Supplementary Information:

Synthesis and characterization of core-shell NMC microparticles as cathode materials for Li-ion batteries: insights from *ex-situ* and *in-situ* microscopy and spectroscopy techniques

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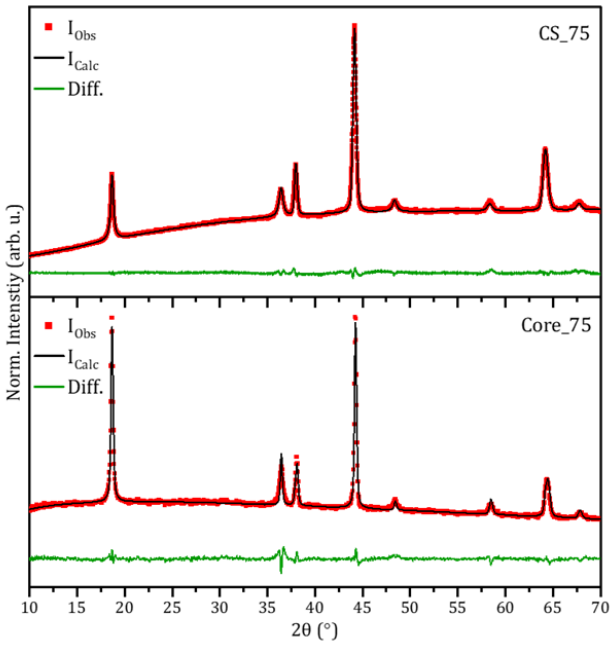

Fig. S1. Rietveld refinements of the XRD measurements for samples Core_75 and CS_75

Table S1.Parameters obtained from the Rietveld refinements shown in Figure S1.

Sample	Core_75	CS_75
a (Å)	2.886	2.892
c (Å)	14.221	14.262
c / a	4.928	4.932
z_{oxy}	0.236	0.251
$d_{M\text{-}O\ Int.}$ (Å)	1.938	2.060
$d_{M\text{-}O\ Vert.}$ (Å)	3.751	3.547
R_{wp} (%)	2.75	1.53
R_p (%)	1.93	1.21
χ^2	2.118	2.185
Ni (3b)	0.65	0.56
Mn (3b)	0.10	0.32
Co (3b)	0.10	0.09
Li (3b)	0.15	0.04
Li (3a)	0.68	0.73
Ni (3a)	0.15	0.04
O (6c)	0.88	0.92

Occupation of the 3b positions were only constrained to maintain a total sum of transition metal and Li equal to 1. Li (3a) was allowed to vary in the range of 0.5 - 1. Ni (3a) and Li (3b) were constrained to the same values.

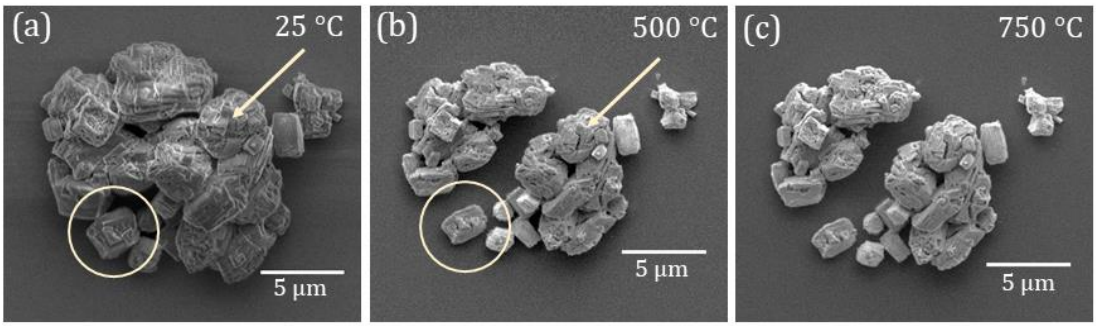

Fig. S2. In-situ SEM images of the untreated core-shell sample (a) without annealing and annealed at (b) 500 °C and (c) 750 °C.

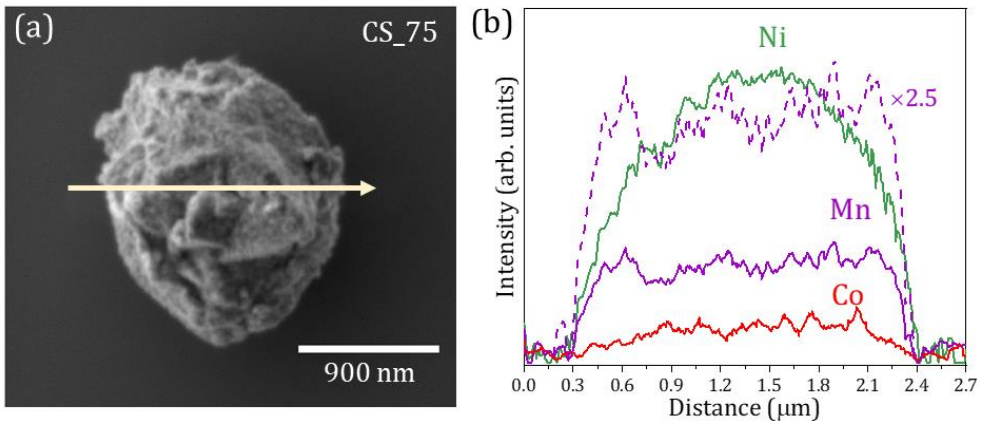

Fig. S3. (a) SEM image of a CS_75 particle and (b) the corresponding EDS profiles acquired along the arrow marked in (a)

Table S2. Atomic (%) concentration and Ni/Mn/Co ratio from Core_75 and CS_75 estimated from ICP-OES analysis

Sample	**Li (at. %)**	**Ni (at. %)**	**Mn (at. %)**	**Co (at. %)**	**Ni/Mn/Co**
Core_75	39.0 ± 0.2	49.0 ± 1.5	6.0 ± 0.3	6.0 ± 0.2	8.0/1.0/1.0
CS_75	37.1 ± 0.2	46.7 ± 1.5	10.4 ± 0.2	5.8 ± 0.2	7.4/1.7/0.9

Table S3. Parameters derived from the deconvolution of the Raman signal from samples Core_75 and CS_75.

Band	**Position (cm^{-1})**	**FWHM (cm^{-1})**	**Area (%)**
Core_75			
Ni (E_g)	359.4	97.3	8.8
Co (E_g)	433.7	90.4	18.0
Co (A_g)	482.0	70.8	24.1
Ni (A_g)	513.4	55.9	12.8
Mn (E_g)	544.2	51.7	14.8
Mn (A_g)	580.3	54.2	21.5
CS_75			
Ni (E_g)	356.2	57.7	2.5
Co (E_g)	433.3	93.3	17.1
Co (A_g)	487.6	71.9	15.6
Ni (A_g)	516.3	33.7	3.1
Mn (E_g)	545.3	50.2	18.6
Mn (A_g)	589.7	63.5	31.9
LO (R-S)	567.9	33.8	11.1

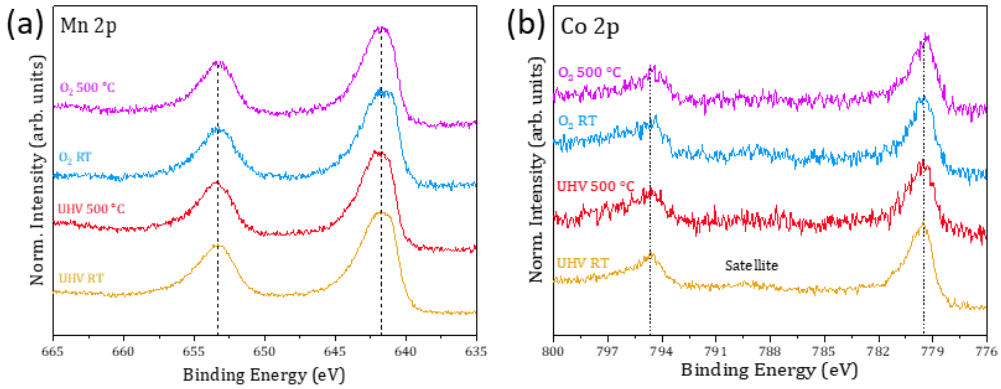

Fig. S4. In-situ XPS spectra from (a) Mn2p, (b) Co2p core levels acquired at 984 eV photon energy at room temperature and 500 °C, and under UHV and O_2 atmospheres.