Supporting Information

Nanoscale control and tri-element co-doping toward 4.6V $LiCoO_2$ with excellent rate capability and long-cycling stability for lithium-ion batteries

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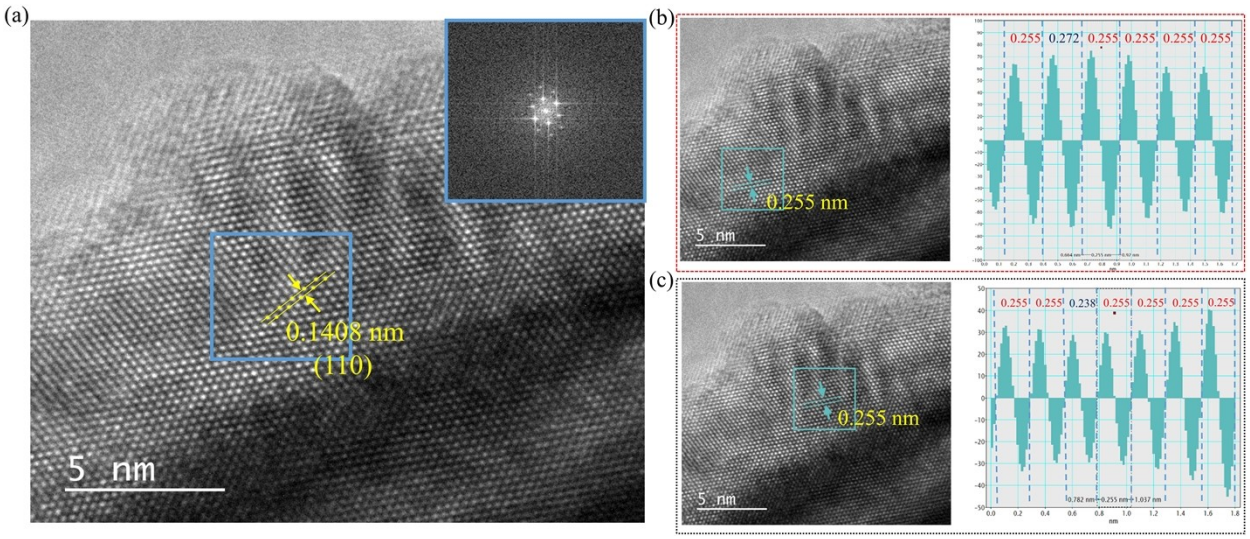

Figure S1. (a) Interplanar crystal spacings of crystal plane (110) and corresponding fast Fourier transformation (FFT) calculated from the blue marked regions of CDLCO; (b) TEM image of CDLCO together with the measured lattice spacing for the marked region; (c) TEM image of CDLCO together with the measured lattice spacing for another marked region.

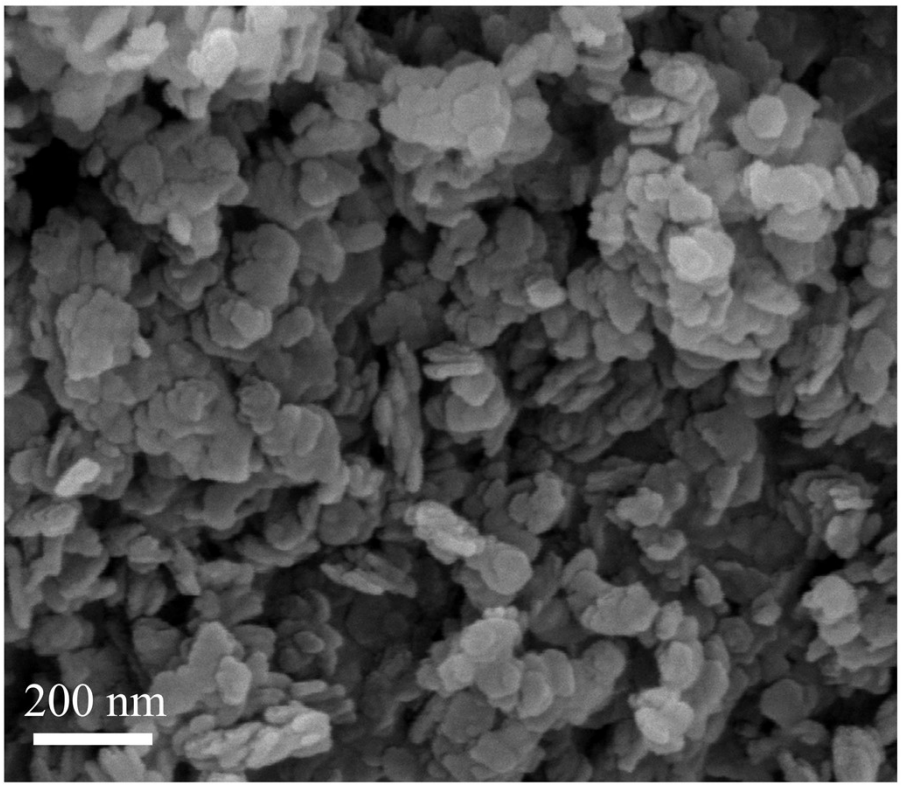

Figure S2. SEM image of nano-CoOOH.

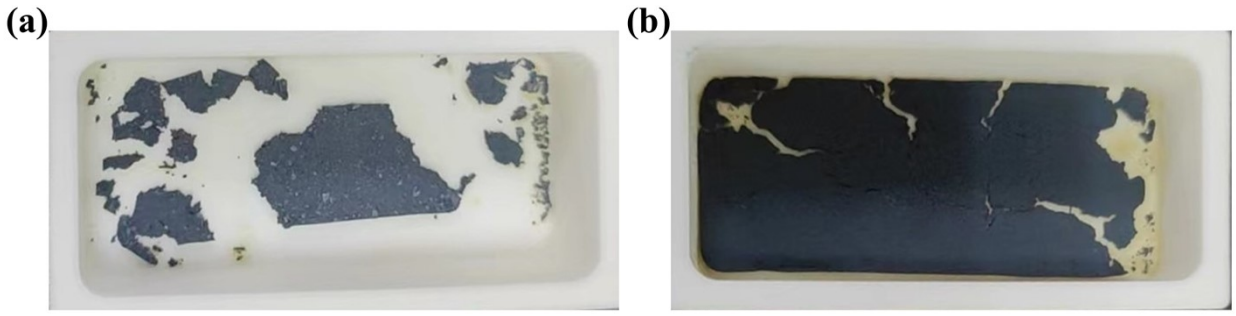

Figure S3. Materials synthesized with different precursors under the same reaction conditions: (a) CDLCO by nano-CoOOH precursors, (b) ATMLCO by Co_3O_4 precursors.

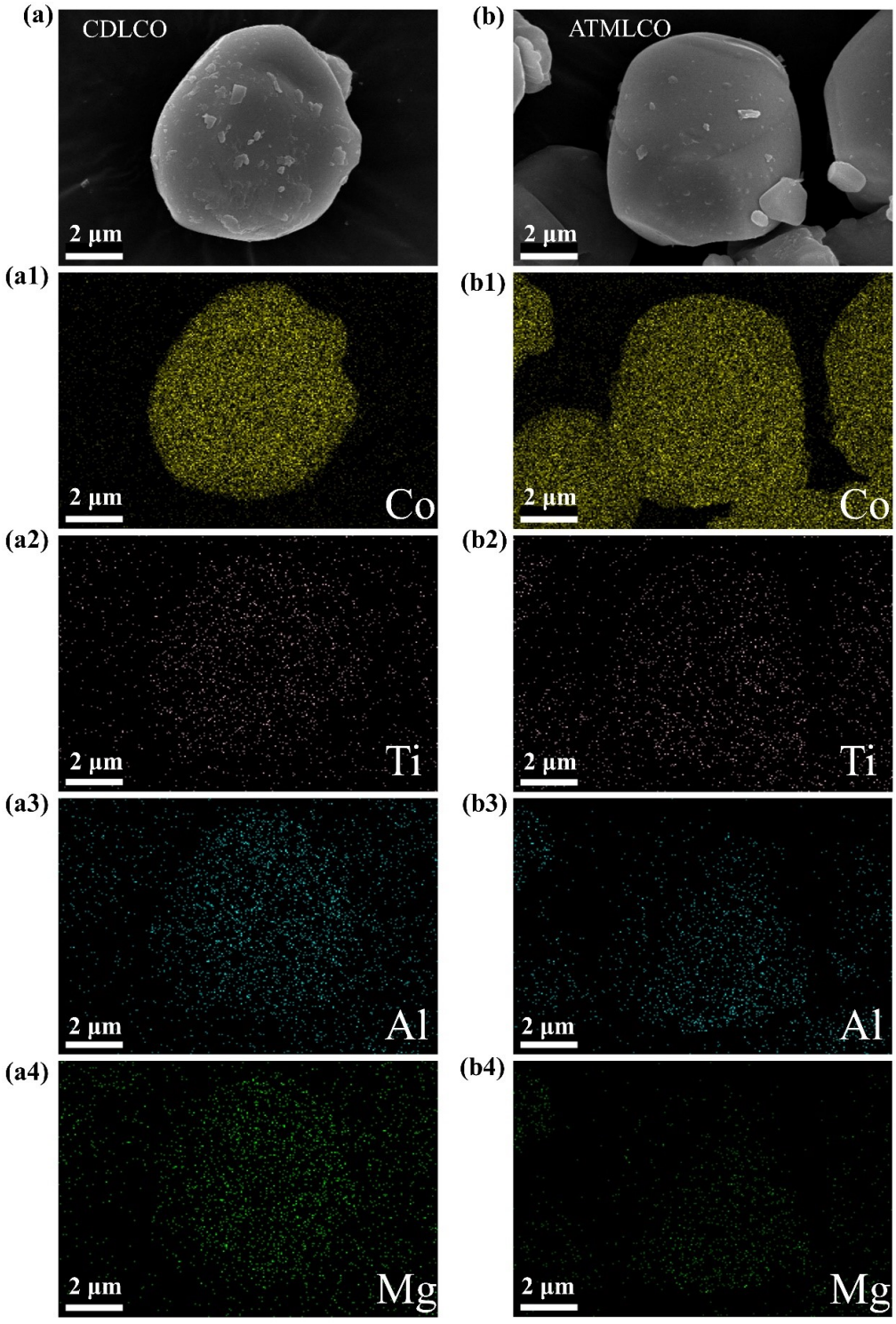

Figure S4. SEM and EDS elemental mappings of Co, Ti, Al, Mg: (a-a4) CDLCO, (b-b4) ATMLCO.

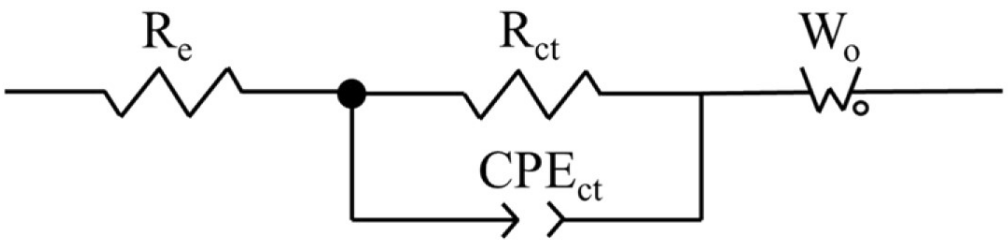

Figure S5. The equivalent circuit models used for the fitting of EIS data.

Table S1. The doping concentration of Al, Mg, Ti in BLCO and CDLCO obtained from ICP.

Samples	ICP wt%		
	Al	Mg	Ti
BLCO	0	0	0
CDLCO	0.4908	0.1083	0.0971

Table S2. Atoms occupancy of BLCO from Rietveld refinement by the XRD.

Atom	Site	x	y	z	Occupancy
Li	3a	0	0	0	1
Co	3b	0	0	0.5	1
O	6c	0	0	0.24454	1

Table S3. Atoms occupancy of CDLCO from Rietveld refinement by the XRD.

Atom	Site	x	y	z	Occupancy
Li	3a	0	0	0	0.996
Mg	3a	0	0	0	0.004
Co	3b	0	0	0.5	0.980
Al	3b	0	0	0.5	0.018
Ti	3b	0	0	0.5	0.002
O	6c	0	0	0.2437	1

Table S4. Comparison of electrochemical properties of the reported $LiCoO_2$-based LIBs at the high cut-off voltage of 4.6 V.

Modified strategies	Current density	Cycle number	Capacity retention	Ref.
Mg-doping	270 $mA \cdot g^{-1}$	100	84% (158 $mAh \cdot g^{-1}$)	[1]
W-doping	274 $mA \cdot g^{-1}$	100	72.3% (146 $mAh \cdot g^{-1}$)	[2]
Mn doping	185 $mA \cdot g^{-1}$	100	55% (112.2 $mAh \cdot g^{-1}$)	[3]
Ni-Mn co-doping	185 $mA \cdot g^{-1}$	100	52% (103.48 $mAh \cdot g^{-1}$)	[3]
Al-Zn co-doping	185 $mA \cdot g^{-1}$	500	65% (119.6 $mAh \cdot g^{-1}$)	[4]
Al-doping, F coating	27.4 $mA \cdot g^{-1}$	200	81.8% (170.7 $mAh \cdot g^{-1}$)	[5]
Mg doping, ZrO_xF_y coating	155 $mA \cdot g^{-1}$	100	76.3% (136.6 $mAh \cdot g^{-1}$)	[6]
Ti, Mg, Al co-doping	137 $mA \cdot g^{-1}$	100	86% (174 $mAh \cdot g^{-1}$)	[7]
Al-Ti bulk co-doping, Mg surface doping	70 $mA \cdot g^{-1}$	200	78% (169.9 $mAh \cdot g^{-1}$)	[8]
This work	1 C (1 C=150 $mA \cdot g^{-1}$)	100	94.3% (183.5 $mAh \cdot g^{-1}$)	
This work	5 C	200	98.7% (146.1 $mAh \cdot g^{-1}$)	
This work	5 C	600	91% (134.8 $mAh \cdot g^{-1}$)	

References

1. Y. Huang, Y. Zhu, H. Fu, M. Ou, C. Hu, S. Yu, Z. Hu, C.-T. Chen, G. Jiang, H. Gu, H. Lin, W. Luo and Y. Huang, *Angew. Chem. Int. Edit.*, 2021, **60**, 4682-4688.
2. J.-N. Zhang, Q.-H. Li, Q. Li, X.-Q. Yu and H. Li, *Chinese Phys. B*, 2018, **27**, 088202.
3. Y. Wang, T. Cheng, Z. Yu, Y. Lyu and B. Guo, *J. Alloys Compd.*, 2020, **842**, 155827.
4. T. Cheng, Z. Ma, R. Qian, Y. Wang, Q. Cheng, Y. Lyu, A. Nie and B. Guo, *Adv. Funct. Mater.*, 2021, **31**, 2001974.
5. J. Qian, L. Liu, J. Yang, S. Li, X. Wang, H. L. Zhuang and Y. Lu, *Nat. Commun.*, 2018, **9**, 4918.
6. Z. Wang, Z. Wang, H. Guo, W. Peng, X. Li, G. Yan and J. Wang, *J. Alloys Compd.*, 2015, **621**, 212-219.
7. J.-N. Zhang, Q. Li, C. Ouyang, X. Yu, M. Ge, X. Huang, E. Hu, C. Ma, S. Li, R. Xiao, W. Yang, Y. Chu, Y. Liu, H. Yu, X.-Q. Yang, X. Huang, L. Chen and H. Li, *Nat. Energy*, 2019, **4**, 594-603.
8. L. Wang, J. Ma, C. Wang, X. Yu, R. Liu, F. Jiang, X. Sun, A. Du, X. Zhou and G. Cui, *Adv. Sci.*, 2019, **6**, 1900355.