

Supporting Information

Facile template-guided synthesis of conformal Bi₂O₃-coated LiMn₂O₄ hollow microspheres for enhanced stability of lithium-ion battery cathodes

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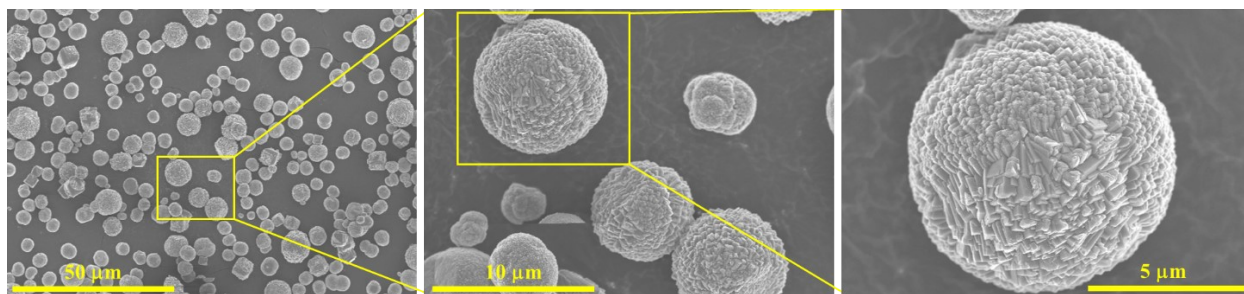


Fig. S1 SEM images showing the morphology of MnCO_3 microspheres as an intermediate product.

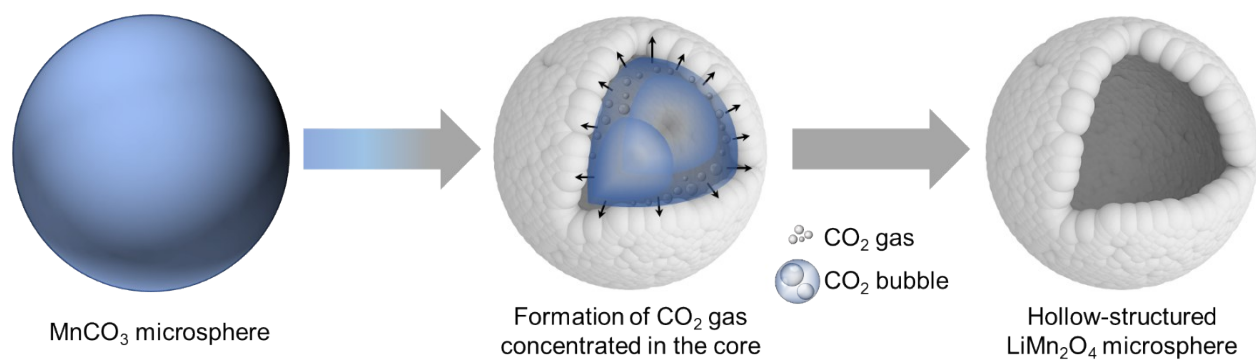


Fig. S2 Schematic illustration of the growth mechanism for LiMn_2O_4 hollow microspheres.

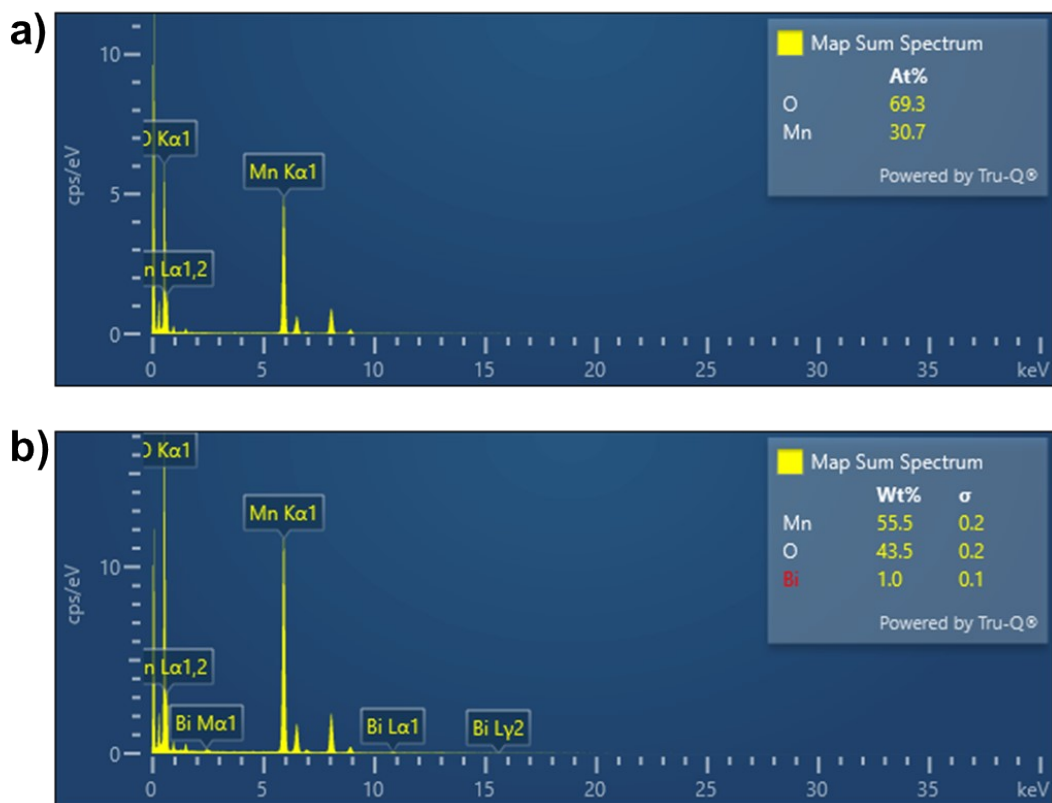


Fig. S3 EDS spectra of (a) LMOhms, and (b) BiLMOhms detect the Bi loading amount during TEM measurement.

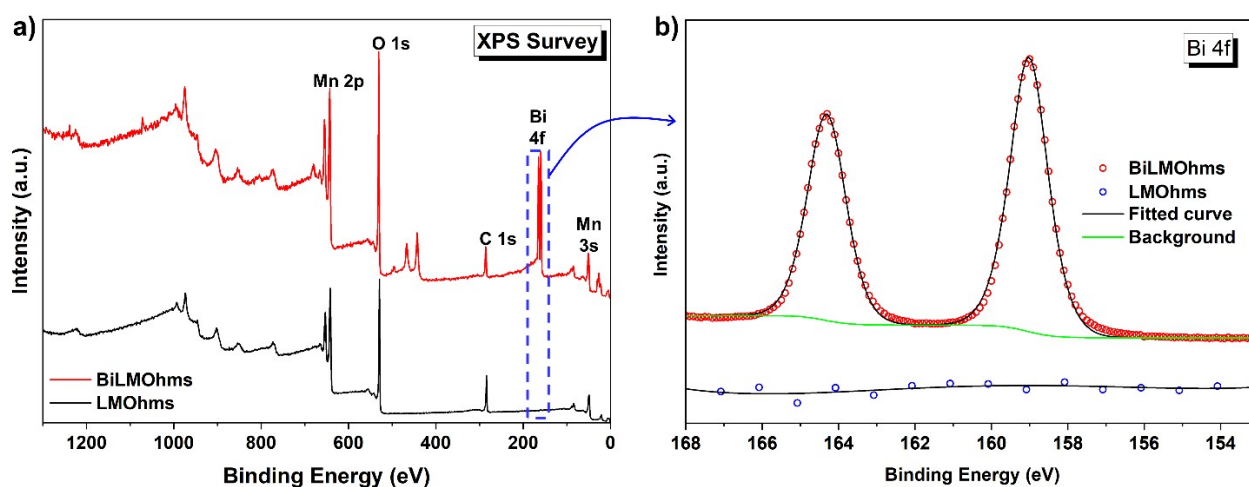


Fig. S4 XPS spectra of BiLMOhms compared to pristine LMOhms. (a) XPS survey spectra, (b) the enlarge spectra of the Bi 4f peak, as indicated by the blue rectangular area.

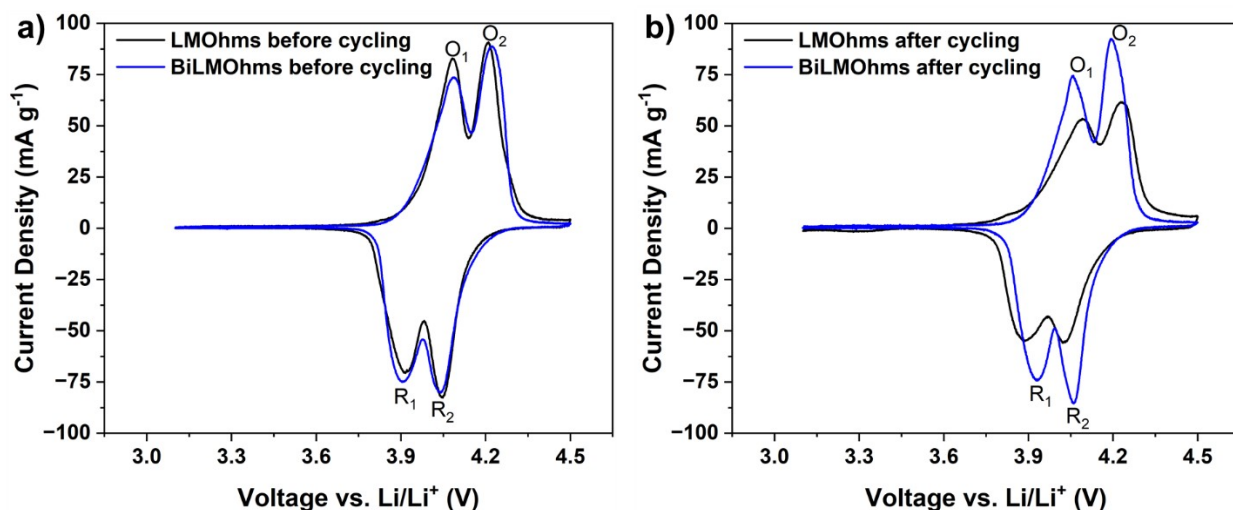


Fig. S5 Cyclic voltammetry of BiLMOhms and pristine LMOhms in half-cell configuration: (a) before cycling, and (b) after 50 cycles.

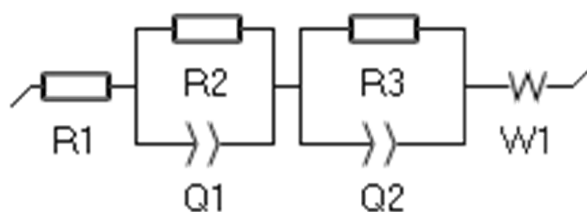


Fig. S6 Equivalent circuit model used for EIS data fitting. R_1 represents the solution resistance (R_s), corresponding to the bulk resistance of the electrolyte. R_2 denotes the surface film resistance (R_{sf}), corresponding to thin interfacial layers such as the coating layer or the cathode–electrolyte interface (CEI). R_3 is the charge transfer resistance (R_{ct}), associated with the Li^+ insertion/extraction process. W_1 represents the Warburg impedance, reflecting Li^+ diffusion within the bulk of the cathode material.

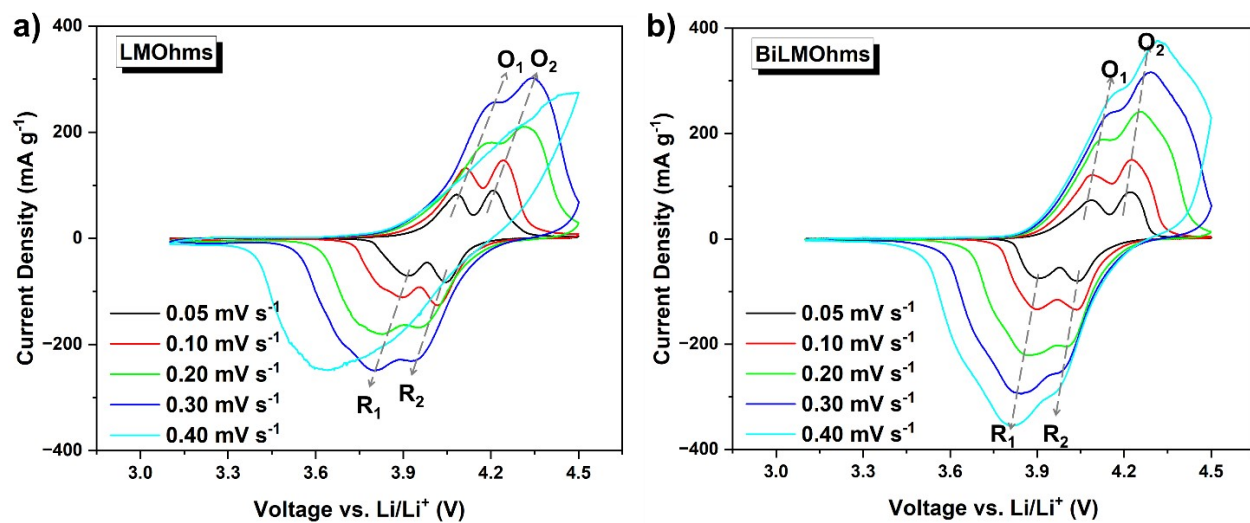


Fig. S7 Cyclic voltammetry at different scan rate of (a) LMOhms and (b) BiLMOhms.

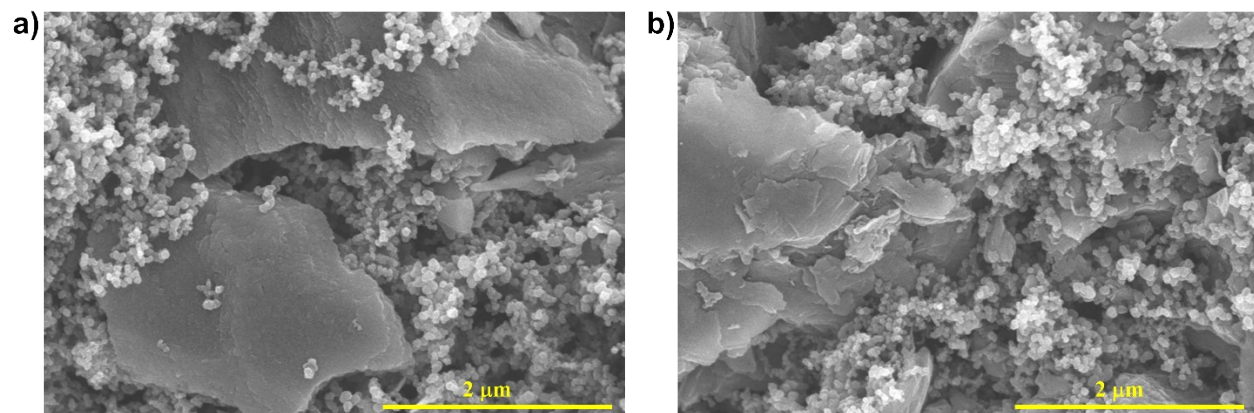


Fig. S8 SEM images of graphite anodes before cycling: (a) from the LMOhms||Graphite cell and (b) from the BiLMOhms||Graphite cell.

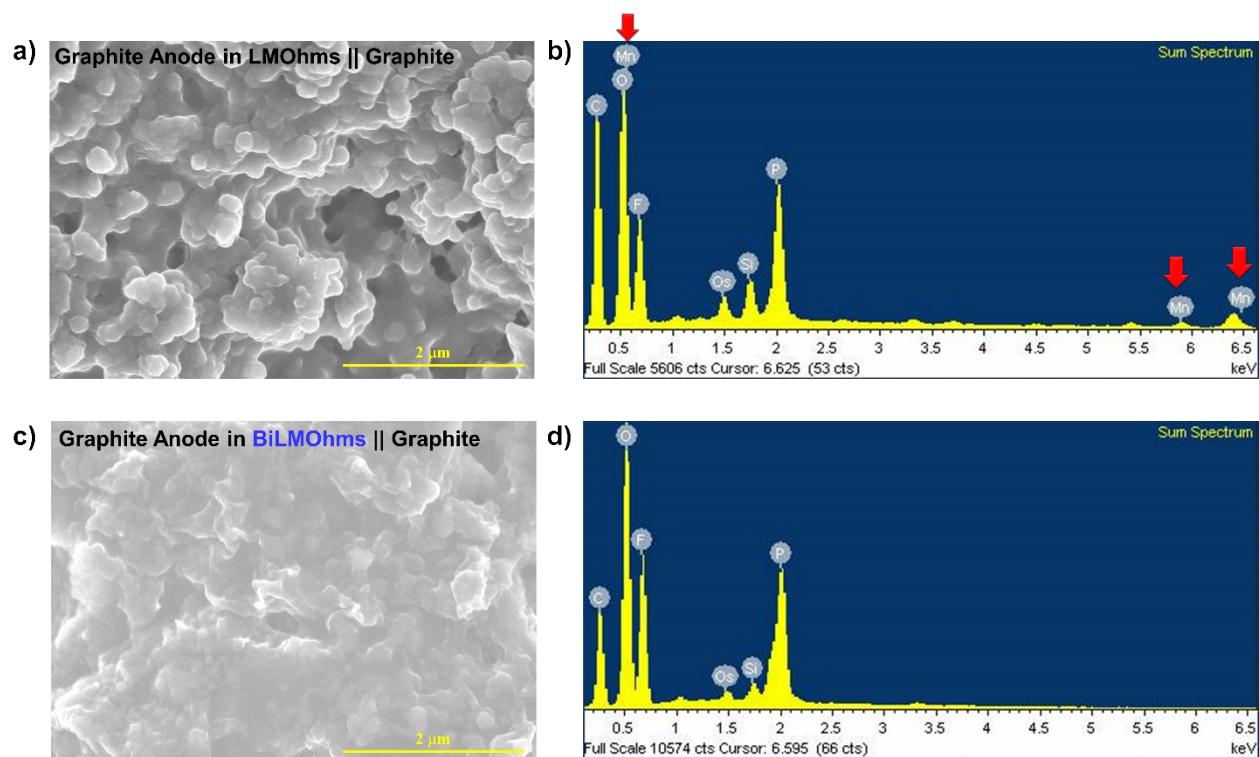


Fig. S9 Post-mortem analysis of graphite anodes after long-term cycling. (a) SEM image of the graphite anode from the LMOhms||Graphite cell and its (b) EDS spectrum. (c) SEM image of the graphite anode from the BiLMOhms||Graphite cell and its (d) EDS spectrum.

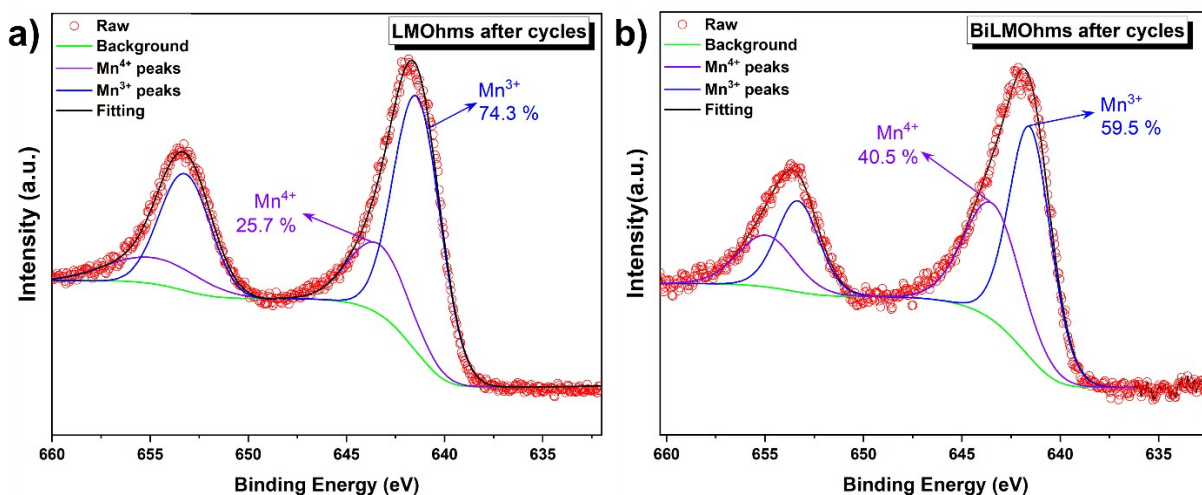


Fig. S10 Post-mortem analysis of XPS spectra after cycles: (a) LMOhms, and (b) BiLMOhms.

Table S1. Elemental composition of LMOhms and BiLMOhms determined by inductively coupled plasma (ICP) analysis.

Element	LiMn ₂ O ₄		Bi ₂ O ₃ -LiMn ₂ O ₄	
Bi	< 0.01 wt.%		1.18 wt.%	0.005 at.%
Li	3.98 wt.%	0.57 at.%	3.98 wt.%	0.57 at.%
Mn	57.9 wt.%	1.05 at.%	61.4 wt.%	1.12 at.%

Table S2. Electrochemical half-cell performance of LiMn₂O₄ cathodes with various surface coating materials reported in the literature for comparison.

No	Coating Material	Initial specific capacity (mAh g ⁻¹)	C-rate (C)	No. of cycle(N)	Capacity retention (pristine/coated)	Retention enhancement	Ref.
1	LiTaO ₃	103.0	2.03	500	65.7% / 95.0 %	29.3%	1
2	Li ₃ PO ₄	125.0	1	300	80.8% / 90.8%	10.0%	2
3	MnBO ₃	112.7	1	1000	56.8% / 85.2%	28.4%	3
4	Al ₂ O ₃ /ZrO ₂ composite	113.6	1	100	97.4% / 98.7%	1.3%	4
5	Al ₂ O ₃	120.4	1	100	72.9% / 93.5%	20.6%	5
6	ZnO	97.5	0.5	500	57.5% / 84.1%	26.6%	6
7	TiO ₂	127.3	0.5	250	80.3% / 90.1%	9.8%	7
8	LaBO ₃	119.4	1	200	76.8% / 89.5%	12.7%	8
9	Sm ₂ O ₃	101.6	1	200	76.3% / 94.7%	18.4%	9
10	Li ₂ MnO ₃	113.3	1	500	72.1% / 94.2%	22.1%	10
11	F-SnO ₂	114.9	1	100	84.1% / 97.1%	13.0%	11
12	Carbon	103.6	0.75	1000	76.0% / 82.0%	6.0%	12
13	PEDOT	115.0	1	100	79.0% / 83.0%	4.0%	13
14	PVDF	112.4	0.75	500	67.7% / 80.0%	12.3%	14
15	Bi₂O₃	97.4	1	1000	45.8% / 80.1%	34.3%	This work

Table S3. Electrochemical performance of LiMn₂O₄||Graphite full cells reported in the literature for comparison.

No	Sample label	C-rate (C)	No. of cycle(N)	Capacity retention (pristine/threated)	Retention enhancement	Ref.
1	LMO@C	1	900	46.1% / 67.2%	21.1%	15
2	LR-LMO	0.1	50	69.0% / 86.0%	17.0%	16
3	CoLi-LMO	2	300	62.0% / 94.0%	32.0%	17
4	CXL-LMO	1	500	73.0% / 84.0%	11.0%	18
5	BiLMOhms	1	100	39.6% / 87.4%	47.8%	This work

Table S4. Elemental composition of LMOhms and BiLMOhms determined by XPS.

LiMn ₂ O ₄ (LMOhms)				Bi ₂ O ₃ -LiMn ₂ O ₄ (BiLMOhms)			
Name	Peak BE	Area (P) CPS.eV	at. %	Name	Peak BE	Area (P) CPS.eV	at. %
Li1s	62.93	7218.56	7.66	Li1s	54.29	1499.63	7.63
Mn2p	642.61	2444379.73	19.08	Mn2p	642.57	527113.24	18.76
O1s	529.92	1435481.28	43.74	O1s	529.98	298064.48	50.25
C1s	284.80	400016.72	29.51	C1s	284.80	54023.33	3.07
				Bi4f	159.07	152797.39	20.29

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