Supporting information for

Highly ordered staging structural interface between $LiFePO_4$ and $FePO_4$

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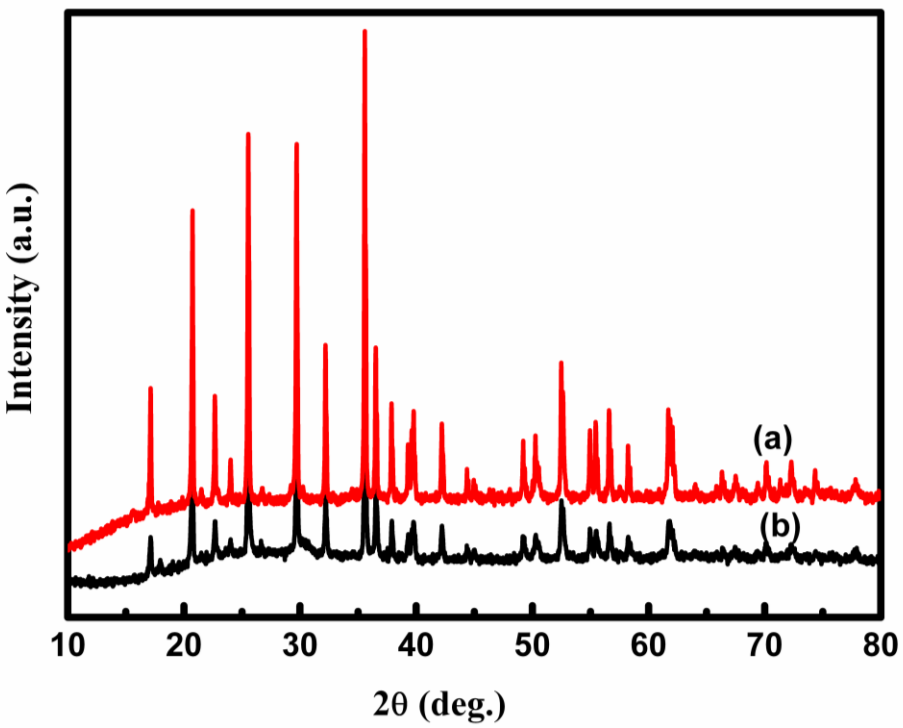

Figure S1 XRD patterns of (a) the pristine Nb-doped $LiFePO_4$ and (b) chemical delithiation (10 atom %) $LiFePO_4$ sample (nominal).

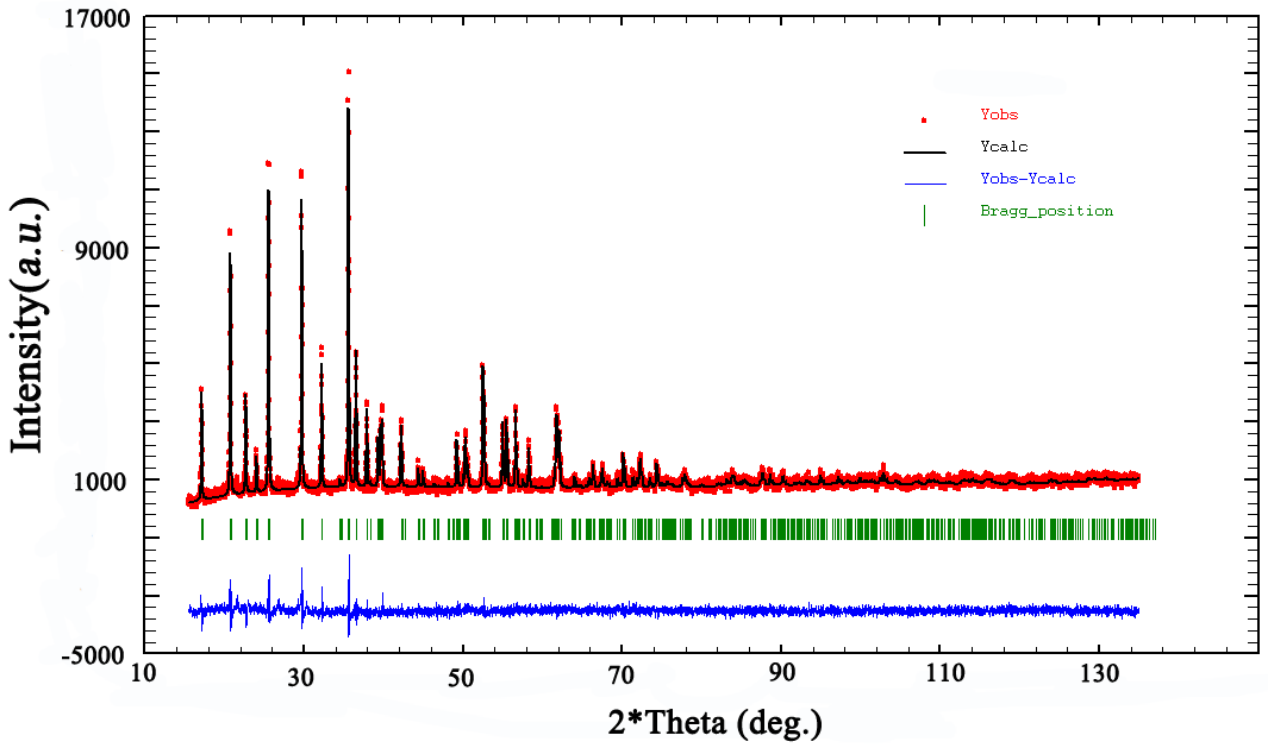

Figure S2 Rietveld patterns of Nb-doped $LiFePO_4$ sample. Observed (red circles) and calculated (black solid line), Bragg reflection peaks (brown solid ticks) and the difference curve (below) are shown. The structural parameters are a = 4.6943 Å, b = 10.3270 Å and c= 6.0048 Å, R*p*: 8.17, R*wp*: 10.7, R*exp*: 3.16 (not corrected for background).

Atomic occupancies of Nb-doped $LiFePO_4$

Atoms	*a*	*b*	*c*	Biso.	Occ.
Li	0.00000	0.00000	0.00000	5.02627	0.47858
Nb					0.01719
Fe	0.97556	0.28238	0.25000	0.10024	0.46296
P1	0.41722	0.09310	0.25000	0.64297	0.5
O1	0.74860	0.10563	0.25000	0.69497	0.5
O2	0.20553	0.45332	0.25000	1.19660	0.5
O3	0.28404	0.16680	0.04259	1.28510	1.0

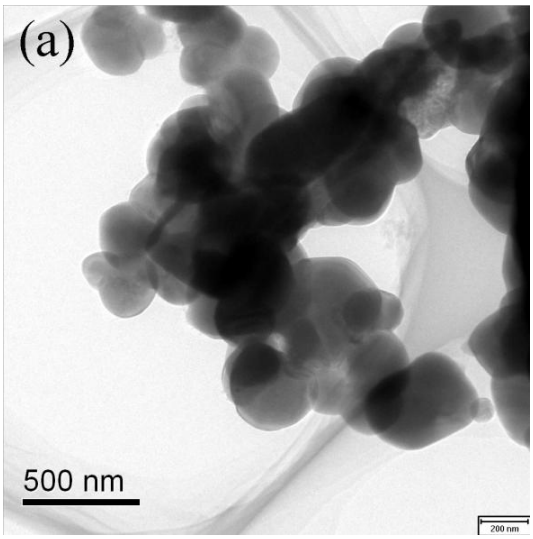

Figure S3. TEM image of the pristine Nb-doped $LiFePO_4$

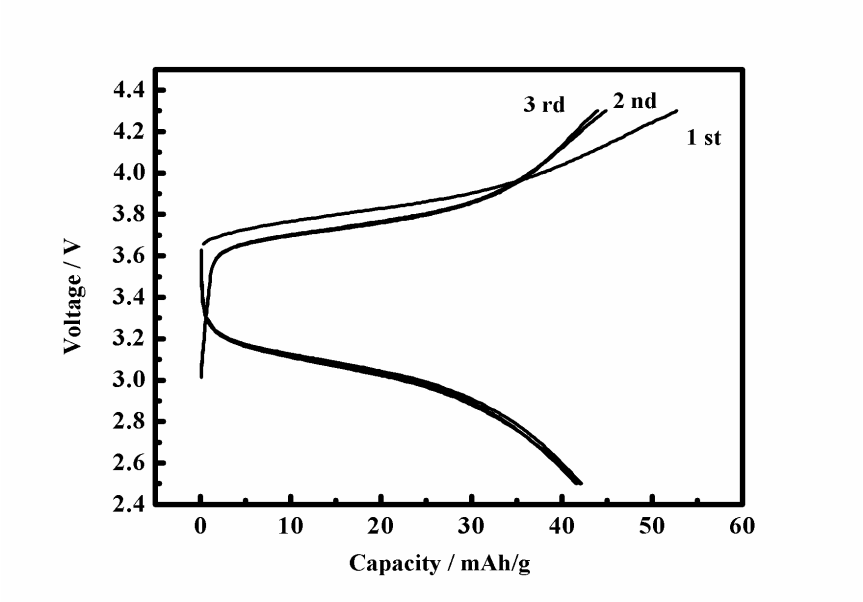

Figure S4 Charge and discharge curves of the as-prepared Nb-doped $LiFePO_4$ sample

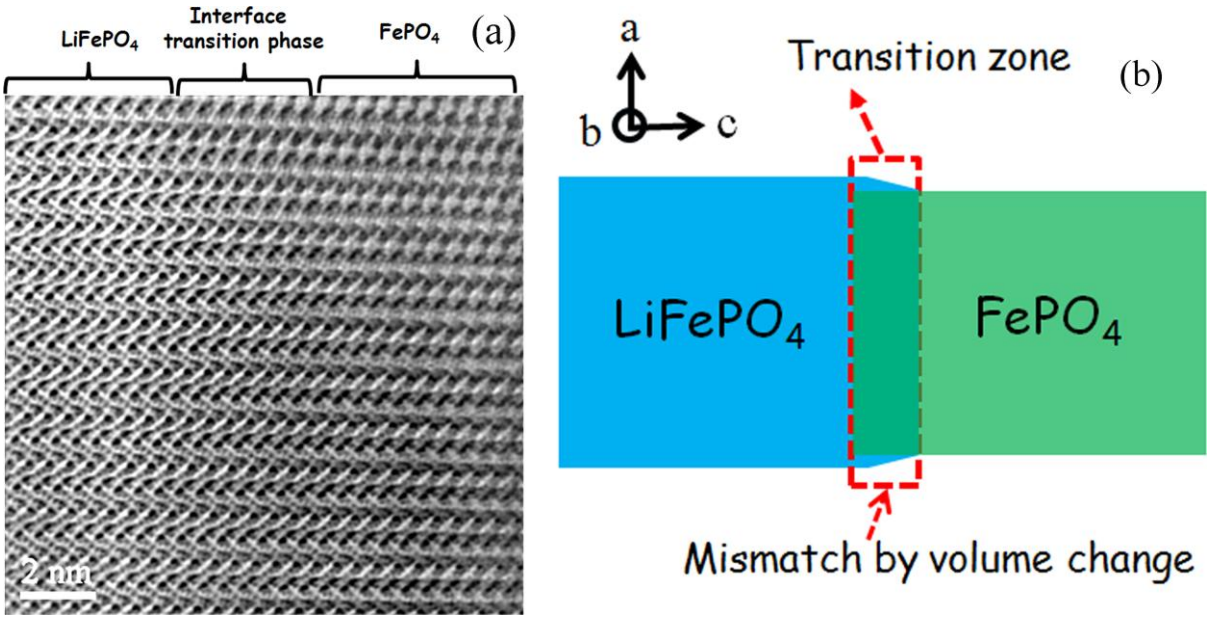

Figure S5 (a) The unmarked ABF-STEM image (Figure 1a) at [010] zone axis and (b) schematic views of the mismatch of two phases ($LiFePO_4$, $FePO_4$).

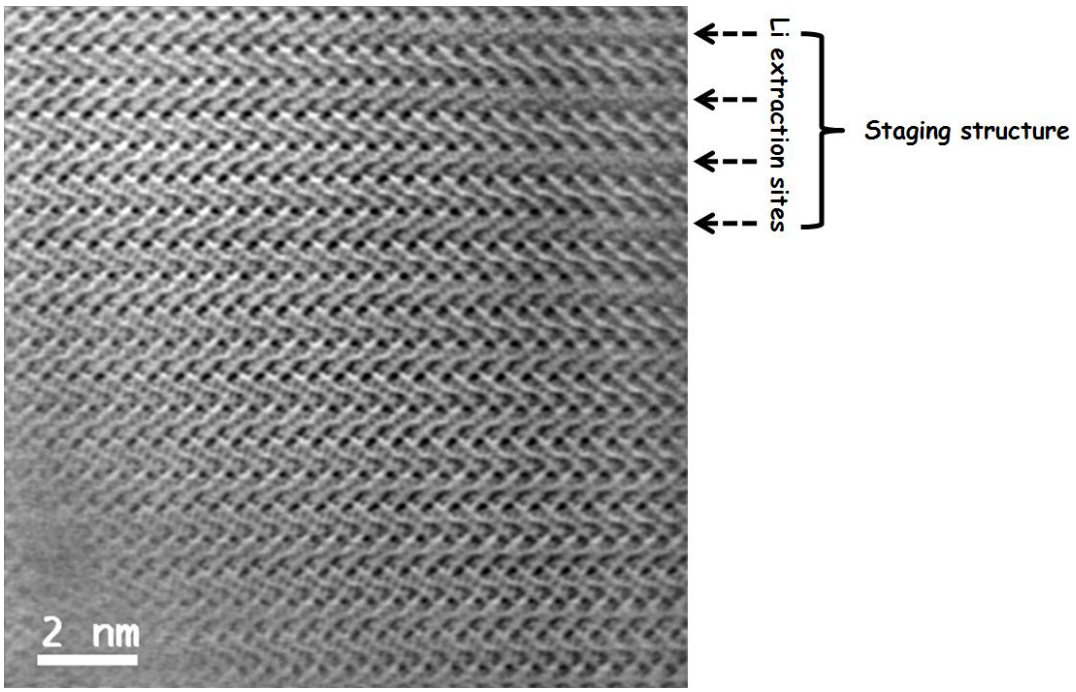

Figure S6 The unmarked ABF-STEM image (Figure 2a) at [010] zone axis.

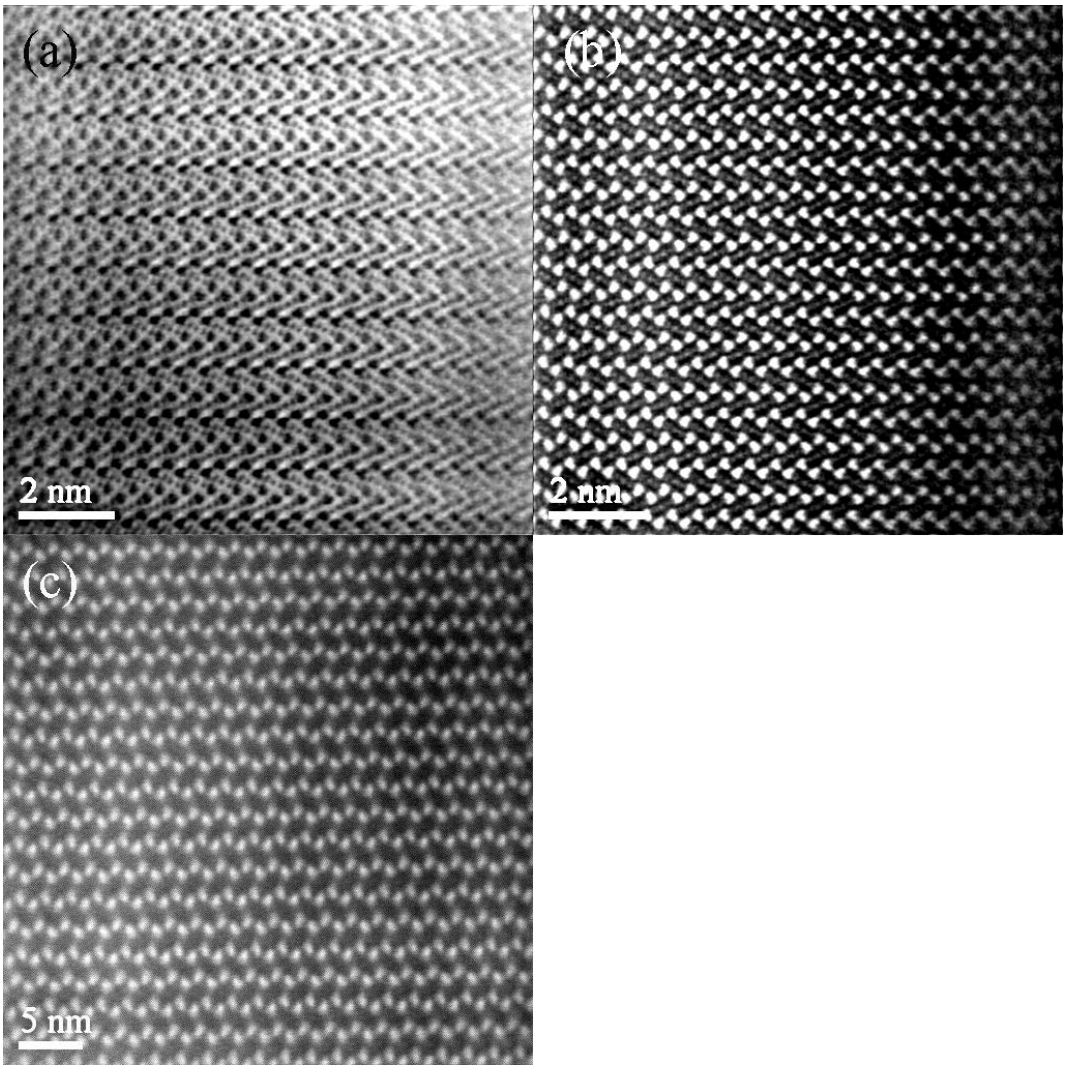

Figure S7 Filtered STEM images of Nb-doped $LiFePO_4$. (a) ABF mode, (b) HADDF mode with Nb occupied in lithium site) and (c) HADDF mode with no Nb occupied in lithium site at [010] zone axis.

Table S1 Standard ICP elemental analysis of the pristine Nb-doped $LiFePO_4$ and chemical delithiation (10 atom % Lithium ion) of Nb-doped$LiFePO_4$

Sample	Atomic ratio of elements			
	Li	**Fe**	**Nb**	**P**
The initial design	0.90	1.00	0.02	1
2% Nb-doped $LiFePO_4$	0.91	1.03	0.02	1
Chemical delithiated 10%	0.81	1.02	0.02	1