## Nanocrystal Heterostructures of LiCoO2 with Conformal Passivating Shells

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## **Supplementary information**



Figure S1. A scheme for the preparation of heterostructure  $LiCoO_2$  nanocrystals with conformal shells.



Figure S2. X-ray diffraction patterns of (a) CoO and (b) core-shell CoO nanocrystals.



Figure S3. TEM images of (a)  $LiCoO_2$ -1h and (b)  $LiCoO_2$ -30h nanocrystals used to measure the populations with spherical or platelet morphology. Representative TEM images of spherical (c) and faceted (plate-like) (d) morphologies in the  $LiCoO_2$  nanocrystals.



![](_page_4_Figure_1.jpeg)

Figure S4. SEM image and corresponding EDX spectrum of (a) CS-LiCoO<sub>2</sub>-1h and (b) CS-LiCoO<sub>2</sub>-30h nanocrystals.

![](_page_5_Figure_0.jpeg)

Figure S5. (a) LAADF and (b) ABF images of CS-LiCoO<sub>2</sub>-30h nanocrystals

	Charge capacity above 3.9 V (mAh/g)	Charge capacity below 3.9 V (mAh/g)	% capacity of LT
LCO 1h	<i>84.1</i> ± <i>0.3</i>	59.6 ± 2.1	<i>41.5</i> ± <i>0.8</i>
CS-LCO 1h	70.6 ± 1.4	<i>41.4</i> ± <i>2.6</i>	36.9 ± 1.7
LCO 30h	<i>93.6</i> ± <i>1.8</i>	58.6 ± 3.7	38.5 ±1.6
CS-LCO 30h	73.4 ± 0.4	<i>49.3</i> ± <i>0.8</i>	40.2±0.3

Table S1. Specific capacities below and above 3.9 V during the first charge. These values are considered qualitatively representative of the ratio of HT- and LT-phase in the nanocrystals. Percent capacities of LT-phase were calculated as (LT\*100/(HT+LT)). All values were taken by averaging three cells.

![](_page_7_Figure_0.jpeg)

Figure S6. Alternate view of the <sup>7</sup>Li MAS NMR spectra of bare and core shell LiCoO<sub>2</sub>, presented in the manuscript.

![](_page_8_Figure_0.jpeg)

Figure S7. XRD patterns of (a)  $Co_3O_4$  prepared by calcination of CoO nanocrystals at 300 °C for 4 hours and (b) spinel LiCoO<sub>2</sub> nanocrystals.

![](_page_9_Figure_0.jpeg)

Figure S8. (a) Voltage versus specific capacity profiles, (b) corresponding dQ/dV plots of spinel LiCoO<sub>2</sub> nanocrystals (Figure S5) and (c) evolution of normalized specific capacity (solid symbol) and Coulombic efficiency (open symbol) when cycling with a discharge cutoff voltage of 2.0 V and a charge cutoff voltage of 4.2 V vs Li<sup>+</sup>/Li<sup>0</sup> at C/20 rate.

![](_page_10_Figure_0.jpeg)

Figure S9. Evolution of discharging specific capacity (solid symbol) and Coulombic efficiency (open symbol) when cycling at C/20.

![](_page_11_Figure_0.jpeg)

Figure S10. (a) Voltage versus specific profiles, (b) corresponding dQ/dV plots, (c) normalized specific capacity (solid symbol) and coulombic efficiency (open symbol), and (d) absolute discharge capacity (solid symbol) and coulombic efficiency of bare and core-shell LiCoO<sub>2</sub> nanocrystal electrodes when cycled at C/20 in an electrolyte consisting of 1.2 M LiPF<sub>6</sub> in a 3:7, w/w, mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC).

![](_page_12_Figure_0.jpeg)

Figure S11. dQ/dV plots of (a) LiCoO<sub>2</sub>-1h, (b) CS-LiCoO<sub>2</sub>-1h, (c) CS-LiCoO<sub>2</sub>-30h, and (d) CS-LiCoO<sub>2</sub>-30h in the 1<sup>st</sup> (black) and 100<sup>th</sup> cycle (red), corresponding to the cells in Figure 6.