Supplementary Information

In-Depth Mesocrystal Formation Analysis of Microwave-Assisted Synthesis of $LiMnPO_4$ Nanostructures in Organic Solution

P. Voepel,[a] C. Suchomski,[*a] A. Hofmann,[a] S. Gross,[b,c] P. Dolcet,[b,c] and B. M. Smarsly,[*a]

Table S1. Refined structural parameters of $LiMnPO_4$ obtained by Rietveld analysis (a) 60 mmol L^{-1} (undiluted), (b) 30 mmol L^{-1} and (c) 20 mmol L^{-1} (diluted approaches).

Phase	$LiMnPO_4$ (a)	$LiMnPO_4$ (b)	$LiMnPO_4$ (c)
Space group	*Pmnb* (#62)		
Lattice parameters, (Å)	a = 6.1037 b = 10.4467 c = 4.7461	a = 6.1025 b = 10.4467 c = 4.7468	a = 6.1012 b = 10.4430 c = 4.7446
Unit–cell volume ($Å^3$)	302.6275	302.613	302.303
Calc. density (g cm^{-3})	3.443	3.443	3.447
Average grain size (nm)	65 ± 5	37 ± 3	35 ± 5
Average maximum microstrain ($\times 10^{-4}$)	15.6208	15.0789	19.2749
R_{wp} [Bragg contributions] (%)	12.9	6.29	14.8
Goodness of fit, χ^2	3.024	2.03	2.59

Table S2. GC-MS results.

Retention time (min)	Compound	m/z [MP]	m/z [BP]	m/z [FP]
1.570	Ar, CO_2	40, 44	-	-
4.868	Styrene	104	103	78, 77, 51
7.159	1-Phenylethanol ((±)-α-Methylbenzyl alcohol)	122	107	79, 77, 51
7.248	1-Phenylethyl chloride (α-Methylbenzyl chloride)	140	105	107, 79, 77
8.750	1-Phenylethyl acetate (α-Methylbenzyl acetate)	164	104	122, 73, 43
12.806, 12.936	(SS or RR) and (RS) Bis(α-methylbenzyl) ether	164	104	122, 105, 43

MP = molecule peak, BP = base peak, FP = fragment peak, m/z = mass-to-charge ratio

Table S3. Atomic percentages of O, C, Li, P and Mn obtained by XPS analysis.

Sample	%O	%C	%Li	%P	%Mn	[Mn]:[Li] (atomic ratio)	[P]:[Mn] (atomic ratio)	Formula*
65 nm	50.1	20.1	8.2	11.5	9.8	1.2 (1)	1.2 (1)	$Li_{0.884}Mn_{0.057}MnPO_4$
35 nm	39.9	33.7	7.2	9.4	9.4	1.3 (1)	1.0 (1)	$Li_{0.831}Mn_{0.085}MnPO_4$

Theoretical values are given in parentheses. [∗] By neglecting the atomic P to Mn ratio.

Table S4. XPS peak analysis data.

Core level	Peak position (eV)*	
	65 nm	35 nm
Mn 2$p_{3/2}$	641.85	641.81
Mn 2$p_{1/2}$	653.77	653.74
Mn 2*p* shake up satellite	646.20, 658.56	646.15, 658.51
Mn 3*s*	89.44	89.64
O 1*s*	531.26	531.35 (lattice oxygen)
	532.81	533.33 (H_2O)
Li 1*s*	55.38	55.35
P2p	133.44	133.51
C 1*s*	284.60	284.60 (C−C)
	−	285.81 (C−O)
	287.65	288.55 (C=O)

[*] error margin: ±0.15 eV

Table S5. Structural parameters of $LiMnPO_4$ for 35 nm grain size obtained by fitting of Mn K-edge EXAFS data.

Atom Label	Number	Distance from Mn absorber	Distance (crystal structure)	σ^2 (10^{-3})
O1	2	(2.09 ± 0.01) Å	2.14 Å	(3.7 ± 1.2) Å
O2	1	(2.12 ± 0.01) Å	2.17 Å	(3.7 ± 1.2) Å
O3	3	(2.21 ± 0.01) Å	2.26 Å	(4.1 ± 1.8) Å
P1	1	(2.87 ± 0.01) Å	2.87 Å	(7.0 ± 3.1) Å
P2	4	(3.32 ± 0.01) Å	3.32 Å	(10.1 ± 2.7) Å

σ = Debye-Waller factor

Table S6. Structural parameters of $LiMnPO_4$ for 65 nm grain size obtained by fitting of Mn K-edge EXAFS data.

Atom Label	Number	Distance from Mn absorber	Distance (crystal structure)	σ^2 (10^{-3})
O1	2	(2.09 ± 0.01) Å	2.14 Å	(2.4 ± 1.4) Å
O2	1	(2.12 ± 0.01) Å	2.17 Å	(2.4 ± 1.4) Å
O3	3	(2.21 ± 0.01) Å	2.26 Å	(2.7 ± 2.0) Å
P1	1	(2.89 ± 0.01) Å	2.87 Å	(11.4 ± 4.7) Å
P2	4	(3.34 ± 0.01) Å	3.32 Å	(12.3 ± 5.4) Å

σ = Debye-Waller factor

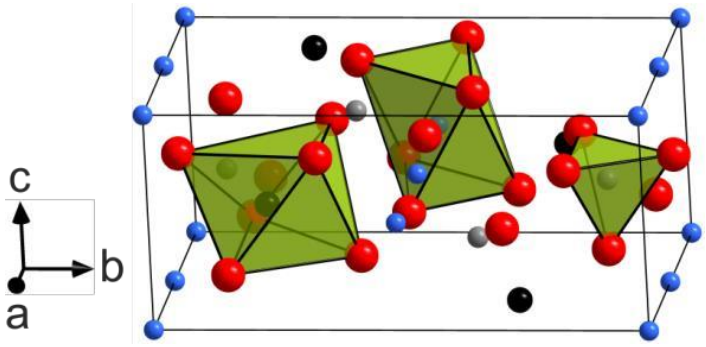

Fig. S1. Unit–cell of $LiMnPO_4$ with orthorhombic space group *Pmnb* (#62). P^{5+} ions occupying the tetrahedral 4(*c*) sites are shown in gray, Li^{+} and Mn^{2+} metal ions on both octahedral 4(*a*) and 4(*c*) sites represented in blue and black, and O^{2-} ions on 4(*c*), 4(*c*) and 8(*d*) sites in red, respectively. The different coordination sites are indicated by colored polyhedra.

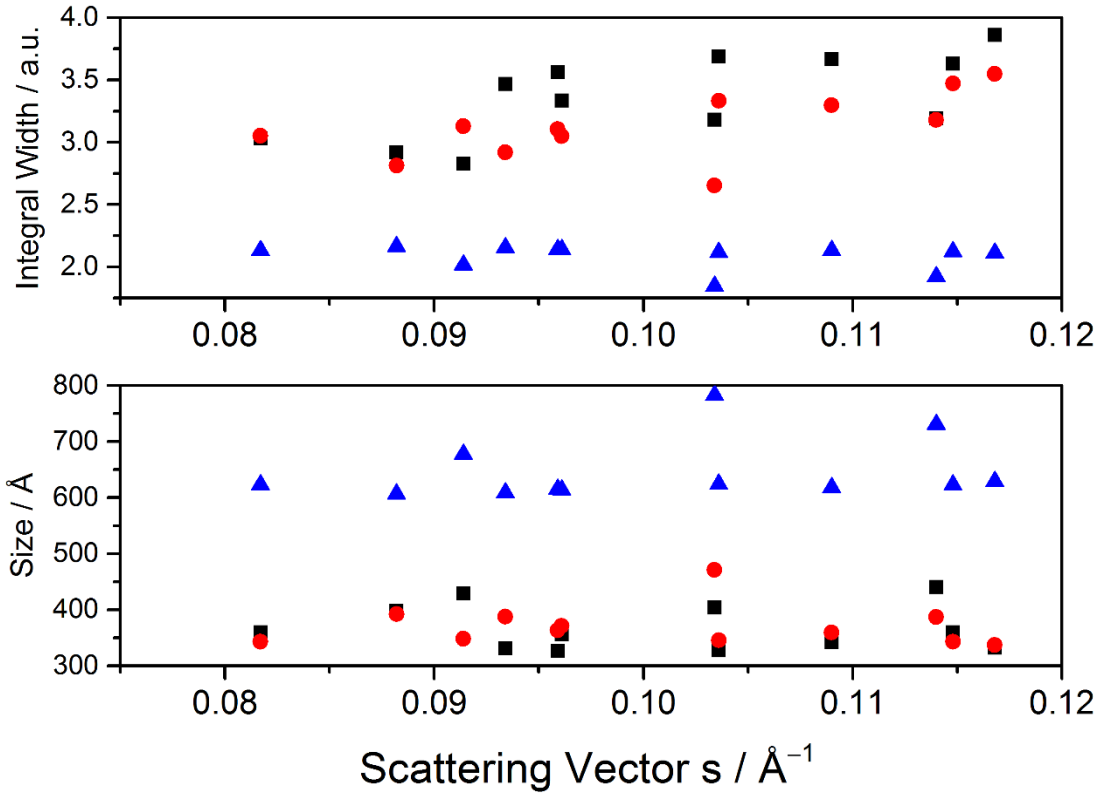

Fig. S2. Integral peak width and the calculated average grain size of the most prominent peaks for the 60 mmol L^{-1}(▲), 30 mmol L^{-1} (●) and 20 mmol L^{-1} (■) approaches.

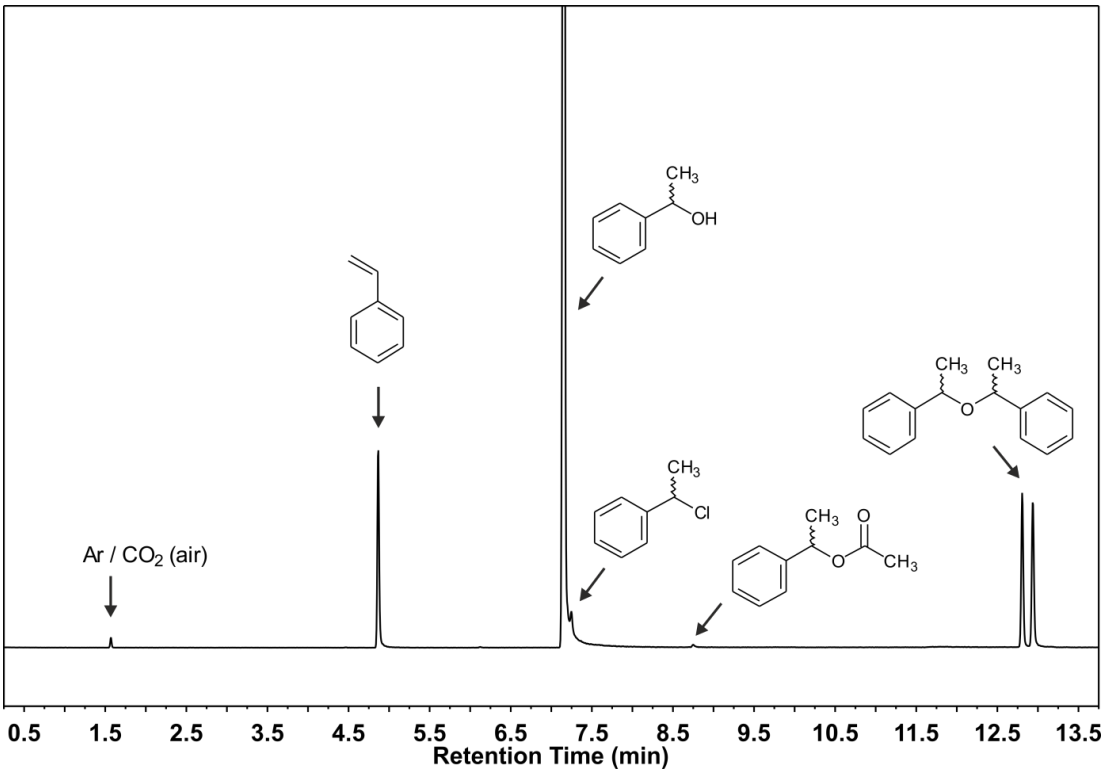

Figure S3. Gas chromatogram of the reaction mixture using *rac*-1-phenylethanol as reaction medium (diluted approach). **Table S2** below summarizes the GC−MS data.

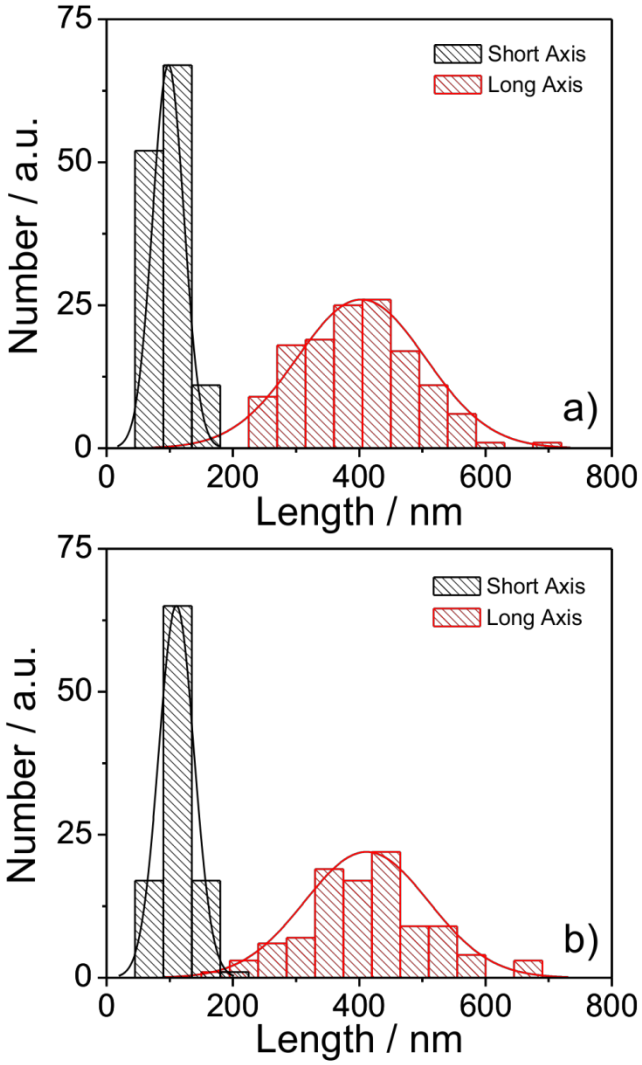

Figure S4. Size distribution on the particles based on SEM. Dilution factor 2 (a) and dilution factor 3 (b).

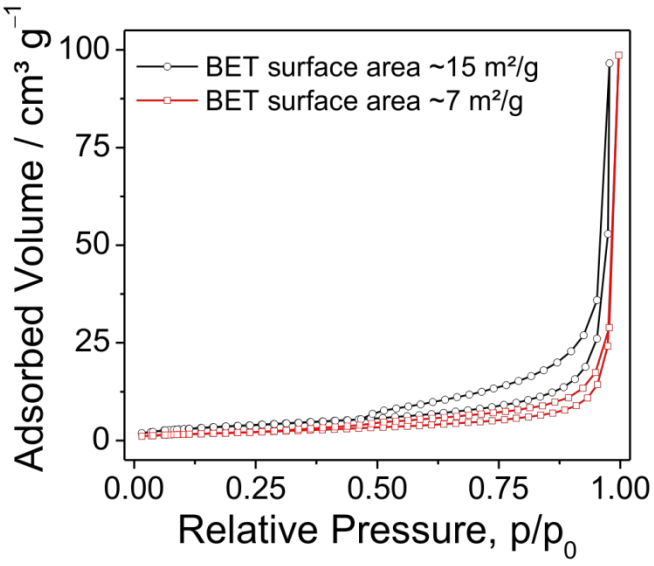

Figure S5. N_2 adsorption and desorption isotherms recorded at 77 K of synthesized $LiMnPO_4$ nanocrystals for grain sizes of approx. 35 nm (①) and 65 nm (⓿), respectively.

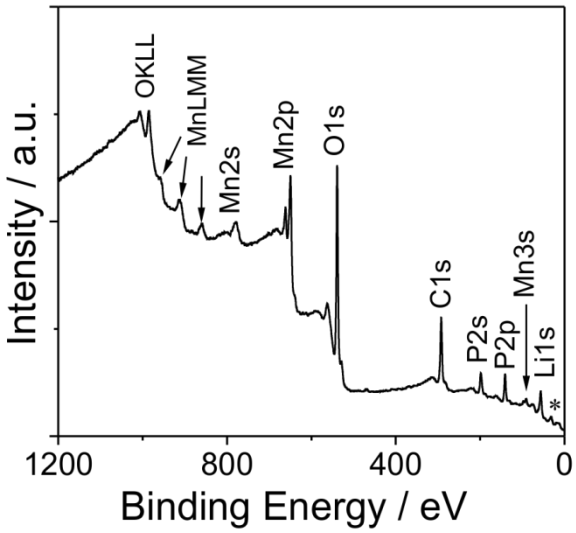

Fig. S6. XPS survey spectra of $LiMnPO_4$ for a grain size of 35 nm. Apart from a strong C 1*s* peak, which we associate with trace amounts of both acetate and 1-phenylethanol, only lithium, manganese, phosphorus and oxygen core levels can be observed. The O 2*s* region is indicated by an asterisk.

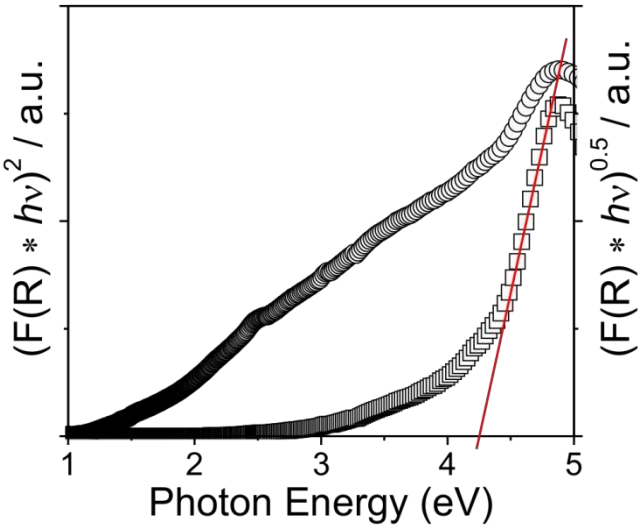

Fig. S7. Direct (□) and indirect (○) optical transitions in nanocrystalline $LiMnPO_4$ particles with an average crystalline domain size of 35 nm. The intercept of the red line with the abscissa yields to a direct band gap of $E_g = (4.25 \pm 0.05)$ eV. Moreover, a weak indirect optical transition at photon energies of approx. 2.50 eV (equivalent to 495 nm) can be identified and attributed to crystal field *d*-*d* transition of Mn^{2+} ions on octahedral sites.

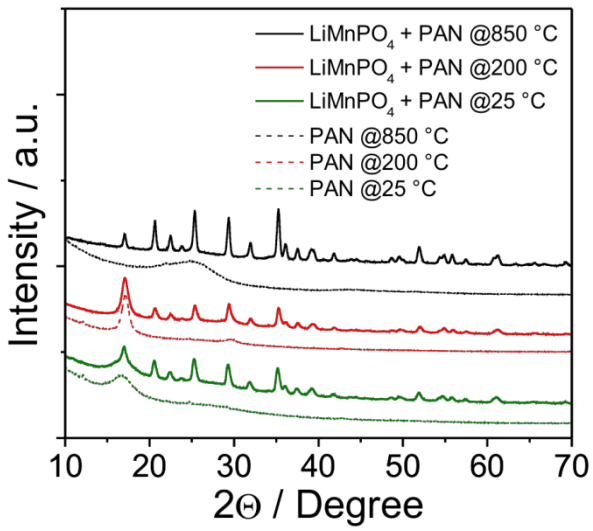

Figure S8: XRD data of the PAN/$LiMnPO_4$ composite fiber material after different heat treatments (as made, stabilized and after carbonization).