Supporting Information

Zirconium-doped precursor regulates surface-bulk structure of $LiCoO_2$ for stable 4.5 V performance

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$$CoSO_4 + 2NH_4HCO_3 \rightarrow CoCO_3\downarrow + (NH_4)_2SO_4 + H_2O + CO_2\uparrow$$

$$6CoCO_3 + O_2 \rightarrow 2Co_3O_4 + 6CO_2$$

$$4Co_3O_4 + 6Li_2CO_3 + O_2 \rightarrow 12LiCoO_2 + 6CO_2$$

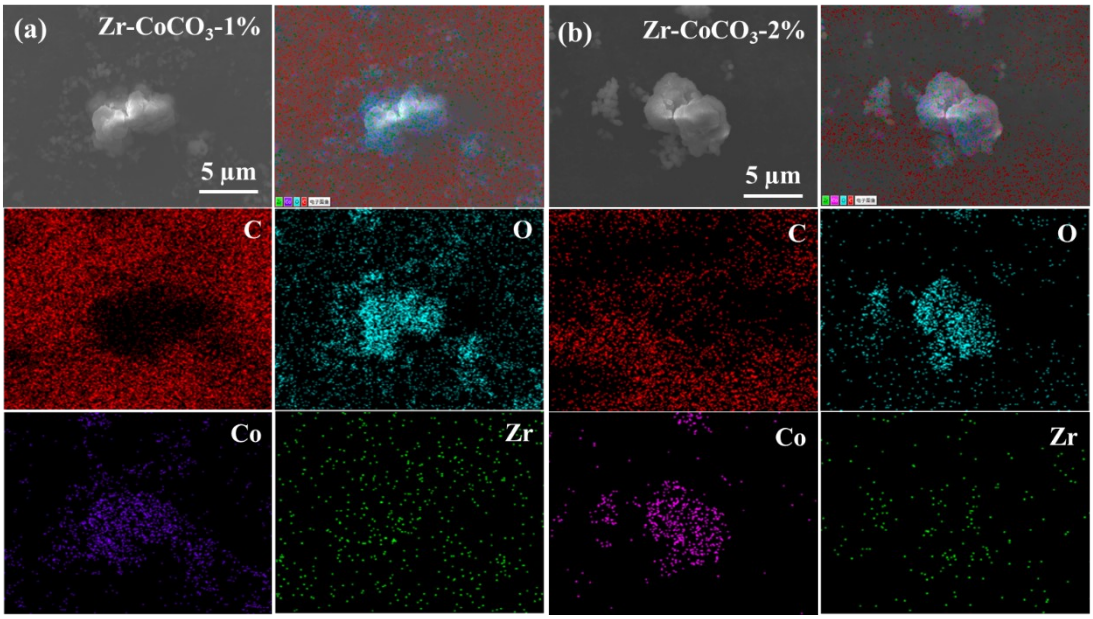

Figure S1 EDS mapping of (a) Zr-$CoCO_3$-1% and (b) Zr-$CoCO_3$-2%

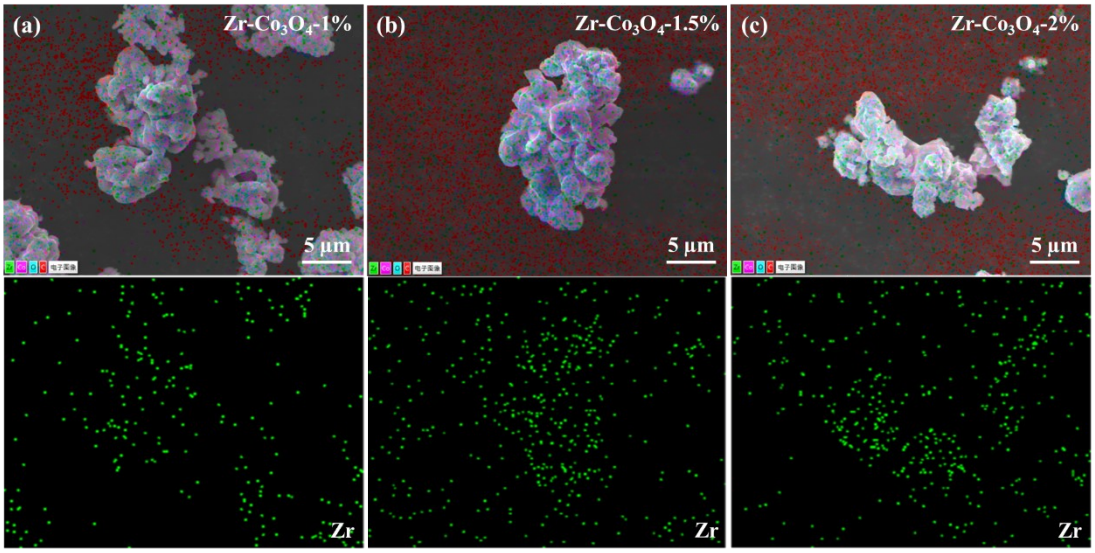

Figure S2 EDS mapping of (a) Zr-Co_3O_4-1%, (b) Zr-Co_3O_4-1.5% and (c) Zr-Co_3O_4-2%

Table S1 Tap density test data for $LiCoO_2$ and Zr-$LiCoO_2$ samples

	Tap density (g cm^{-3})
$LiCoO_2$	2.74
Zr-LCO-1	2.78
Zr-LCO-2	2.78
Zr-LCO-3	2.98

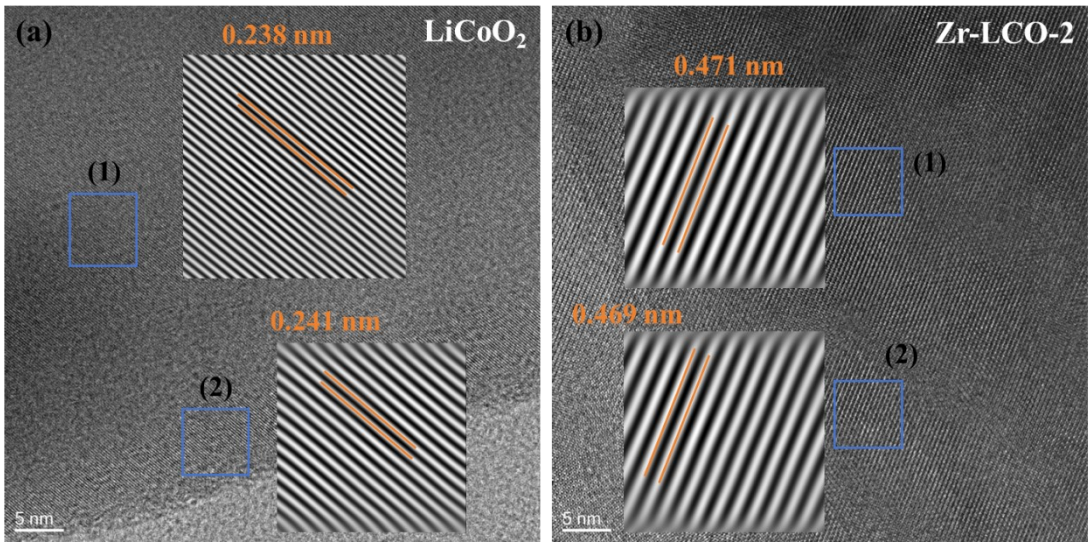

Fig. S3 HRTEM images of (a) $LiCoO_2$ and (b) Zr-LCO-2

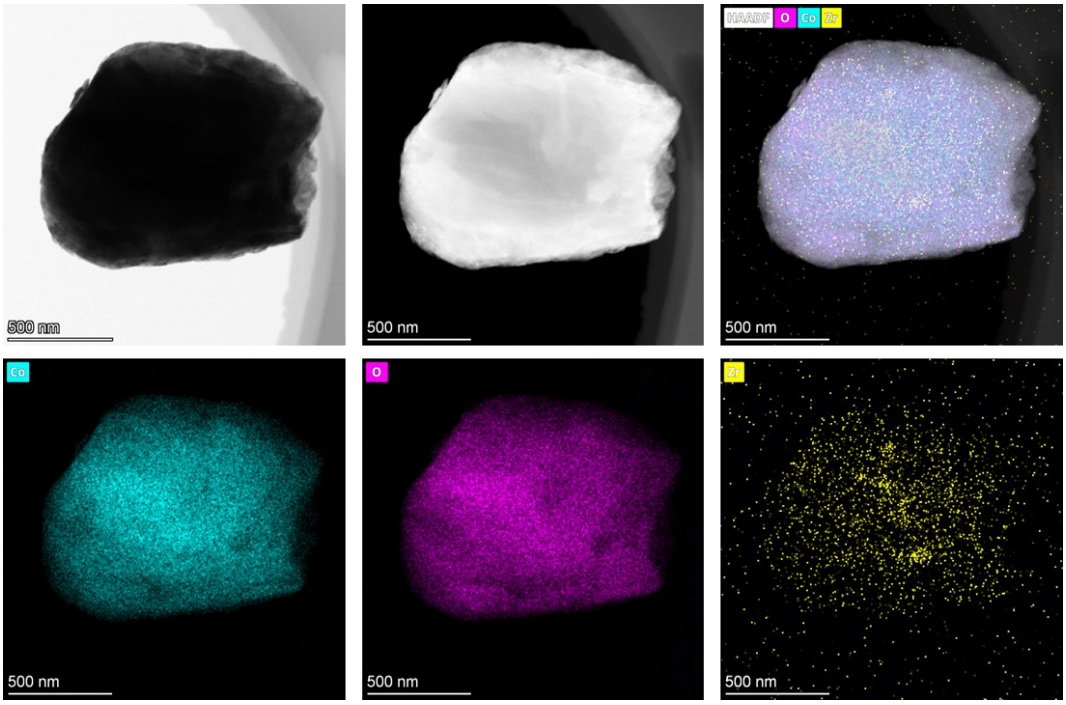

Fig. S4 EDS mapping of Zr-LCO-2

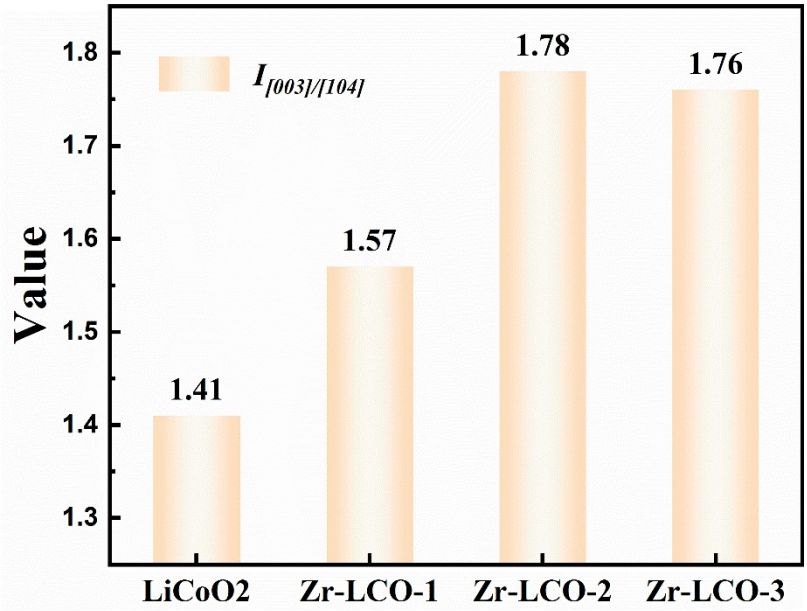

Figure S5 $I_{[003]/[104]}$ value of $LiCoO_2$ samples

Table S2 Cell parameters of refined $LiCoO_2$ samples

Sample	a	b	c	volume	c/a
$LiCoO_2$	2.811049	2.811049	14.02094	95.95	4.98779637
Zr-LCO-1	2.812326	2.812326	14.03545	96.137	4.99069062
Zr-LCO-2	2.812015	2.812015	14.02883	96.07	4.98888911
Zr-LCO-3	2.812114	2.812114	14.03132	96.094	4.98959893

Table S3 Content of Co^{2+} and Co^{3+} in XPS test data

Sample	Co^{3+}	Co^{2+}	Co^{3+}/Co^{2+}
$LiCoO_2$	45.97%	54.03%	0.85
Zr-LCO-1	42.58%	57.42%	0.74
Zr-LCO-2	40.93%	59.07%	0.69
Zr-LCO-3	37.68%	62.32%	0.60

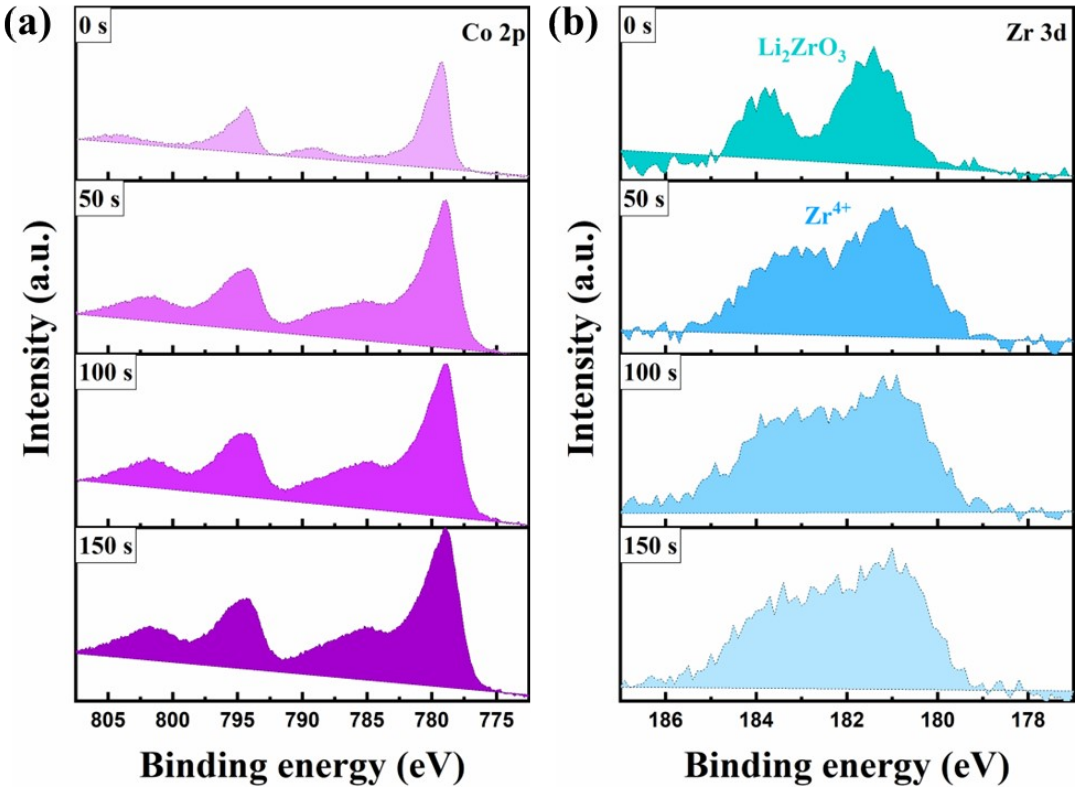

Fig. S6 (a) Co 2p and (b) Zr 3d XPS spectra of Zr-LCO-2

Table S4 Content of $O_{lat.}$ and $O_{ads.}$ in XPS test data

Sample	$O_{lat.}$	$O_{ads.}$	$O_{ads.}/O_{lat.}$
$LiCoO_2$	41.03%	58.97%	1.44
Zr-LCO-1	27.84%	72.16%	2.59
Zr-LCO-2	22.52%	77.48%	3.44
Zr-LCO-3	19.44%	80.55%	4.14

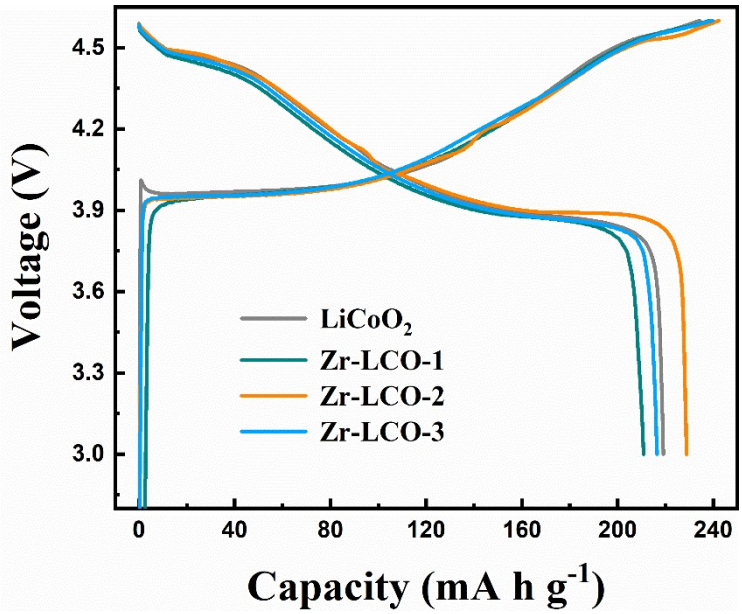

Figure S7 Reversible Capacity of $LiCoO_2$ in the 3.0-4.6 V

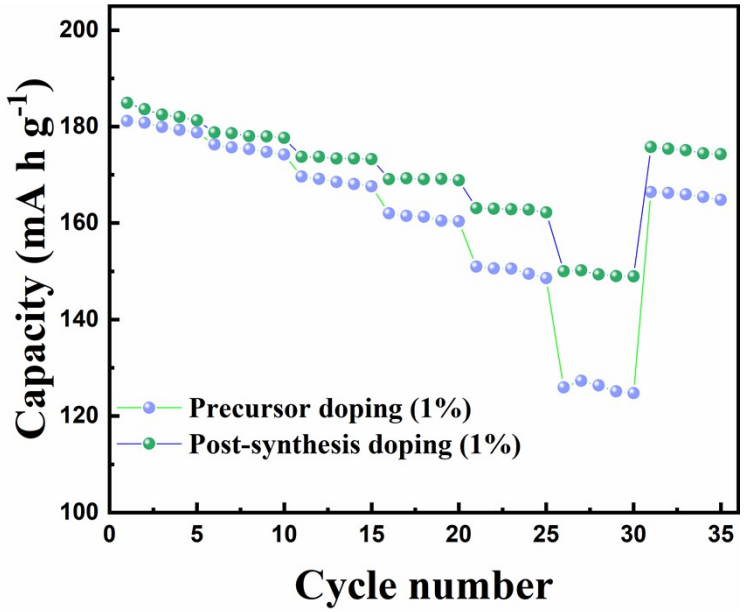

Fig. S8 Rate performance of $LiCoO_2$ samples doped during precursor synthesis and post-synthesis

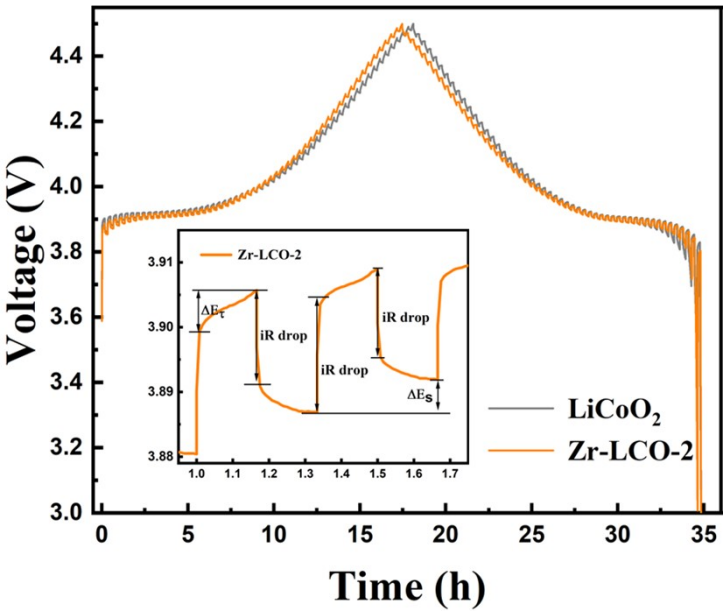

Figure S9 GITT curves of $LiCoO_2$ and Zr-LCO-2

Table S5 ICP test data for Zr-$LiCoO_2$ samples

	Co	Li	Zr
Zr-LCO-1	56.84	7.04	0.3618
Zr-LCO-2	57.64	6.84	0.6957
Zr-LCO-3	56.82	7.11	1.1077