## **Supplementary Information**

## Enabling uniform lithiation in solid-state synthesis by preventing pre-matured surface grain coarsening through grain boundary engineering

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**Figure S1**.TGA and XRD analysis. (a) Bare-NCM(OH)<sub>2</sub> TGA curve from 25°C to 600°C at a ramping rate of 3°C/min. (b) Bare-NCM(OH)<sub>2</sub> TGA curve from 25°C to 200°C at a ramping rate of 3°C/min and 200°C holding for 2h. Both of these two TGA experiment are performed in O<sub>2</sub> atmosphere. (c) XRD patterns of the Bare-NCM(OH)<sub>2</sub> at 200°C and 350°C holding for 3 hours. The precursor shows a mixture of hydroxide phase and rocksalt phase. (d) XRD patterns of the fully calcined WO<sub>3</sub>-coated samples (10W-NCM90, 25W-NCM90, 50W-NCM90 and 100W-NCM90) at 750°C in O<sub>2</sub> with LiOH·H<sub>2</sub>O for 12h. The I<sub>(003</sub>/I<sub>(104)</sub> ratio decreases as WO<sub>3</sub> coating amount increases.



**Figure S2**. ALD deposited W molar amount of 25W-NCM(OH)<sub>2</sub>, 50W-NCM(OH)<sub>2</sub>, 100W-NCM(OH)<sub>2</sub>, 200W-NCM(OH)<sub>2</sub>, and 300W-NCM(OH)<sub>2</sub> obtained from ICP-OES. The deposition amount shows linear relationship to ALD cycle with an amount of about 0.11‰ molar ratio of tungsten to transition metal plus tungsten per cycle.



**Figure S3**: XPS spectra of h-NCM(OH)<sub>2</sub>, 25W-NCM(OH)<sub>2</sub> and 25W-NCM90. (a) O 1s spectra for h-NCM(OH)<sub>2</sub>, (b) Ni 2p spectra for 25W-NCM(OH)<sub>2</sub> and (c) Ni 2p spectra for 25W-NCM90. The W/Ni ratio are 2.32% and 2.12% for 25W-NCM(OH)<sub>2</sub> and 25W-NCM90 each, calculated from XPS spectra.



Figure S4. SEM images of (a) a Bare-NCM $(OH)_2$  secondary particle and (b) a Bare-NCMO secondary particle. (c-e): SEM-EDS mapping of a 25W-NCM90 particle. Deep blue and green represent Ni, W signal respectively. W is "uniformly distributed in primary particles" in SEM-EDS mode.



**Figure S5**. HADDF-STEM images for a center primary particle of Bare-NCM90 and the surface of a primary particle of Bare-NCM90 and 25W-NCM90 (a) Position of inner rock salt particle in Bare-NCM. (b) Magnified lattice structure of (a) shows a rock salt phase. (c) Lattice structure of Bare-NCM surface primary particles. (d) Lattice structure of 25W-NCM surface primary particles. All HAADF-STEM images were captured along the <100> zone axis in the R<sup>3</sup>m lattice.



**Figure S6**. Contours plots of the *operando* HTXRD pattern from room temperature to  $600^{\circ}$ C with a temperature ramping rate of 2°C/min. No obvious change except for LiOH·H<sub>2</sub>O dehydration are observed below 200°C



**Figure S7**: Rate capability of Bare-NCM90, 10W-NCM90 and 25W-NCM90 at 0.1C, 0.2C, 0.5C, 1C, 2C and 5C.



**Figure S8**: (a) The estimated average volume of lithiated particle and (b) relative amount of lithiated particle for Bare-NCMO and 25-NCMO during *operando* HTXRD calcination with  $LiOH \cdot H_2O$ .



**Figure S9**: Geometry phase analysis (GPA) of Bare-NCM90 and 25W-NCM90. (a, b) HAADF-STEM image of a particle in Bare-NCM90 and 25W-NCM90. (c, d) Lattice distortion  $\varepsilon_e$  of Bare-NCM90 and 25W-NCM90 respectively. Red area represents lattice shrinkage and blue area represent stretching. All GPA results have cut off the top and bottom atoms layer to avoid calculation error at atom layer boundaries.

Table	<b>S1</b> :	Chemical	composition	of	purchased	$NCM(OH)_2$	hydroxide	precursor
determ	ined	by ICP-OE	ES.					

Chemical composition of NCM(OH) <sub>2</sub>								
Elements	Ni	Со	Mn					
Concentration (ppm)	580.706	32.859	30.345					
Atoms percentage (%)	89.91%	5.07%	5.02%					