

## Supplementary information

### Direct evidence for the influence of lithium ion vacancies on polaron transport in nanoscale LiFePO<sub>4</sub>

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**Table S1.** The temperature and time duration used to synthesize different crystallite sized LFP samples

Crystallite size (nm)	Temperature (K)	Time period (hrs.)
40	1023	6
36	1023	4
34	1023	2
30	823	8
27	823	6

**Table S2:-** List of important parameters related to polaronic dc conduction in LFP for various crystallite sizes estimated from Mott fitting and Rietveld refinement.  $\theta_D$  is the Debye temperature,  $\nu_{ph}$  is the optical phonon frequency,  $R$  is the long-range polaron hopping distance,  $E_a^{Lt}$  and  $E_a^{Ht}$  are the activation energy at intermediate and high temperatures, and lithium ion vacancy concentration determined by the XRD Rietveld refinement analysis.

Crystallite Size (nm) $\pm 2$ nm	$\theta_D$ (K)	$\nu$ (Hz) $\times 10^{13}$	$R$ (Å) $\pm E_r$	$E_a^{Lt}$ (eV)	$E_a^{Ht}$ (eV)	Polaron concentration (%) $\pm E_r$	LIV concentration (%)
27	567	1.18	2.79 $\pm 0.05$	0.571	0.651	17.0 $\pm 0.12$	17
30	574	1.19	2.80 $\pm 0.03$	0.587	0.655	11.0 $\pm 0.2$	14.65
34	596	1.24	2.93 $\pm 0.01$	0.595	0.659	8.4 $\pm 0.31$	13.03
36	605	1.26	3.12 $\pm 0.02$	0.601	0.665	7.0 $\pm 0.12$	10.54
40	615	1.29	3.42 $\pm 0.05$	0.645	0.677	6.5 $\pm 0.11$	10.15

**Table S3:** Structure related parameters obtained from the Rietveld refinement for LFP sample with 27 nm crystallite size

Wavelength (Å)		0.78799			
Space group		<i>Pnma</i>			
a (Å)		10.3153			
b (Å)		6.0012			
c (Å)		4.7011			
V (Å <sup>3</sup> )		291.022			
R <sub>p</sub> (%)		3.42			
R <sub>wp</sub> (%)		4.55			
GOF( $\chi^2$ )		6.538			
Site	Wyck.	x/a	y/b	z/c	Occupancy
Li	4a	0 0.0000	0 0.0000	0 0.0000	0.8300
Fe	4c	0 0.2820	0 0.2500	0 0.9731	0.9964
P	4c	0 0.0953	0 0.2500	0 0.4193	1.0000
O	4c	0 0.0962	0 0.2500	0 0.7404	1.0000
O	4c	0 0.4579	0 0.2500	0 0.2056	1.0000
O	8d	0 0.1653	0 0.0491	0 0.2828	1.0000
Fe	4a	0 0.0000	0 0.0000	0 0.0000	0.0050

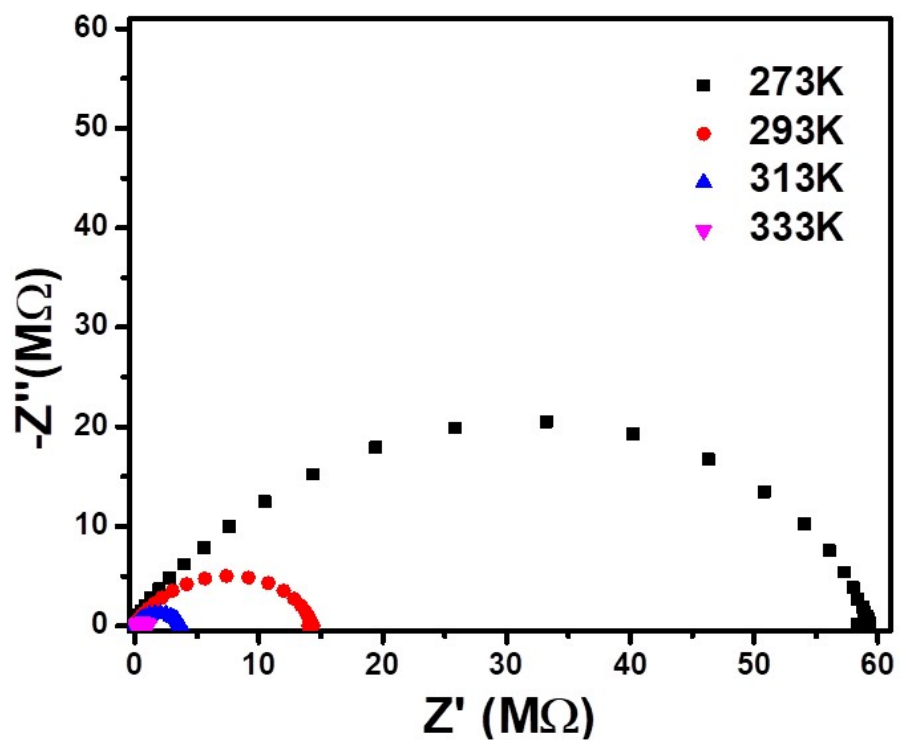
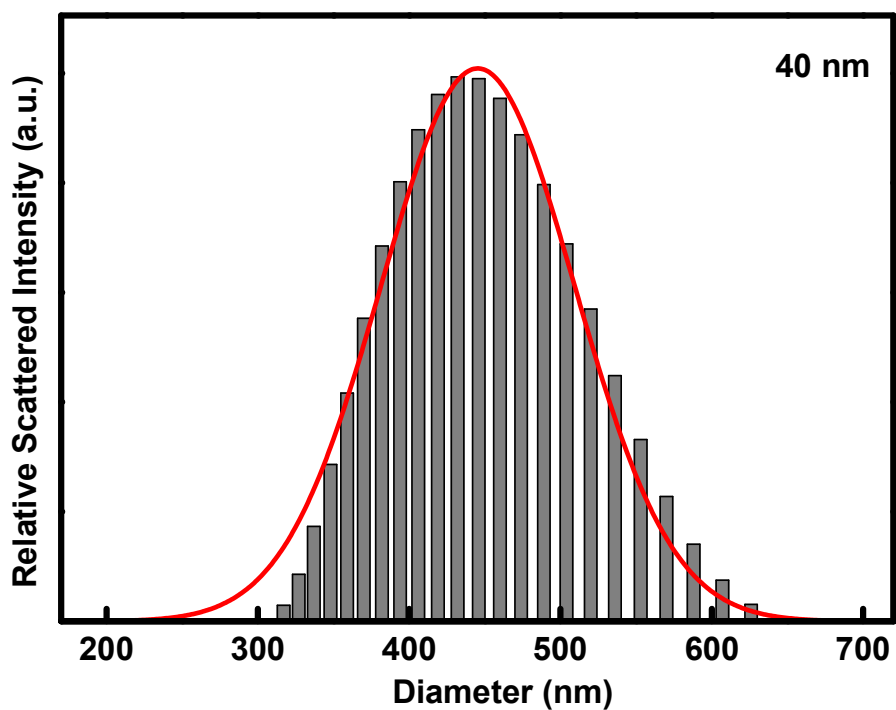
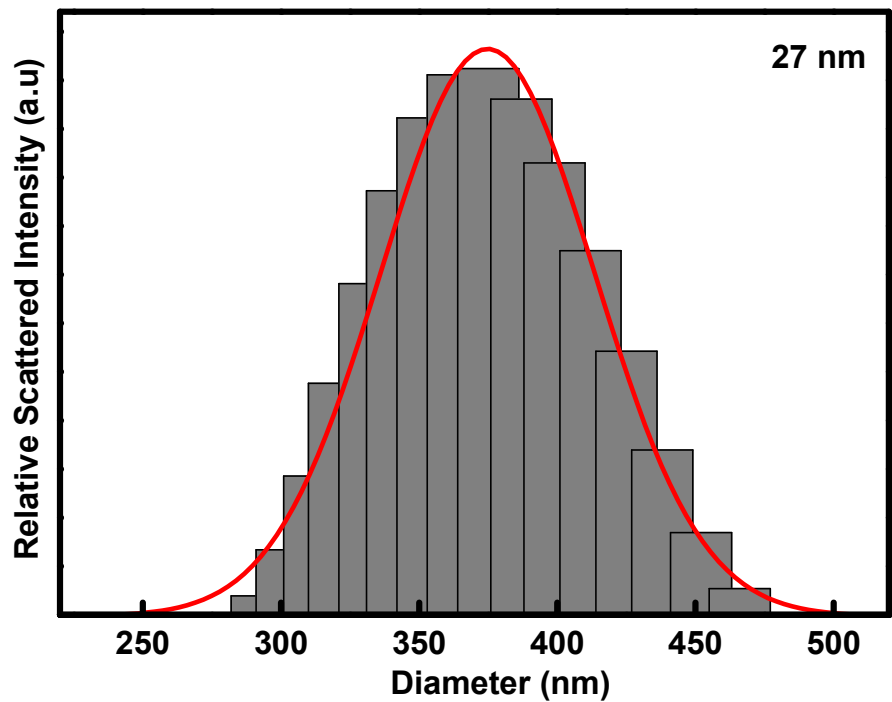


Fig. S1. Nyquist plot for LFP sample with 30 nm crystallite size.



**Fig. S2.** The article size distribution histogram of representative 27 nm and 40 nm crystallite size of LFP sample obtained by dynamic light scattering method.