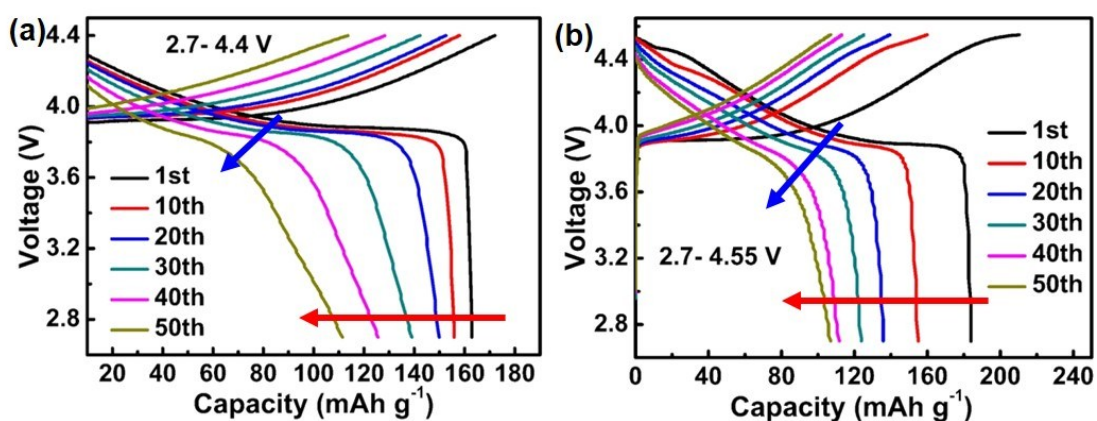


## Supporting information

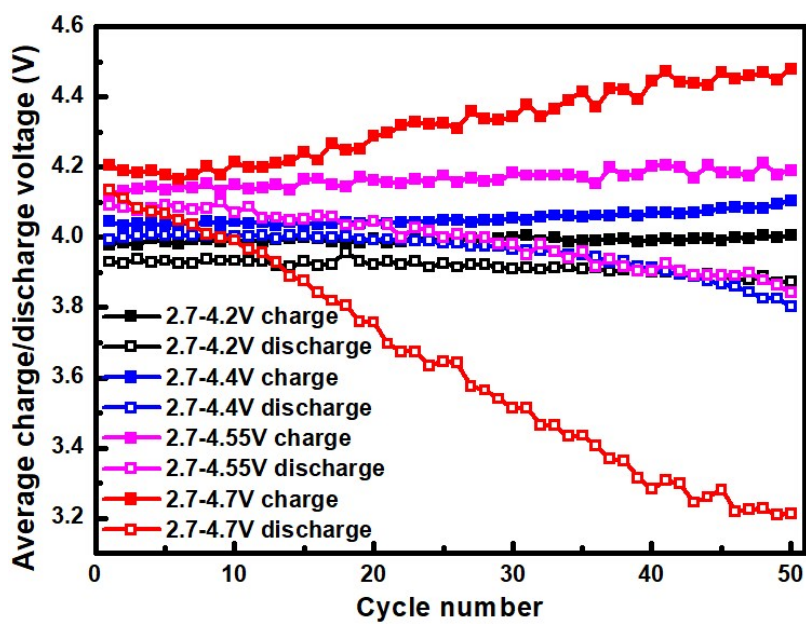
### Origins of capacity and voltage fading of LiCoO<sub>2</sub> upon high voltage cycling

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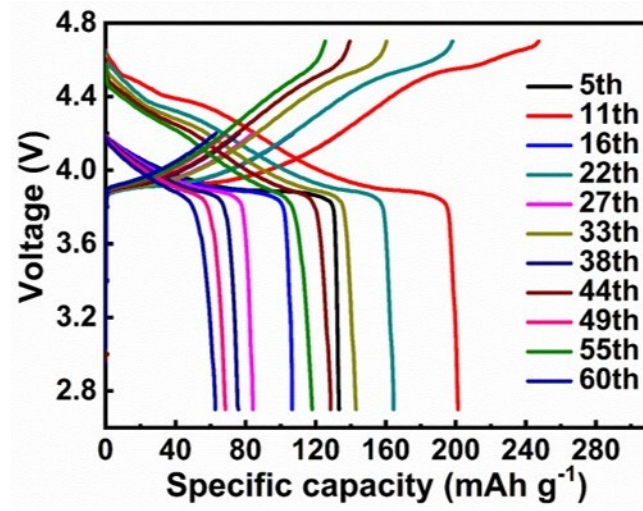
Beijing Key Laboratory of Microstructure and Properties of Solids, Institute of Microstructure and Properties of Advanced Materials, Beijing University of Technology, Beijing 100124, China



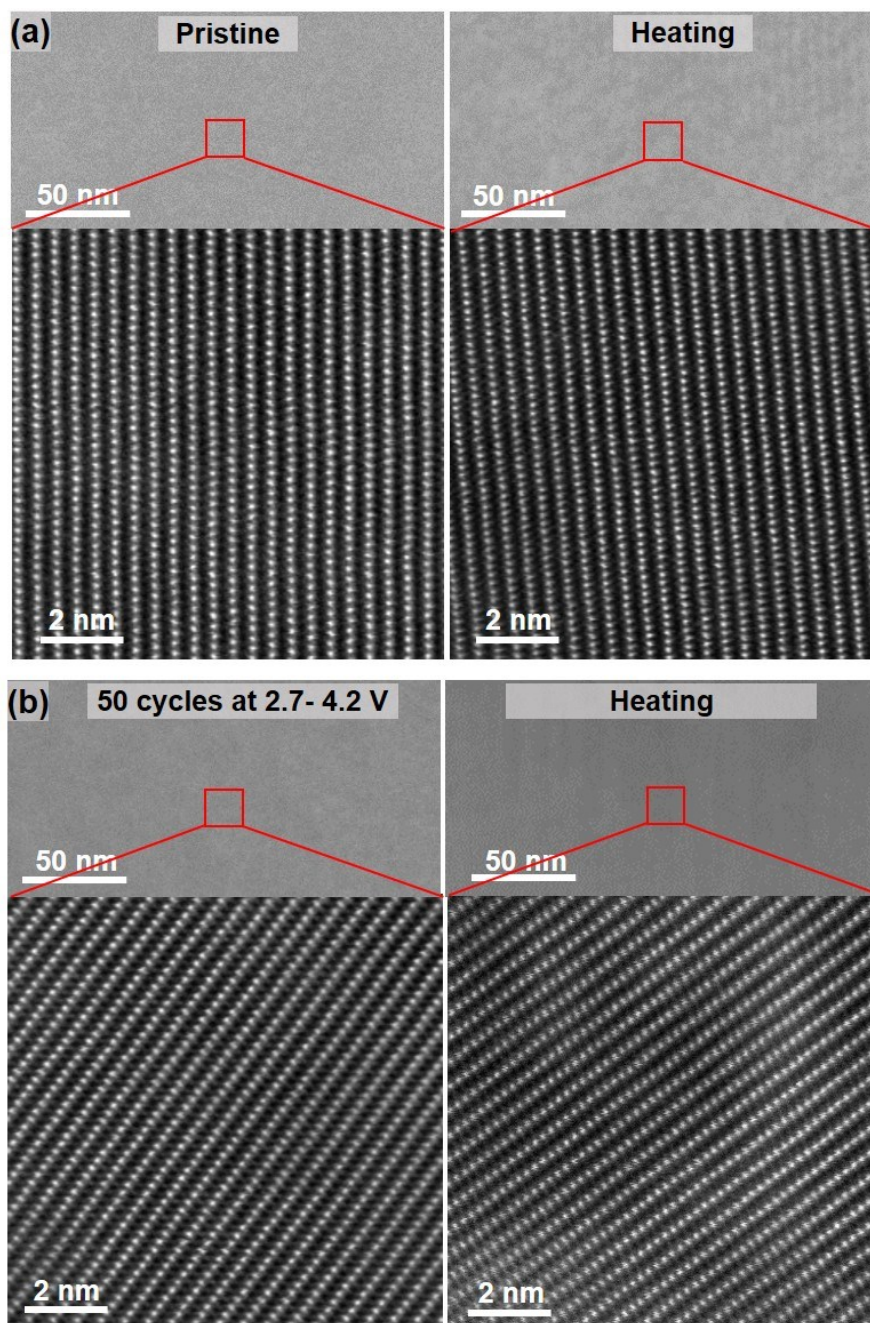
**Figure S1.** (a) Evolution of the charge/discharge voltage profiles cycled at 2.7- 4.4 V.  
(b) Evolution of the charge/discharge voltage profiles cycled at 2.7- 4.55 V.



**Figure S2.** The average charge/discharge voltages of  $\text{LiCoO}_2/\text{Li-metal}$  half-cells when cycled at  $0.2\text{C}$  rate ( $140 \text{ mAh g}^{-1}$ ) with different voltage windows, 2.7-4.2V, 2.7-4.4V, 2.7-4.55V and 2.7-4.7V.

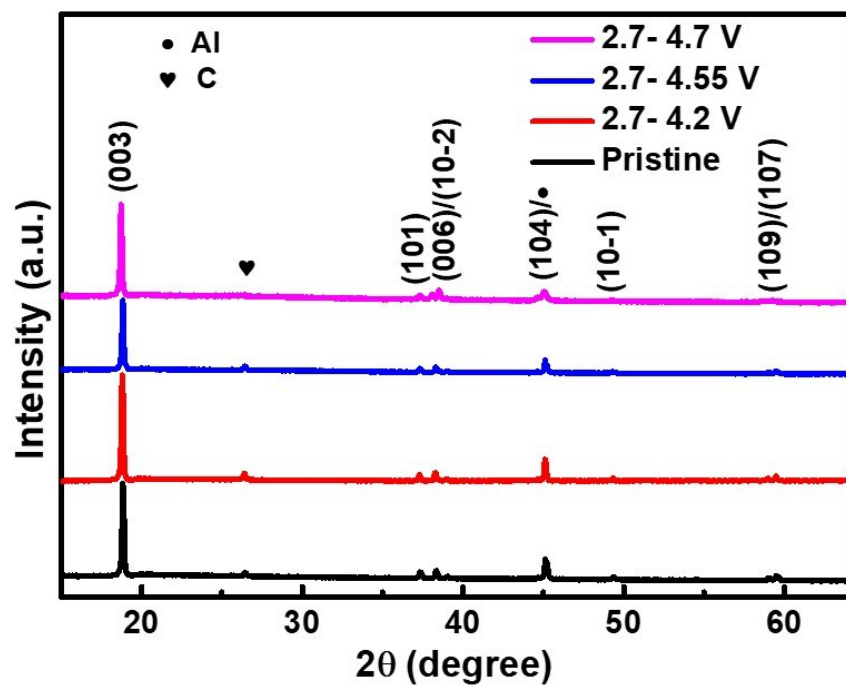


**Figure S3.** The charge/discharge voltage from Figure 1d to show the capacity and voltage fading.

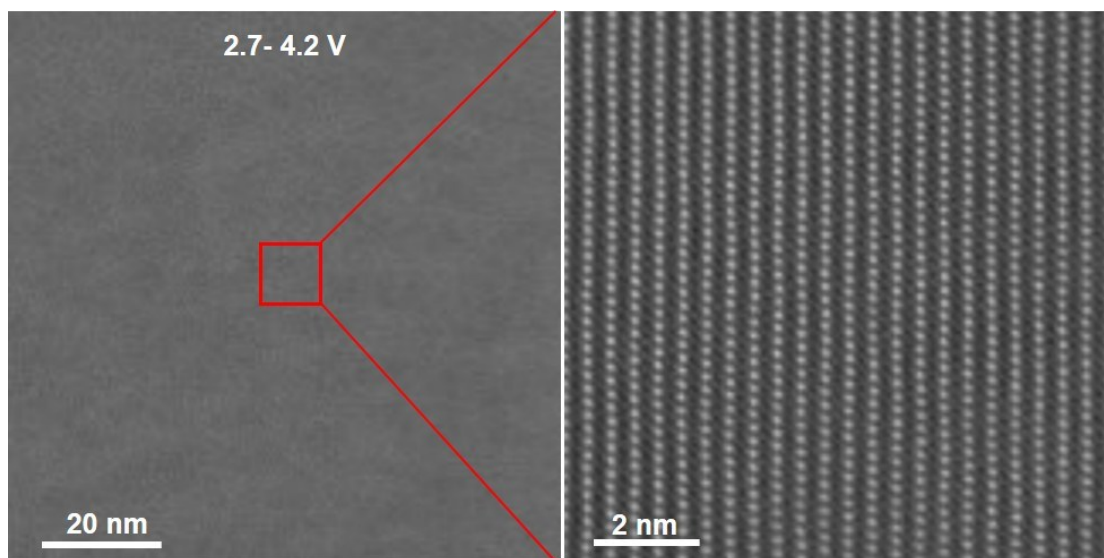


**Figure S4.** STEM-HAADF observation of the bulk structure before and after heat treatment.

(a) A low magnification and enlarged lattice STEM-HAADF image of the pristine LiCoO<sub>2</sub> cathode before heating (left panel) and after heating to 200 °C for 30 minutes (right panel). (b) A low magnification and enlarged lattice STEM-HAADF image of the LiCoO<sub>2</sub> cathode after 50 cycles at 2.7-4.2 V before heating (left panel) and after heating to 200 °C for 30 minutes (right panel). The typical layered structure still maintain after heating for (a) and (b).

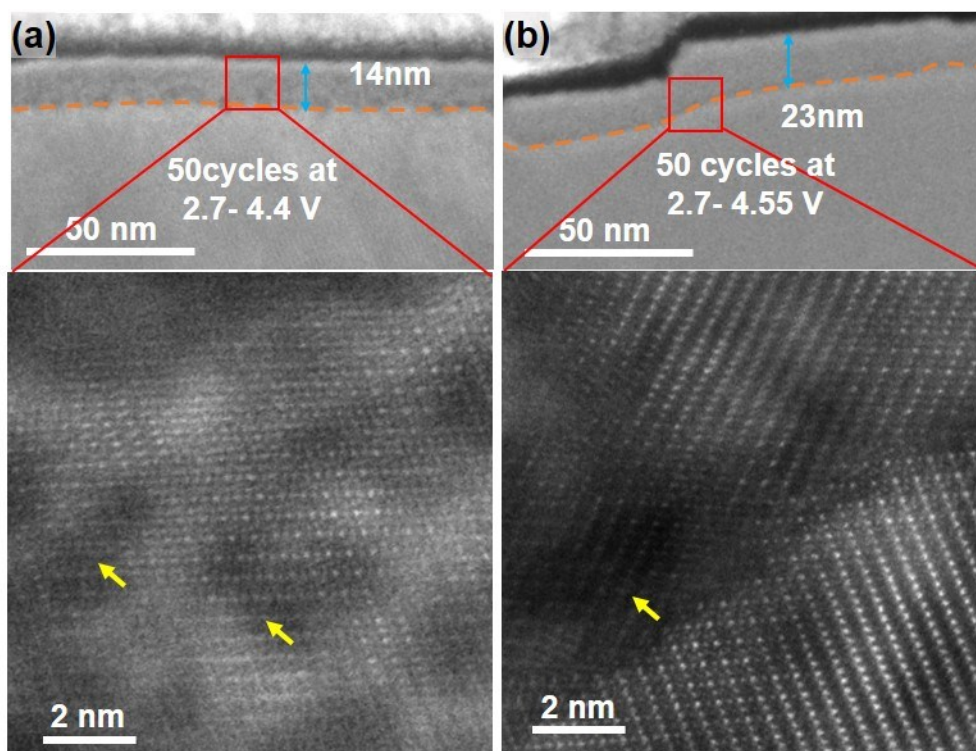


**Figure S5.** The XRD patterns of the pristine LiCoO<sub>2</sub> cathode sample and the samples after 50 cycles in the voltage range of 2.7-4.2 V, 2.7-4.55 V and 2.7-4.7 V.



**Figure S6.** STEM-HAADF images of the sample after 50 cycles in the voltage range of 2.7- 4.2 V.

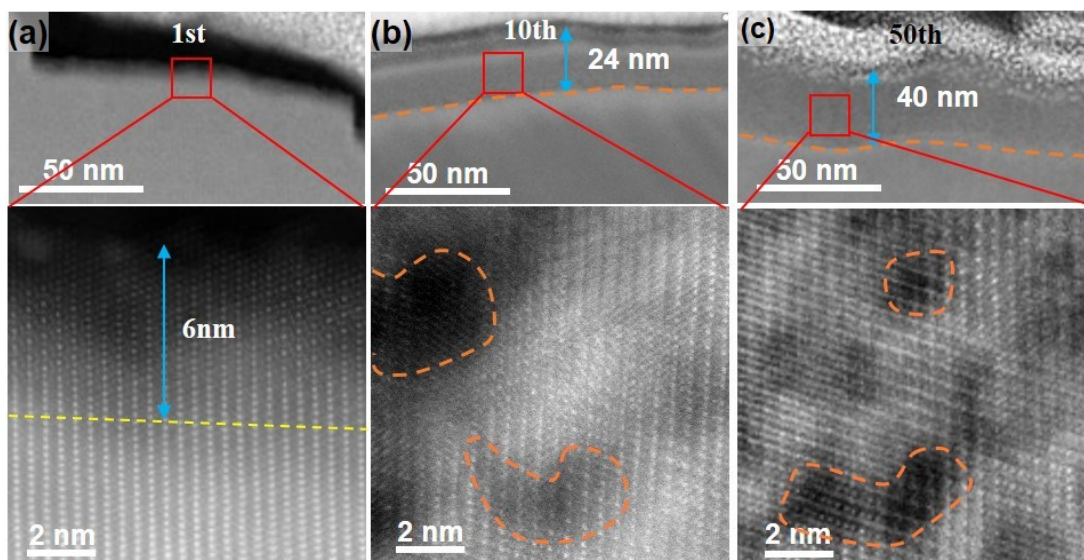




**Figure S7.** STEM-HAADF observation of the surface phase transformation layer of LiCo<sub>2</sub> cathode after electrochemical cycling.

(a) Low and high resolution STEM-HAADF images of LiCo<sub>2</sub> electrodes cycled at 2.7-4.4 V.

(b) Low and high resolution STEM-HAADF images of LiCo<sub>2</sub> electrodes cycled at 2.7-4.55 V.



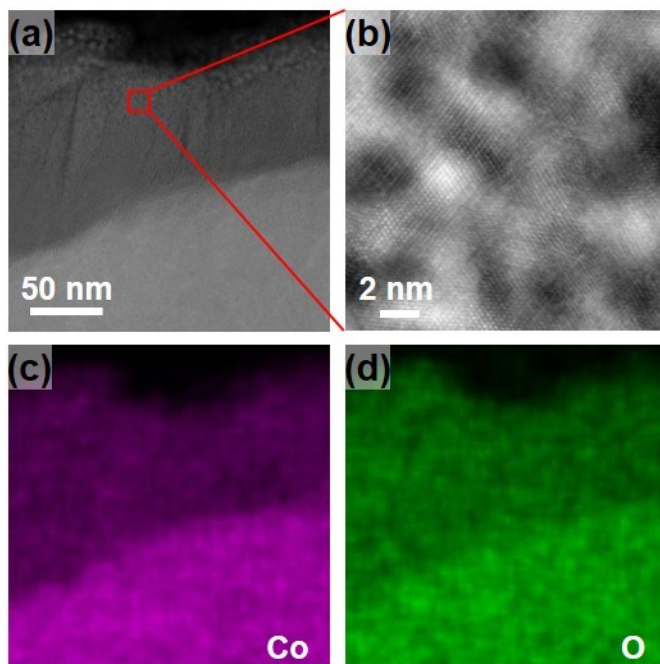
**Figure S8.** STEM-HAADF observation of the surface phase transformation layer of  $\text{LiCoO}_2$  cathode cycled with different cycle numbers.

(a) Low and high resolution STEM-HAADF images of  $\text{LiCoO}_2$  electrodes after one cycle.

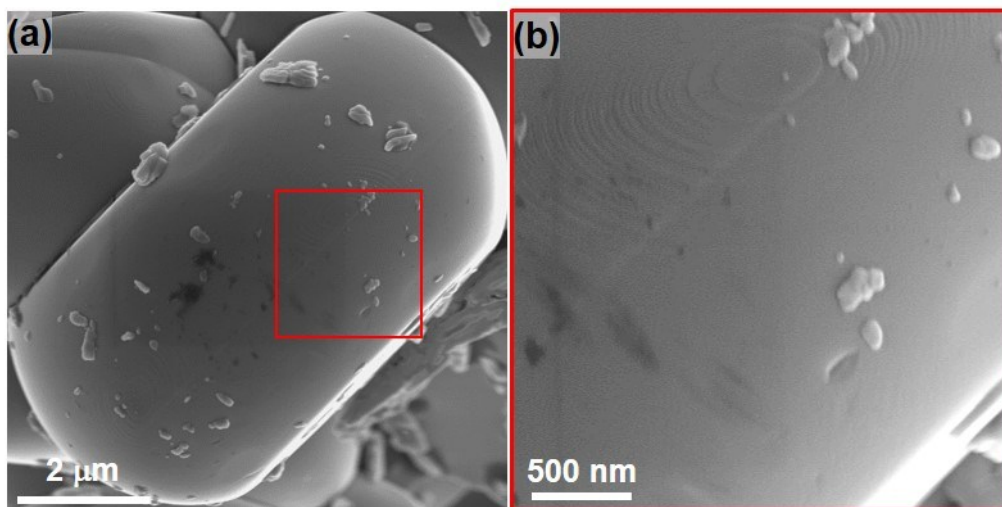
(b) Low and high resolution STEM-HAADF images of  $\text{LiCoO}_2$  electrodes cycled after 10 cycles.

(c) Low and high resolution STEM-HAADF images of  $\text{LiCoO}_2$  electrodes cycled after 50 cycles.

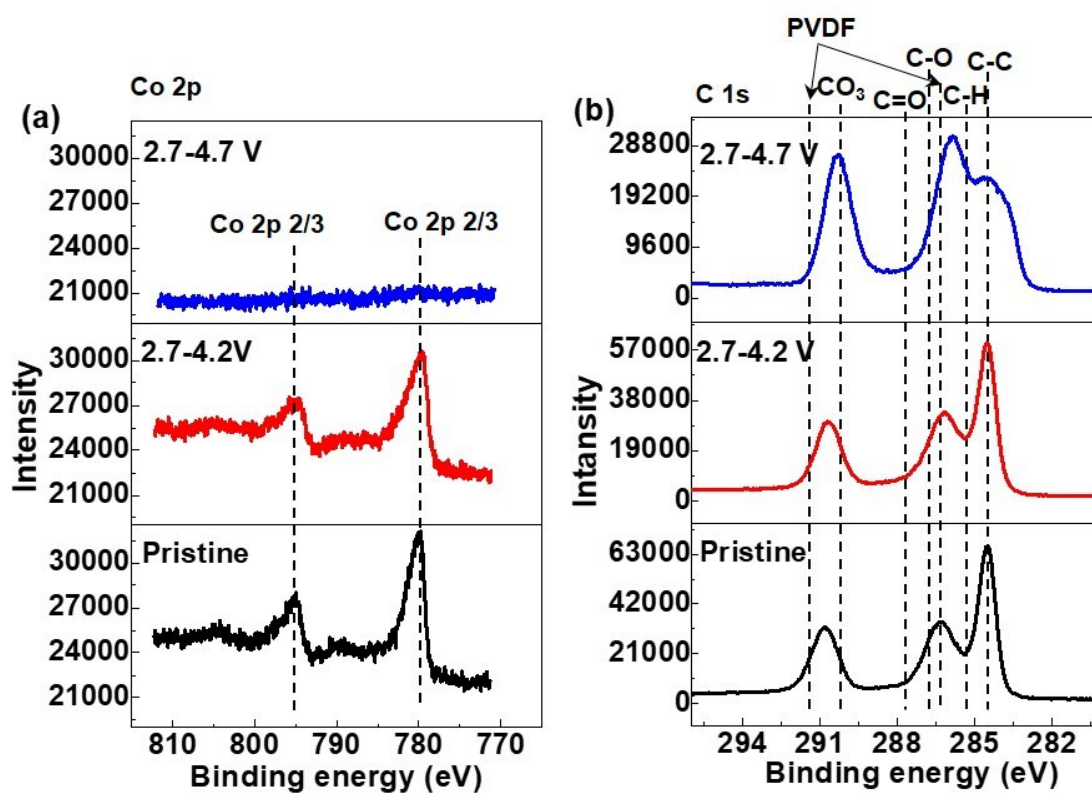




**Figure S9.** Surface corrosion of LiCoO<sub>2</sub> particles after 200 cycles at 2.7-4.2V. (a) Low magnification STEM-HAADF image to show the surface reconstruction layer indicated by the yellow dashed line. (b) Enlarged lattice STEM-HAADF image from (a). (c-d) EDS mapping from (a), showing loss of Co and O at the SRL layer.



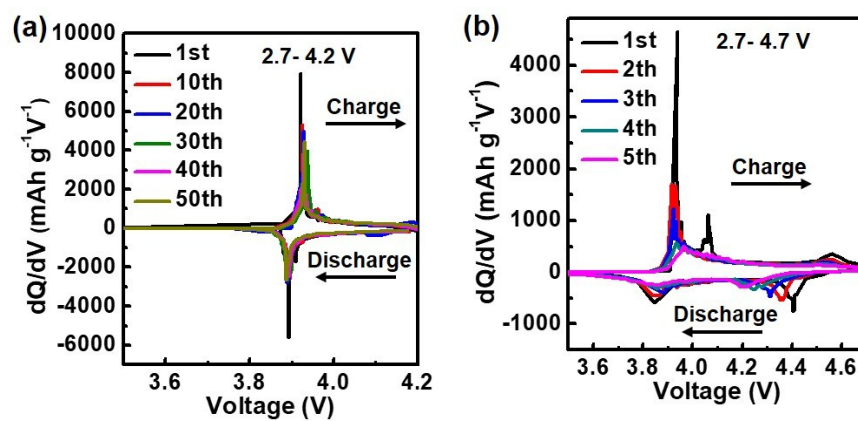
**Figure S10.** SEM images of pristine LiCoO<sub>2</sub>. The particle surface is clear and clean.



**Figure S11.** The component analysis of CEI layer by XPS.

(a) The Co 2p XPS spectra of LiCoO<sub>2</sub> electrode with pristine sample and the samples after 50 cycles in the cycling voltage of 2.7- 4.2 V and 2.7- 4.7 V.

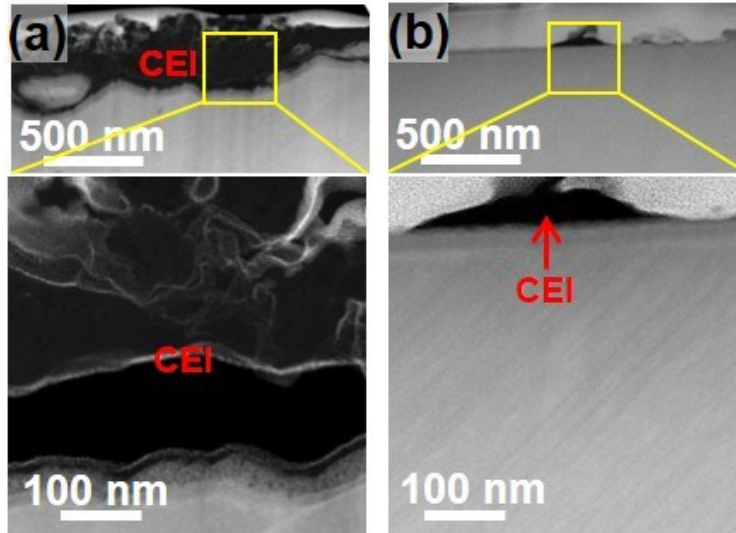
(b) C1s XPS spectra of LiCoO<sub>2</sub> electrode with pristine sample and cycling 50 cycles in the cycling voltage of 2.7- 4.2 V and 2.7- 4.7 V.



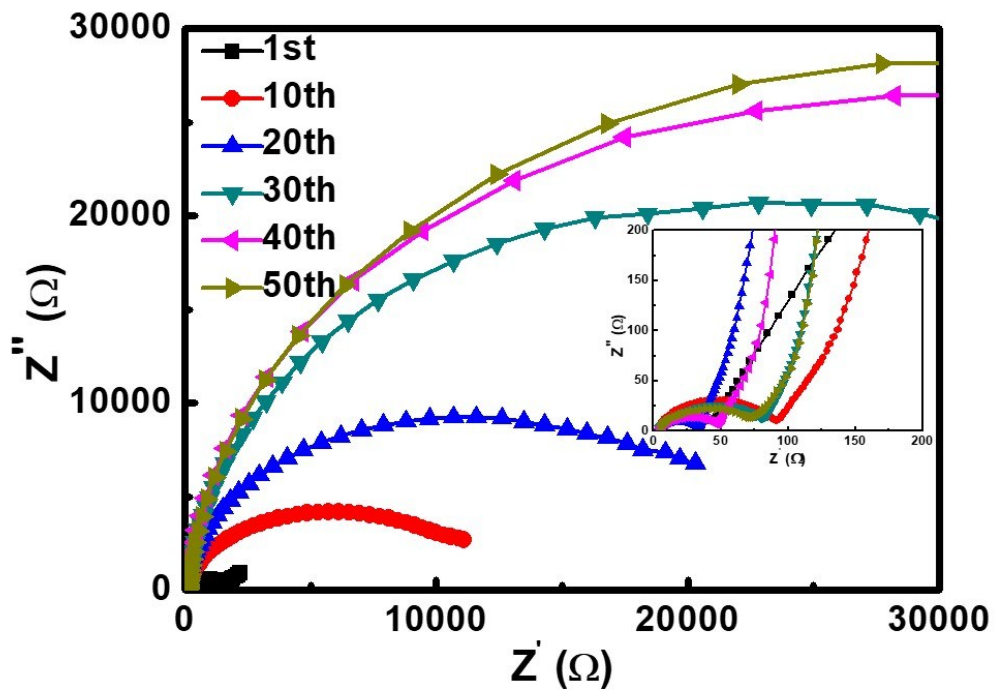
**Figure S12.**  $dQ/dV$  curves of  $\text{LiCoO}_2$  cathode cycled at different voltage windows.

(a)  $dQ/dV$  curves of  $\text{LiCoO}_2$  cathode measured at 1st, 10th, 20th, 30th, 40th, 50th in the cycling voltage of 2.7- 4.2 V.

(b)  $dQ/dV$  curves of  $\text{LiCoO}_2$  cathode measured at 1st, 2th, 3th, 4th, 5th in the cycling voltage of 2.7- 4.7 V.

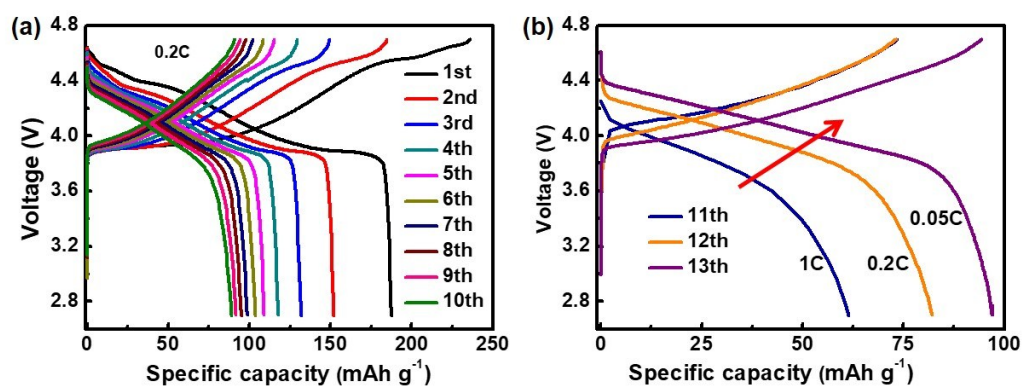


**Figure S13.** Observing the CEI layer evolution when cycled at different voltage windows. (a) STEM-HAADF images of a  $\text{LiCoO}_2$  particle after 10 cycles at 2.7-4.7 V, showing the CEI layer is hundreds of nanometers in thickness. (b) STEM-HAADF images of a  $\text{LiCoO}_2$  particle after 10 cycles at 2.7-4.7 V followed by 10 cycles at 2.7-4.2 V, showing the CEI layer left on particle surface is thin and not uniform.

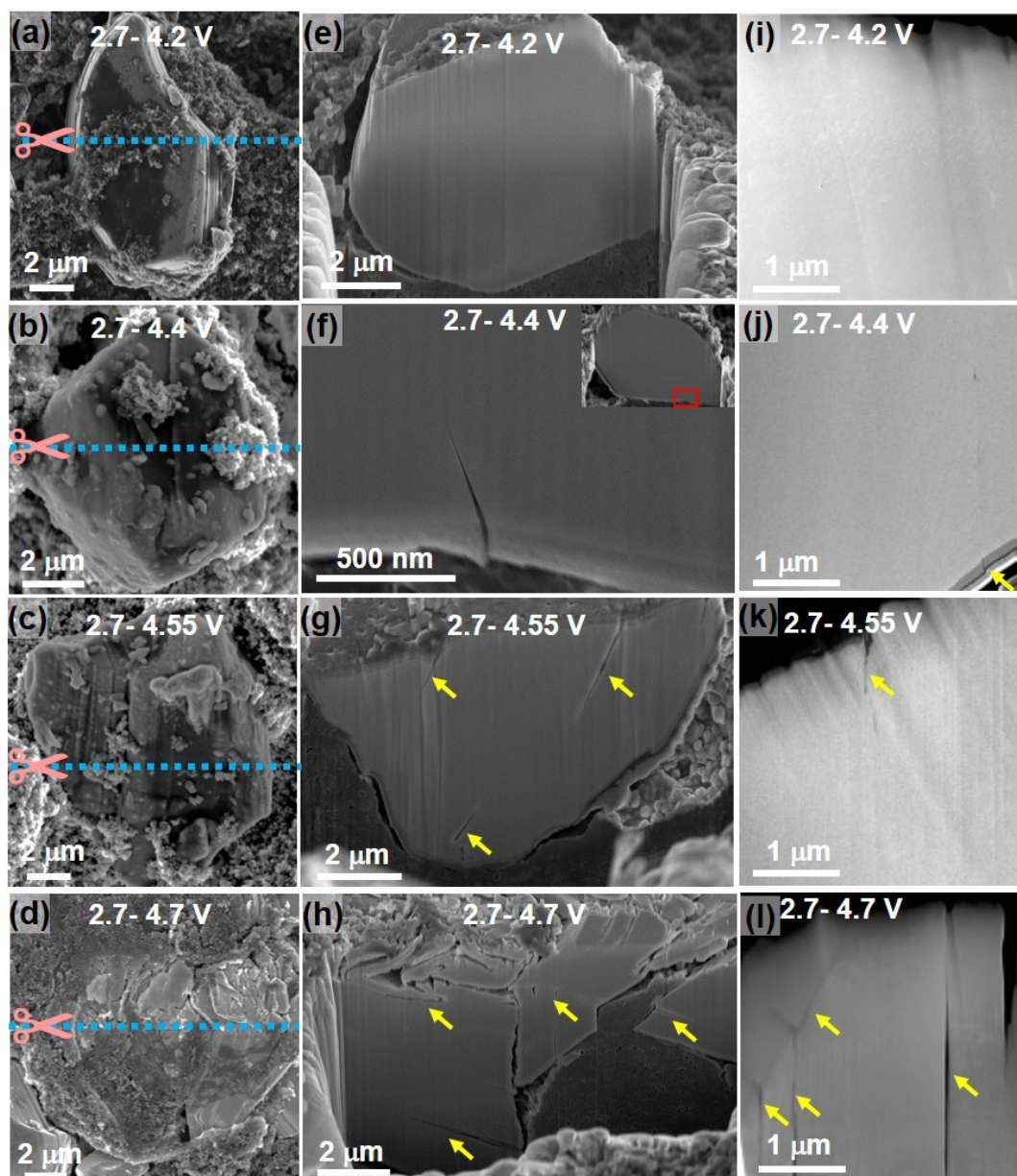


**Figure S14.** The electrochemical impedance spectra of LiCoO<sub>2</sub>/Li-metal Half-cells measured at 1st, 10th, 20th, 30th, 40th, 50th in the cycling voltage of 2.7- 4.7 V.





**Figure S15.** (a) Charge/discharge voltage profiles of a LiCoO<sub>2</sub>/Li-metal Half-cell during the first 10 cycles cycled at 2.7- 4.7 V at 0.2C rate. (b) The charge/discharge voltage profiles at 11<sup>th</sup> cycle (1C rate), 12<sup>th</sup> cycle (0.2C rate) and 13<sup>th</sup> cycle (0.05C rate) followed (a). The red arrow indicates voltage fading is alleviated by reducing cycle current.



**Figure S16.** Observing cracks in  $\text{LiCoO}_2$  samples cycled at different voltage windows.

(a-d) SEM images of surface morphology of  $\text{LiCoO}_2$  electrodes after 50 cycles. (a) 2.7- 4.2 V, (b) 2.7- 4.4 V, (c) 2.7- 4.55 V and (d) 2.7- 4.7 V.

(e-h) Corresponding cross-sectional SEM images from a-d. (e) 2.7- 4.2 V, (f) 2.7- 4.4 V, (g) 2.7- 4.55 V and (h) 2.7- 4.7 V. Cracks are highlighted by yellow arrows.

(i-l) Low resolution STEM-HAADF images of  $\text{LiCoO}_2$  electrodes after 50 cycles. (i) 2.7- 4.2 V, (j) 2.7- 4.4 V, (k) 2.7- 4.55 V and (l) 2.7- 4.7 V. Cracks are highlighted by yellow arrows.