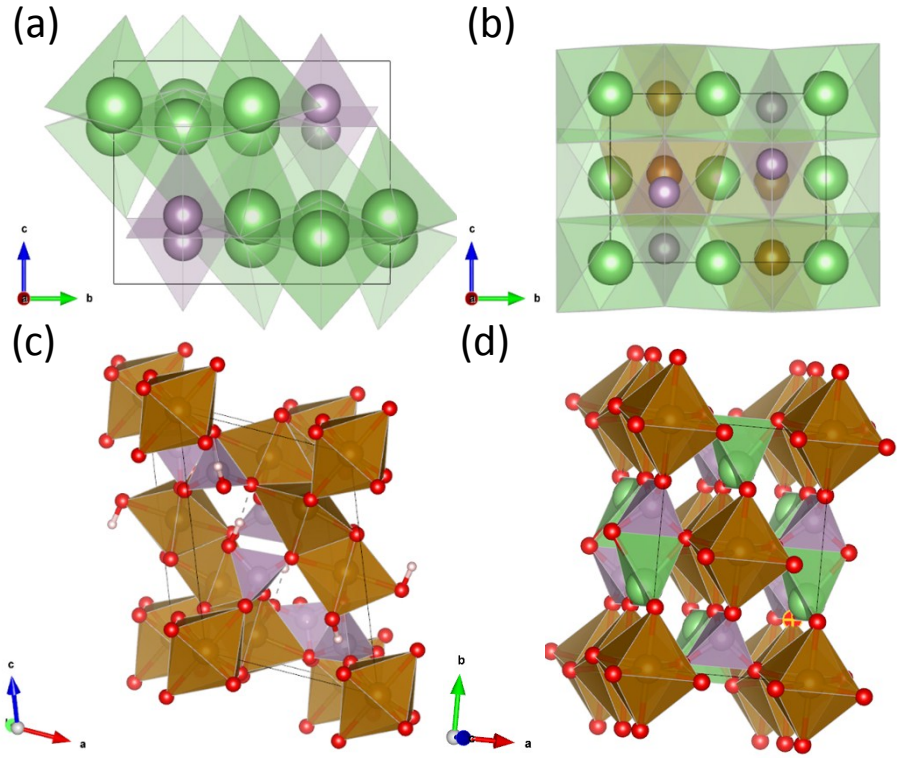

Figure S6. Crystal lattice illustration of **(a)** Li_3PO_4, **(b)** aLFP, **(c)** $Fe_7H_4(PO_4)_6$ and **(d)** bLFP. Li-O polyhedral shown in green, Fe-O octahedral shown in brown, and P-O tetrahedral shown in purple.

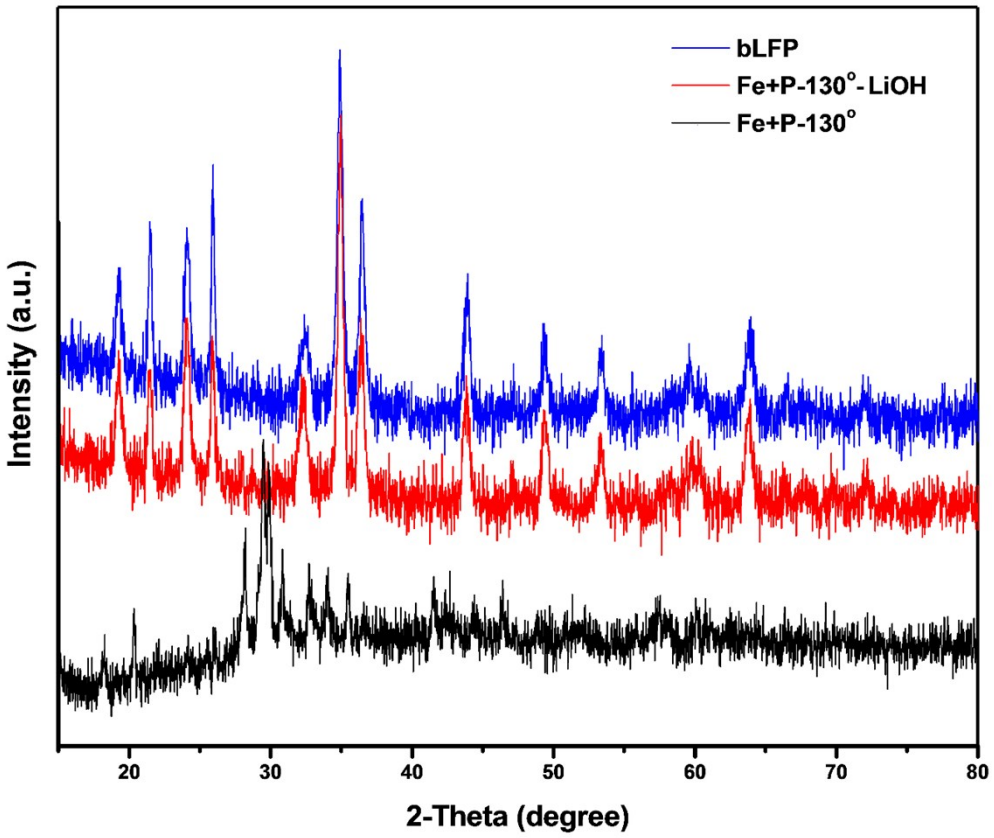

Figure S7. $FeSO_4$ and H_3PO_4 (mole ratio 1:2.5) reacted and became $Fe_7H_4(PO_4)_6$ in temperature of 130 ^oC (shown as black line), which later reacted with LiOH and became bLFP (shown as red line).

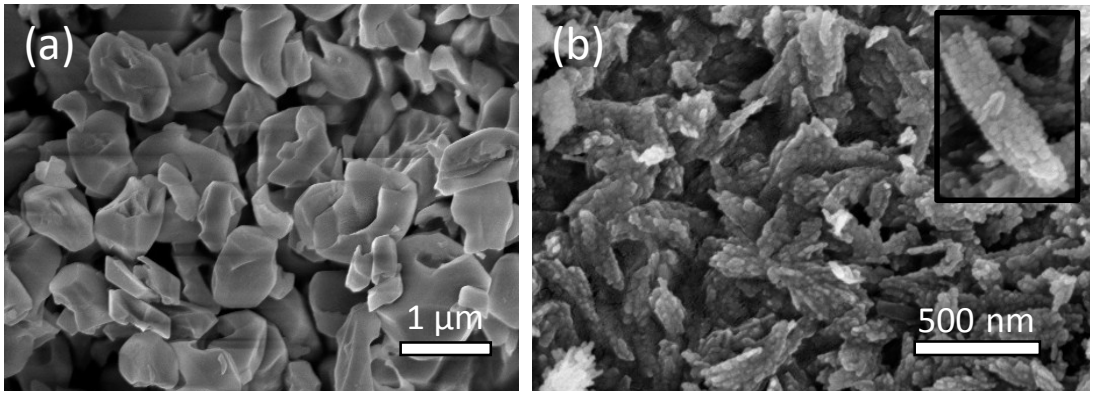

Figure S8. SEM image showing morphologies for (a) intermediate product $Fe_7H_4(PO_4)_6$ and (b) final product bLFP.

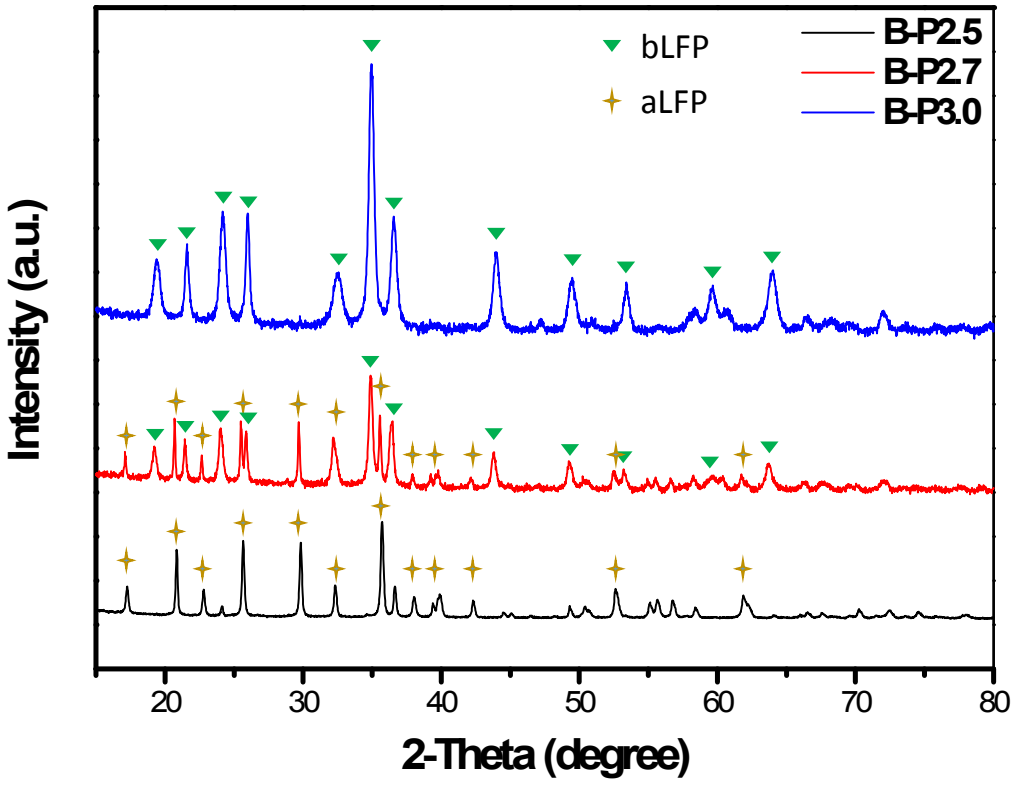

Figure S9. XRD of products from different phosphate acid ratio (from 2.5 to 3.0) experiments with different adding sequences of the reactants.