

Supporting Information

Hydrothermal Control of the lithium-rich Li_2MnO_3 phase in lithium manganese oxide nanocomposites and their application as precursors for lithium adsorbents

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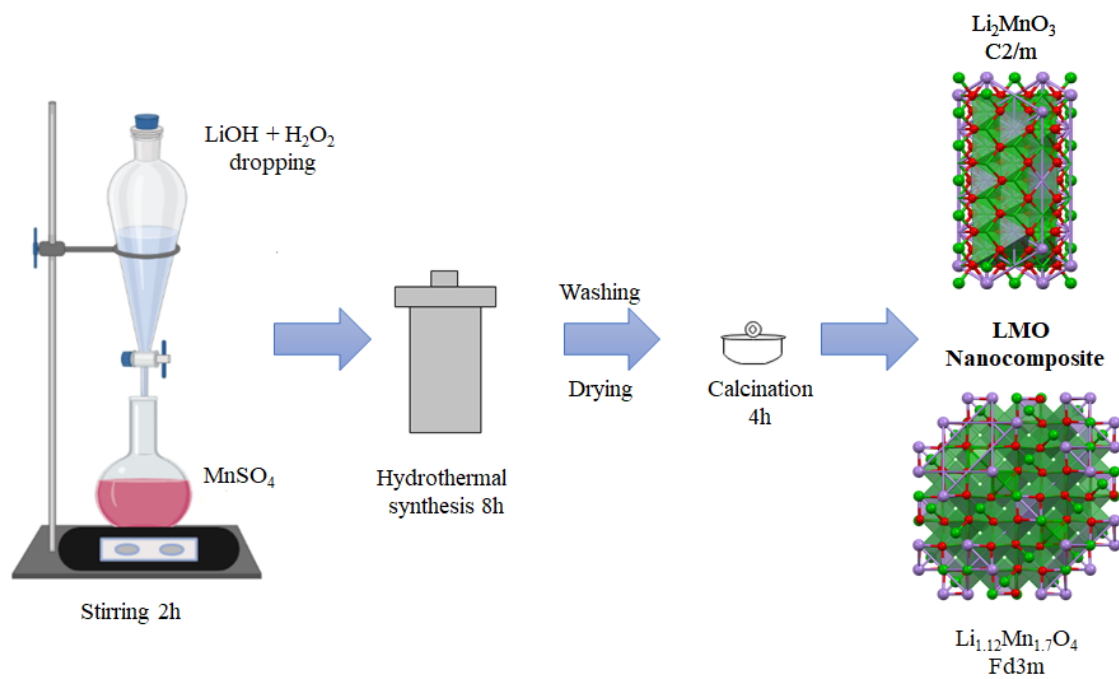


Figure S1 Schematic representation of the hydrothermal synthesis of Li₂MnO₃ · Li_{1.12}Mn_{1.7}O₄ nanocomposites.

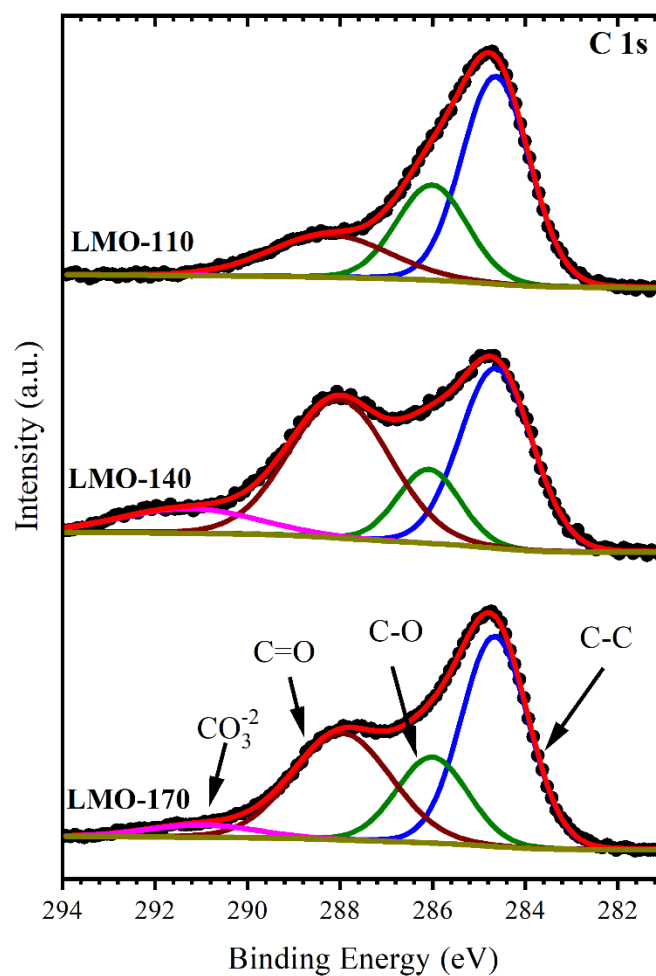


Figure S2 High-resolution XPS spectra of C 1s from the LMO nanocomposites. The peak fitting analysis of C 1s core-level showed the typical C-C (284.60 eV) and C-O (286 eV) components. Moreover, around 288 and 291 eV, other two contributions can be assigned to C=O and CO₃⁻²-like, related to the adsorbed atmospheric carbon and further formation of Li₂CO₃, respectively¹⁻⁴

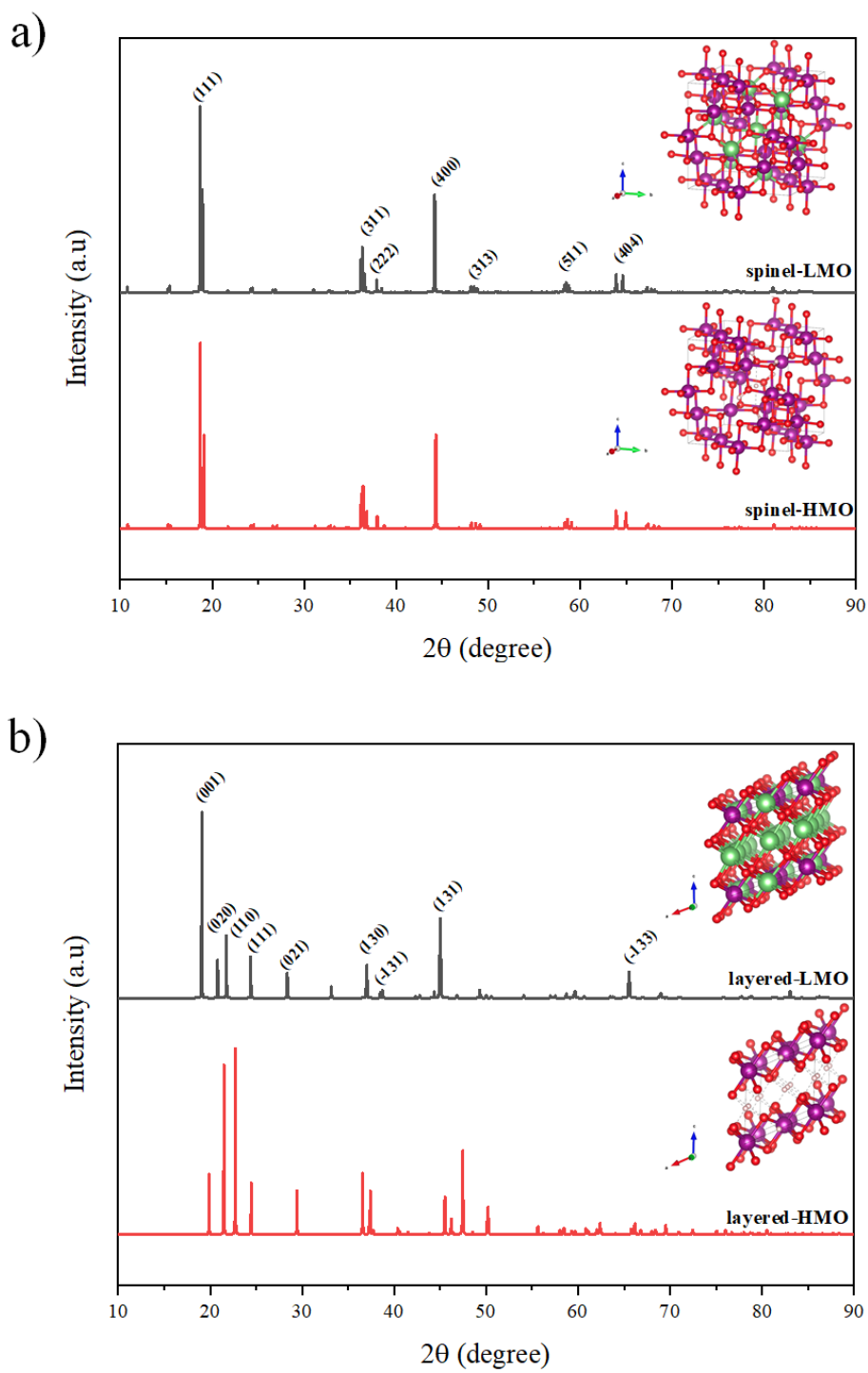


Figure S3 Simulated XRD patterns of adsorbent precursor materials in pure phase.

Layered-LMO (a) and spinel-LMO (b).

Table S1

Structural parameters of LMO nanocomposites determined by Rietveld refinement of XRD data.

Nanocomposite	Phase	a (Å)	b (Å)	c (Å)	β angle(°)	V (Å ³)
LMO-110	Li _{1.12} Mn _{1.7} O ₄	8.1397	-	-	-	539.2955
	Li ₂ MnO ₃	4.9400	8.5277	5.0085	108.800	199.7378
LMO-140	Li _{1.12} Mn _{1.7} O ₄	8.1272	-	-	-	536.8187
	Li ₂ MnO ₃	4.9279	8.5260	5.0108	108.930	199.1424
LMO-170	Li _{1.12} Mn _{1.7} O ₄	8.1366	-	-	-	538.6697
	Li ₂ MnO ₃	4.9303	8.5306	5.0130	108.943	199.4214

Table S2

Quantitative analysis C 1s XPS spectra of LMO nanocomposite

Sample	C-C%	C-O%	C=O%	CO ₃ ²⁻ %
LMO-170	12.1	5.3	9.0	1.1
LMO-140	5.3	1.9	5.8	1.3
LMO-110	9.5	4.6	3.4	0.0

Table S3

DFT optimized cell parameters for simulated LMO and HMO

Structure	Cell parameters				
	a(Å)	b(Å)	c(Å)	β angle (°)	Volume
Li ₉ Mn ₁₅ O ₃₂	8.19191	-	-	-	549.655156
H ₉ Mn ₁₅ O ₃₂	8.16750	-	-	-	544.333233
Li ₈ Mn ₄ O ₁₂	4.93214	8.53083	4.93276	109.5915	195.531518
H ₈ Mn ₄ O ₁₂	4.82884	8.92474	4.58778	115.7690	178.053829

Table S4

Simulated X-ray diffraction data for LMO and HMO

<i>hkl</i>	Li ₉ Mn ₁₅ O ₃₂		H ₉ Mn ₁₅ O ₃₂		Li ₈ Mn ₄ O ₁₂		H ₈ Mn ₄ O ₁₂	
	<i>d</i> (Å)	2 θ	<i>d</i> (Å)	2 θ	<i>d</i> (Å)	2 θ	<i>d</i> (Å)	2 θ
111	4.6822	18.93	4.5978	19.28	-	-	-	-
400	2.0477	44.19	2.0406	44.35	-	-	-	-
001	-	-	-	-	4.6471	19.08	4.1315	21.49
131	-	-	-	-	2.0107	45.05	1.9144	47.45

References

- 1 S.-H. Lee, I.-S. Jo and J. Kim, *Surf. Interface Anal.*, 2014, **46**, 570–576.
- 2 P. Verma, P. Maire and P. Novák, *Electrochim. Acta*, 2010, **55**, 6332–6341.
- 3 D. Aurbach, I. Weissman, A. Schechter and H. Cohen, *Langmuir*, 1996, **12**, 3991–4007.
- 4 L. El Ouatani, R. Dedryvère, J.-B. Ledeuil, C. Siret, P. Biensan, J. Desbrières and D. Gonbeau, *J. Power Sources*, 2009, **189**, 72–80.