Electronic Supplementary Information

Understanding the Mechanochemical Synthesis of the Perovskite $LaMnO_3$ and its Catalytic Behaviour

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Table S1: Percentage composition of La, Mn and Zr (from milling media/jar) during the mechanochemical synthesis of $LaMnO_3$

Sample	% La	% Mn	% Zr
1 h	53.5	23.2	< 0.01
2 h	54.4	22.2	0.11
3 h	55.1	22.1	0.12
4 h	54.6	21.9	0.3

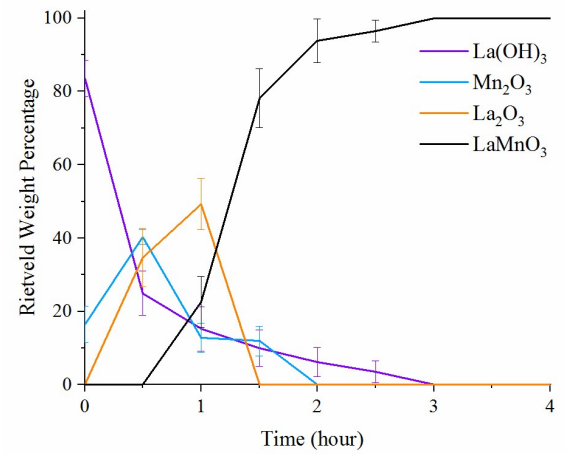

Figure S1: Rietveld weight percentage analysis during the mechanochemical synthesis of $LaMnO_3$

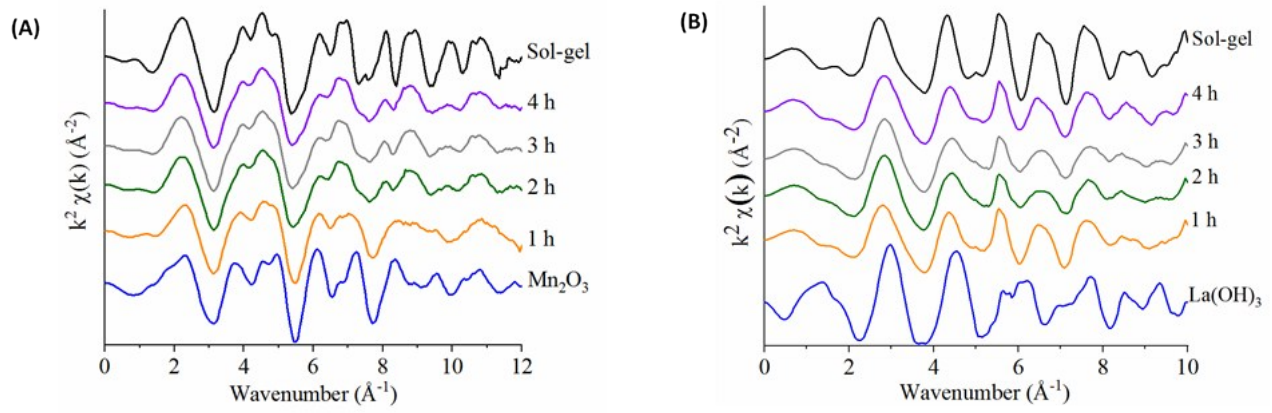

Figure S2: k^2 weighted EXAFS oscillations at the **(A)** Mn K-edge and **(B)** La L_3-edge for $LaMnO_3$ synthesised by sol-gel and by ball milling from 1 h and 4 h compared to precursor Mn_2O_3 and $La(OH)_3$, respectively

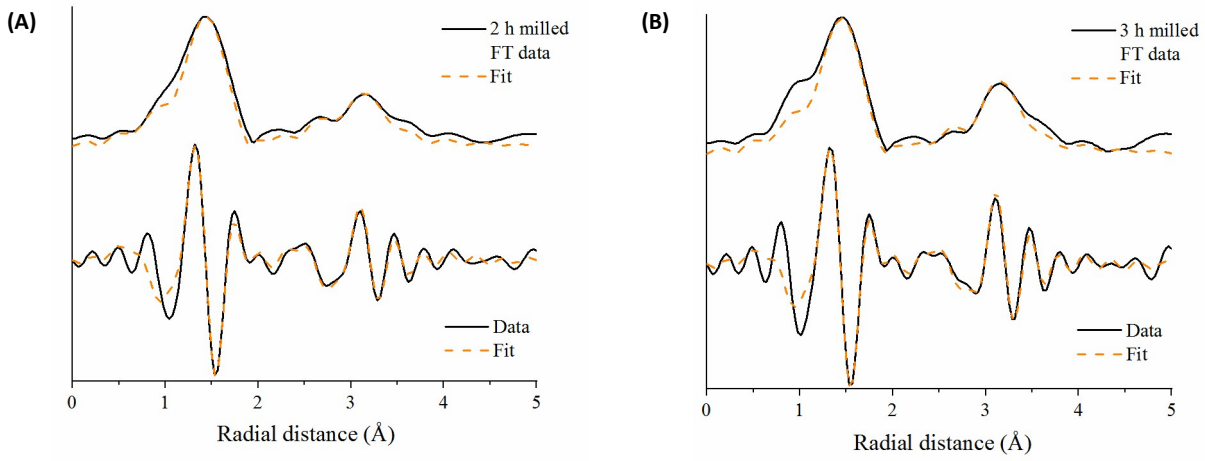

Figure S3: Mn K-edge EXAFS data after (**A**) 2 h and (**B**) 3 h of milling showing the magnitude and imaginary components of the k^2-weighted Fourier transform data and simulated fits

Table S2: EXAFS fitting parameters for the Mn K-edge for spectra collected at 1 h *ex situ* time-slices throughout the mechanochemical syntheses of $LaMnO_3$ compared to precursor Mn_2O_3 and sol-gel synthesised $LaMnO_3$ Fitting parameters: $S_0^2 = 0.7$ as determined by the use of a Mn foil standard; Fit range $3 < k > 11$, $1.2 < R > 3.85$. [a]CN fixed to known structures and the number of scattering paths reduced in order to minimise fitting parameters [b]All refined CN are within 10% error margin

Sample	Bond (Abs-Sc)	CN	E_0 (eV)	σ^2 / Å^2	R / Å
[a]Mn_2O_3	Mn-O1	4.0	-6(2)	0.007(1)	1.92(2)
	Mn-O2	2.0		0.011(6)	2.27(3)
	Mn-Mn1	6.0		0.0070(8)	3.10(2)
	Mn-Mn2	6.0		0.012(3)	3.57(3)
[a]Time 0	Mn-O1	4.0	-6(2)	0.005(1)	1.92(1)
	Mn-O2	2.0		0.009(6)	2.27(3)
	Mn-Mn1	6.0		0.0070(5)	3.09(4)
	Mn-Mn2	6.0		0.012(2)	3.57(1)
[b]Time 1 h	Mn-O1	3.9(3)	-8(7)	0.0038(9)	1.90(1)
	Mn-Mn1	4.1(5)		0.010(1)	3.07(1)
	Mn-Mn2	6.3(6)		0.015(2)	3.58(2)
[b]Time 2 h	Mn-O	5.0(2)	-7(2)	0.0065(4)	1.91(3)
	Mn-La1	5.9(5)		0.013(1)	3.24(4)
	Mn-La2	2.0(2)		0.0039(1)	3.38(1)
[b]Time 3 h	Mn-O	4.9(2)	-6(1)	0.0070(4)	1.92(3)
	Mn-La1	5.9(4)		0.012(2)	3.27(1)
	Mn-La2	1.9(1)		0.003(1)	3.40(1)
[b]Time 4 h	Mn-O	5.0(1)	-7(1)	0.0054(3)	1.90(2)
	Mn-La1	5.9(5)		0.014(1)	3.24(1)
	Mn-La2	2.0(1)		0.0043(3)	3.37(1)
[a]Sol-gel	Mn-O	6.0	-5(2)	0.0058(5)	1.93(4)
	Mn-La1	6.0		0.0071(6)	3.34(6)
	Mn-La2	2.0		0.0020(9)	3.70(9)

Table S3: Surface Atomic percentage ratios of both 3 and 4 h milled $LaMnO_3$ compared to sol-gel synthesised sample

	3 h	4 h	Sol-gel	Expected
La : Mn	1.1 : 1	1.2 : 1	1 : 1	1 : 1
O : La	1 : 0.2	1 : 0.2	1 : 0.2	1 : 0.33
O : Mn	1 : 0.2	1 : 0.2	1 : 0.2	1 : 0.33

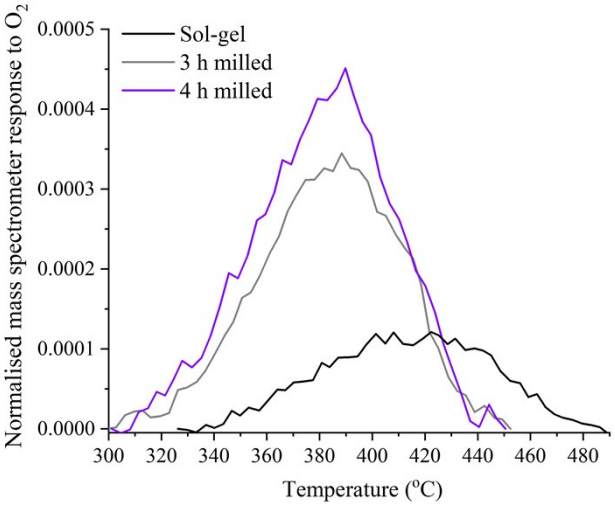

Figure S4: Normalised and base-line corrected O_2-TPD profiles of 3, 4 h milled and sol-gel synthesised $LaMnO_3$

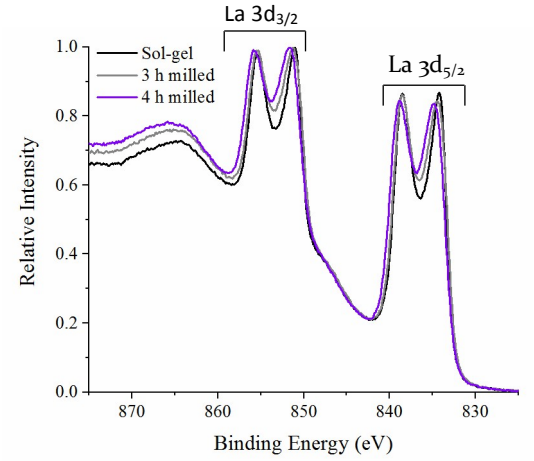

Figure S5: XPS spectra in the La 3d region of 3, 4 h ball milled samples in atmospheric milling environments compared to sol-gel synthesised $LaMnO_3$

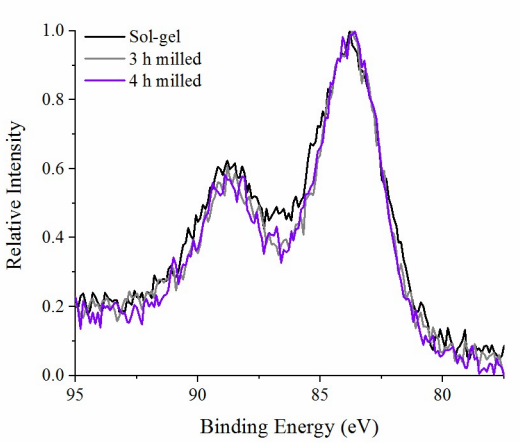

Figure S6: XPS spectra in the Mn 3s region of 3, 4 h ball milled samples compared to sol-gel synthesised $LaMnO_3$

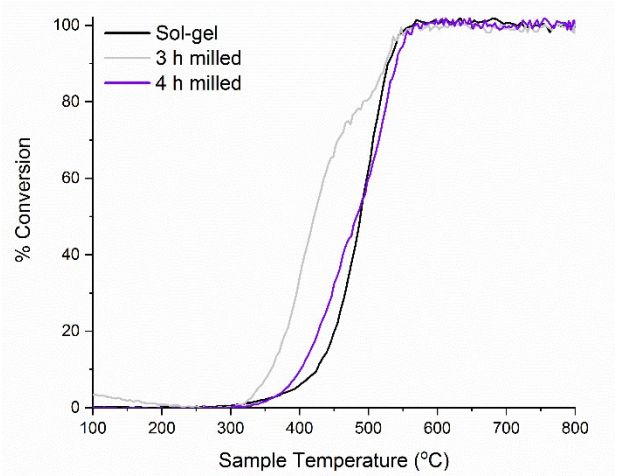

Figure S7: Light-off curve showing the percentage of deN_2O to N_2 over 3 h, 4 h ball milled and sol-gel synthesised $LaMnO_3$ using 0.5% N2O/He at 30 mL min^{-1} with a pre-treatment of He at 30 mL min^{-1}

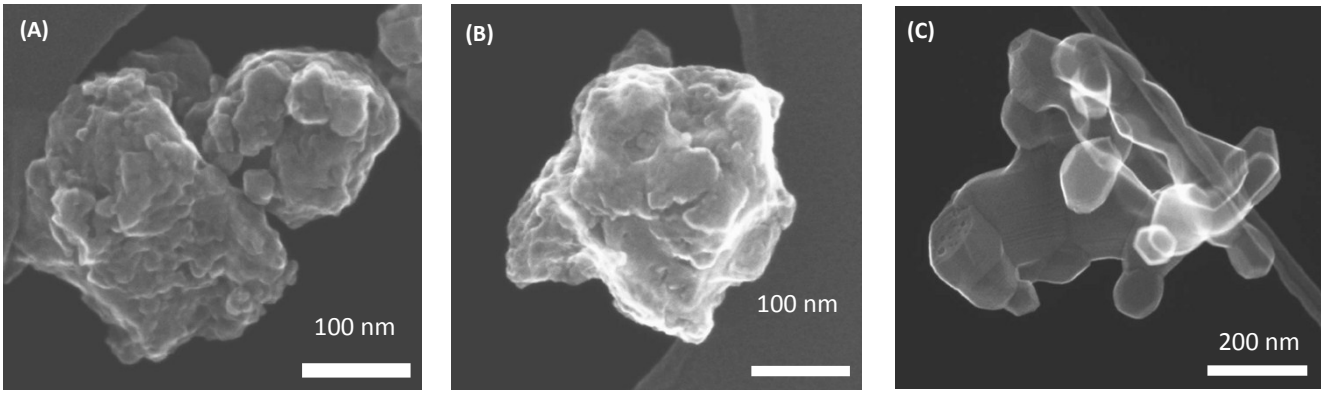

Figure S8: SEI images showing the morphological changes between **(A)** 3 h **(B)** 4 h ball milled and **(C)** sol-gel synthesized $LaMnO_3$

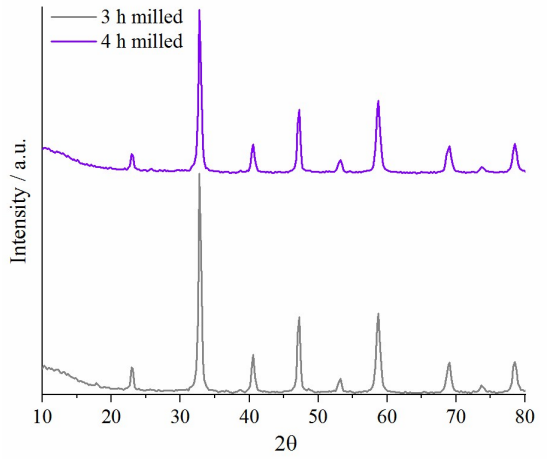

Figure S9: XRD patterns of 3 and 4 h milled $LaMnO_3$ after deN_2O up to 800 °C