

A versatile single molecular precursor for the synthesis of layered oxide cathode materials for Li-ion batteries

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1. Experimental Section

1.1 Preparation of single molecular precursor

All chemicals were analytical grade and used as received without further purification.

- (a) $C_5H_7LiO_2$: lithium foils were added into acetylacetone in an argon-filled glove box. Leave it alone until the lithium foils were completely exhausted to produce white powder $C_5H_7LiO_2$. After centrifugation, it was dried at 60 °C for 12 h in a vacuum oven.
- (b) $LiCo(acac)_3$: $C_5H_7LiO_2$ (3.0000 g, 28.29 mmol) was dissolved in ethanol (135 mL), and $CoCl_2$ (1.2132 g, 9.35 mmol) was dissolved in ethanol (35 mL). $CoCl_2$ solution was slowly added dropwise to $C_5H_7LiO_2$ solution under magnetic stirring. After stirring for 4 h, we can get pink precipitate. It was filtered off, washed with ethanol several times (about 500 mL) and dried at 80 °C overnight in a vacuum oven.
- (c) $LiNi_{0.8}Co_{0.2}(acac)_3$: The procedure is similar with that of $LiCo(acac)_3$. $C_5H_7LiO_2$ (3.0000 g, 28.29 mmol) was dissolved in ethanol (135 mL), $CoCl_2$ (0.2426 g, 1.87 mmol) and $NiCl_2$ (0.9694 g, 7.48 mmol) was dissolved in ethanol (35 mL). Metal salt solution was slowly added dropwise to $C_5H_7LiO_2$ solution with magnetic stirring. After stirring for 4 h, we can get lavender precipitate. It was filtered off, washed with ethanol several times (about 500 mL) and dried under vacuum oven at 80 °C overnight.
- (d) $LiNi_{0.5}Co_{0.2}Mn_{0.3}(acac)_3$: The procedure is similar with that of $LiCo(acac)_3$. $C_5H_7LiO_2$ (3.0000 g, 28.29 mmol) was dissolved in ethanol (135 mL), $CoCl_2$ (0.2426 g, 1.87 mmol), $NiCl_2$ (0.6059 g, 4.68 mmol) and $MnCl_2$ (0.3532g, 2.81 mmol) were dissolved in ethanol (35 mL). Metal salt solution was slowly added dropwise to $C_5H_7LiO_2$ solution with magnetic stirring. After stirring for 4 h, we can get light grey precipitate. It was filtered off, washed with ethanol several times (about 500 mL) and dried under vacuum oven at 80 °C overnight.

The entire synthesis process was clearly shown in [Fig. S1](#).

1.2 Preparation of layered oxide cathode materials

- (a) $LiCoO_2$: The sample was obtained by calcining the pink single molecular precursor, $LiCo(acac)_3$, in a tube furnace at 850 °C for 8 h under air atmosphere.
- (b) $LiNi_{0.8}Co_{0.2}O_2$: The sample was obtained by calcining the lavender single molecular precursor, $LiNi_{0.8}Co_{0.2}(acac)_3$, in a tube furnace at 800 °C for 8 h under air atmosphere.

(c) $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$: The sample was obtained by calcining the light grey single molecular precursor, $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}(\text{acac})_3$, in a tube furnace at 825 °C for 10 h under air atmosphere.

1.3 Materials characterizations

The X-ray diffraction (XRD) patterns of the single molecular precursors and layered oxide materials were measured by a Bruker D8 Advance diffractometer using $\text{Cu-K}\alpha$ radiation at room temperature. The scanning electron microscopy (SEM) images were measured by Zeiss SUPRA-55. Thermogravimetric analysis (TGA) data and differential scanning calorimetry (DSC) data of single molecular precursors were collected on a TGA/DSC1 system at a heating rate of 10 °C/min under air flow. The composition and distribution of chemical elements were observed by energy X-ray spectroscopy (EDX, Oxford X Max 20, 20 kV), and the ICP-AES analysis with use HORIBA JY 2000-2.

1.4 Electrochemical measurements

The composite electrode was prepared by blending 80 wt% LiCoO_2 or $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ or $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ as the cathode active material, 10 wt% carbon black as the conductive additive, and 10 wt% poly(vinylidene fluoride) (PVdF) as the binder in N-methyl-2-pyrrolidone. The slurry was blade-coated onto aluminum foil and dried at 100 °C for 12 h in a vacuum oven. Then electrode was cut into pellets with diameter of 10 mm. Electrochemical tests were performed with CR2032 coin-type cells, which were finally assembled in an argon-filled glove box (Mikrouna Universal 2440/750) with water and oxygen content below 1 ppm. The pure lithium foil was used as the anode. The polypropylene membrane (Celgard 2400) was used as the separator. 1 M LiPF_6 in a mixture of EC, DEC and DMC with a volume ratio of 1:1:1 was used as the electrolyte. The cells were charged and discharged at different rates (1 C=180 mA h g^{-1}) between 2.7 and 4.4 V in the galvanostatic mode. Before the electrochemical measurement, the prepared cells were shelved for 6 h. Galvanostatic discharge/charge tests were performed using a NEWARE battery cycler in the voltage range of 2.7-4.4V (vs. Li^+/Li), all the above data were collected at 25 °C.

2. Figures

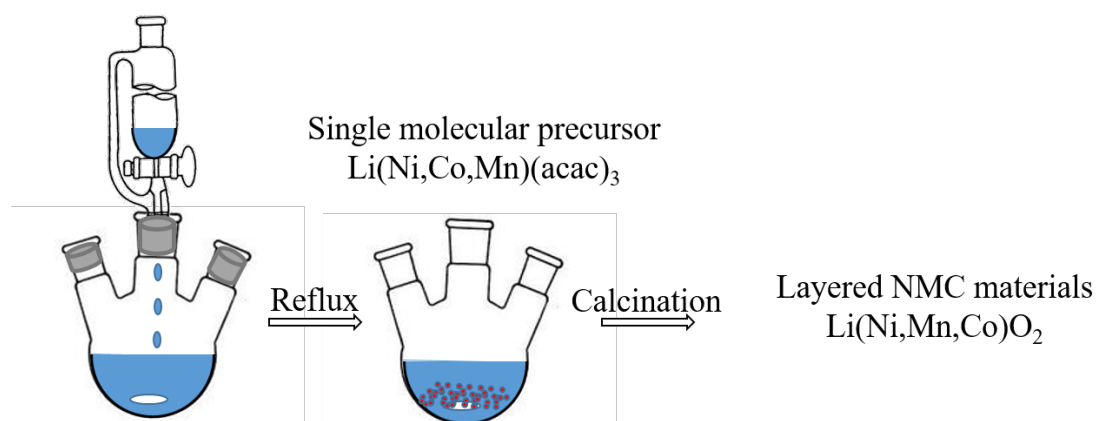


Fig. S1 The schematic for the synthesis of layered NMC materials by the single molecular precursor method.



Fig. S2 Photos of as-synthesized $\text{C}_5\text{H}_7\text{LiO}_2$ (a), $\text{LiCo}(\text{acac})_3$ (b), $\text{LiNi}_{0.8}\text{Co}_{0.2}(\text{acac})_3$ (c), and $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.2}(\text{acac})_3$ (d).

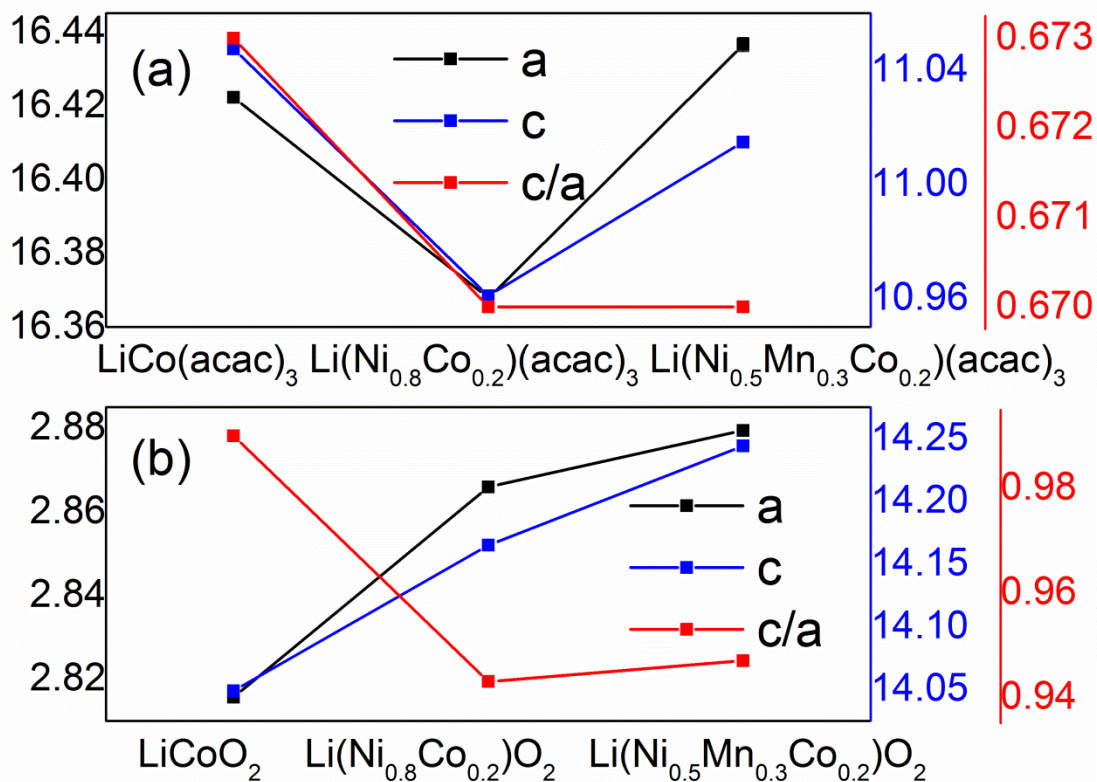


Fig S3 The refined lattice parameters of three precursors (a) and their corresponding layer oxides (b).

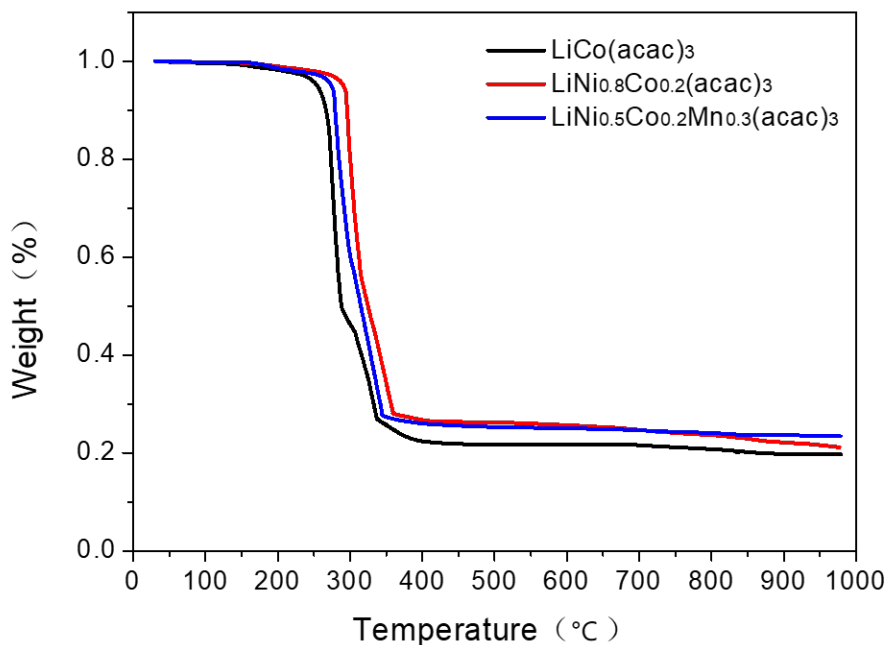


Fig. S4 The TGA curves of $\text{LiCo}(\text{acac})_3$, $\text{LiNi}_{0.8}\text{Co}_{0.2}(\text{acac})_3$, and $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}(\text{acac})_3$.

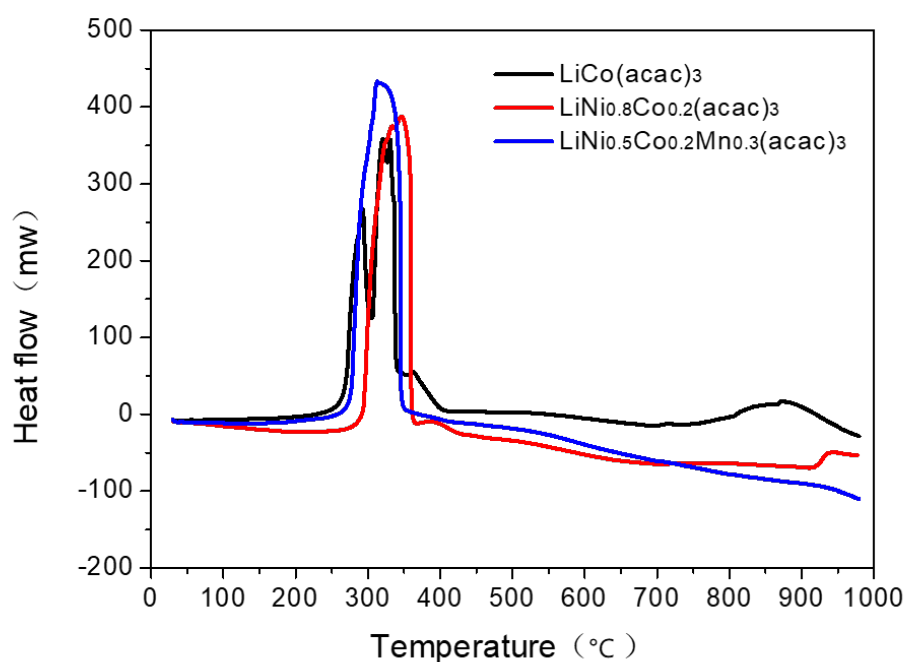


Fig. S5 The DSC curves of $\text{LiCo}(\text{acac})_3$, $\text{LiNi}_{0.8}\text{Co}_{0.2}(\text{acac})_3$, and $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}(\text{acac})_3$.

To investigate the thermal stability of these compounds, thermogravimetric analysis (TGA) accompanied with differential scanning calorimetry (DSC) was performed (Fig. S4 and S5, ESI†). Their weight loss curves are very similar with an abrupt weight loss behavior around 300 °C, which could be attributed to a thermal decomposition process. The experimental weight loss values (all around 75%) are basically consistent with their theoretical values (73.28%, 73.31%, and 73.54%) from precursors to layered oxides. Correspondingly, multiply exothermic peaks were observed in DSC curves (Fig. S5), indicating a multiply-step thermal decomposition process. Among three compounds, $\text{LiNi}_{0.8}\text{Co}_{0.2}(\text{acac})_3$ owned highest thermal decomposition temperature, which showed that Ni substitution enhanced the structure stability.

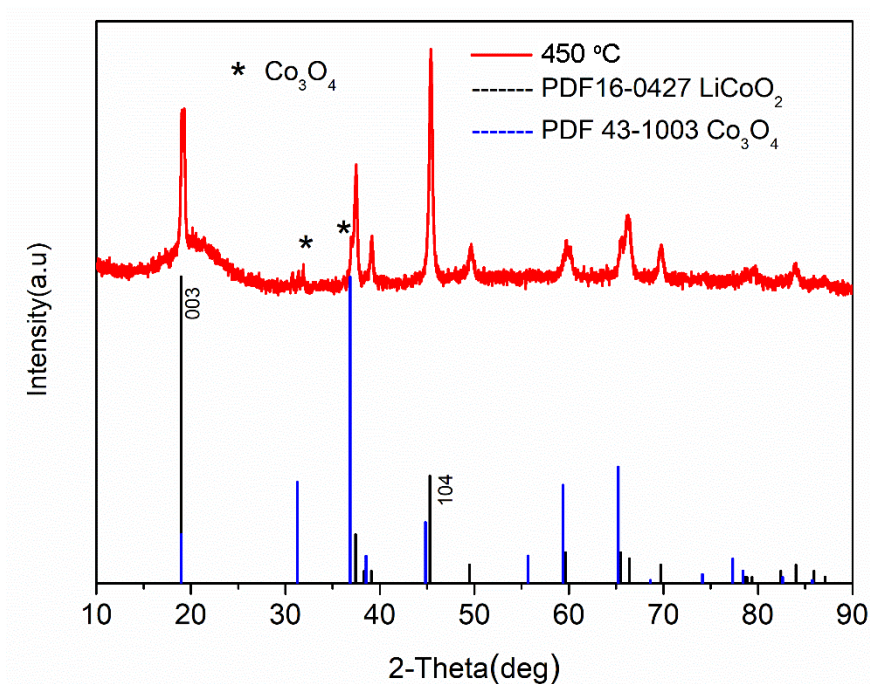


Fig. S6 The experimental XRD pattern of LiCoO₂ prepared at 450 °C for 8 h.

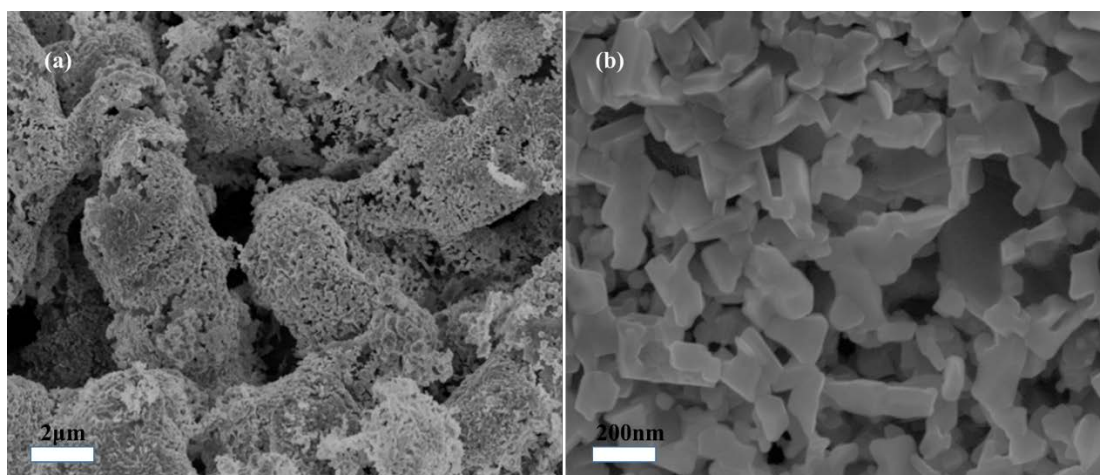


Fig. S7 Low and high magnification SEM images of LiCoO₂ prepared at 450 °C for 8 h.

Based on the analysis of their thermal stability, we try to obtain LiCoO₂ by the thermal decomposition of the LiCo(acac)₃ precursors at 450 °C for 8 h in air atmosphere (see Experimental section in the ESI†). The morphology investigated by SEM (Fig. S7, ESI†) show that we got a nanocrystalline network-like material, which is composed of 100-200 nm nanocrystals. Compare it to the precursor morphology, we further ensure that this unique morphology came from the thermal decomposition process of prism-like precursors. The XRD pattern (Fig. S6, ESI†) showed that the nanocrystalline material has presented a main phase of layered structure with weak

peak intensity, also including tiny intermediate phase Co_3O_4 . To improve the crystalline degree of the layered structure, we increased the sintering temperature. By a lot of experiments, LiCoO_2 and $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ with good crystalline was obtained by calcining $\text{LiCo}(\text{acac})_3$ in a tube furnace at $850\text{ }^\circ\text{C}$ and $800\text{ }^\circ\text{C}$ for 8 h in air atmosphere, respectively.

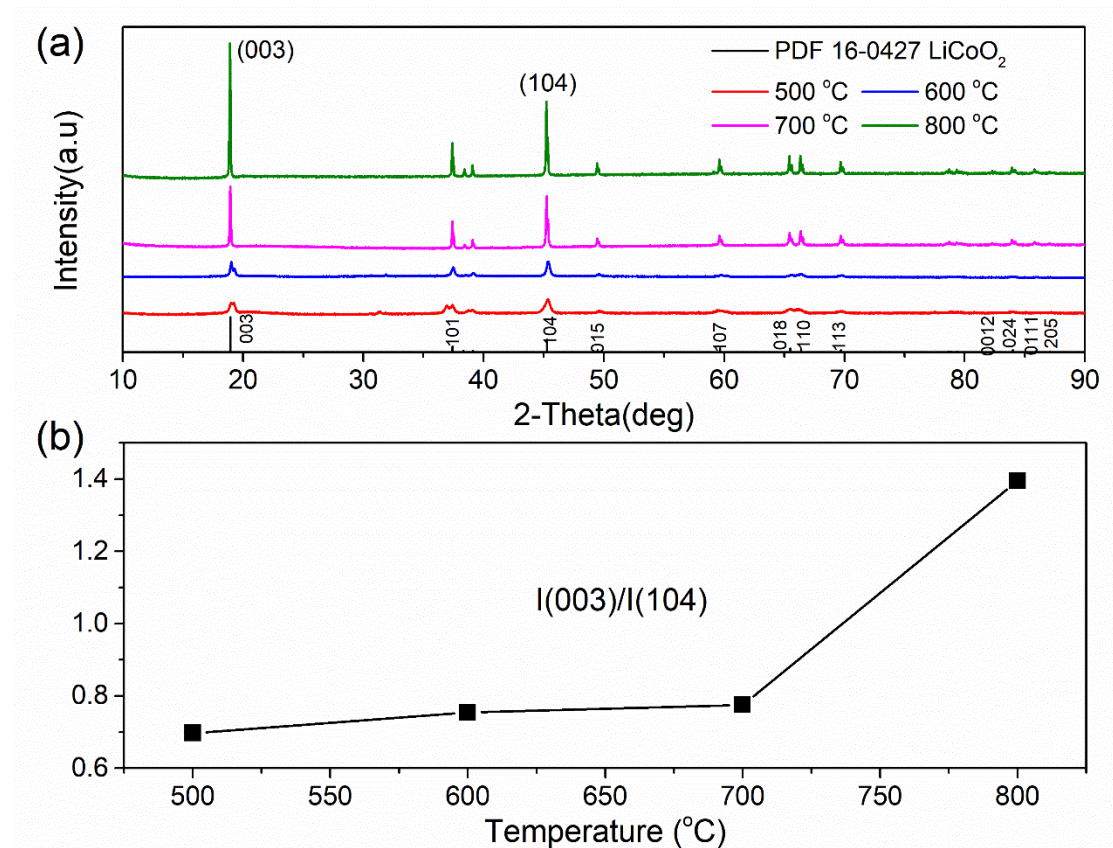


Fig. S8 (a) The XRD patterns of $\text{LiCo}(\text{acac})_3$ calcined at different temperatures; (b) the evolution of $I(003)/I(104)$ as a function of the temperature. Here, $I(003)/I(104)$ represents the ratio between the integrated areas of (003) and (104) peaks.

As shown in Fig. S8a, the XRD patterns were measured after performing calcination at different temperature for 8 hours. It is easy to see that, layered LiCoO_2 has been formed at low temperature $500\text{ }^\circ\text{C}$, with tiny impurity Co_3O_4 . Low peak intensities indicated poor crystallinity at low temperature. The crystallinity was fast increased indicated by the fast increase of peak intensities with the elevating temperature. And also the ratio between the integrated areas of (003) and (104) peaks (denoted as $I(003)/I(104)$) was calculated and shown in Fig. S8b. It increased quickly, indicating the fast decrease of Li/Ni mixing in the layered structure. All these phenomena will beneficial to enhance the electrochemical performance of the final products. In one word, the calcination conditions were roughly optimized to obtain products with high crystallinity and low Li/Ni mixing for better electrochemical performance.

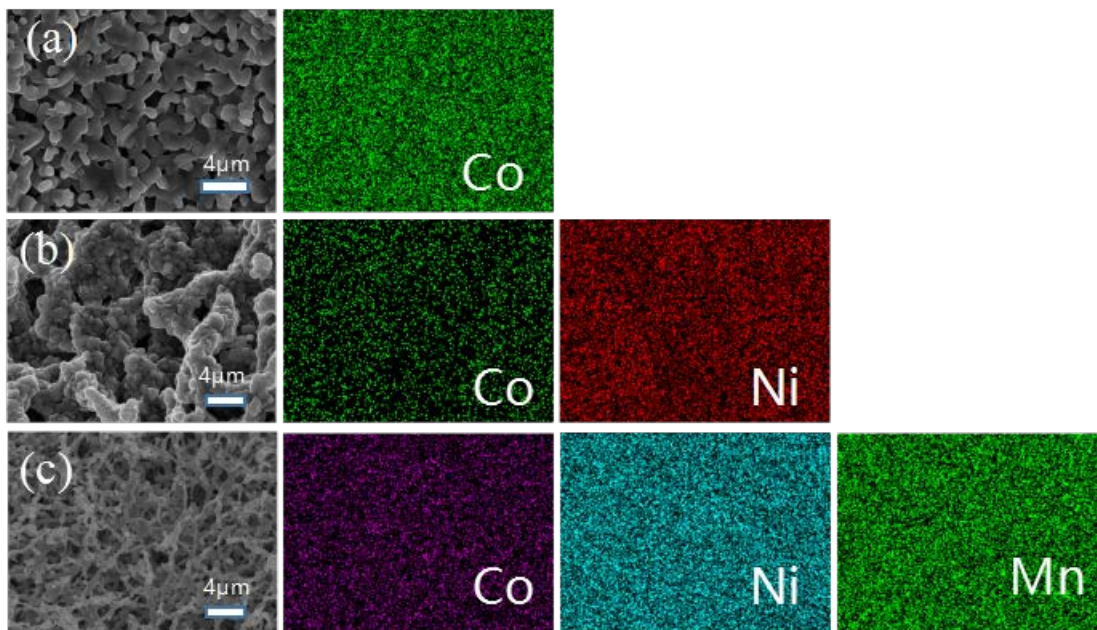


Fig. S9 SEM elemental mappings of LiCoO_2 (a), $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ (b) and $\text{LiNi}_{0.5}\text{Mn}_{0.3}\text{Co}_{0.2}\text{O}_2$ (c).

3. Tables

Table S1. Elemental composition analysis by ICP-AES.

	molar ratio			
	Li	Co	Ni	Mn
LiCo(acac) ₃	1.014(2)	1.000(2)	-	-
Li(Ni _{0.8} Co _{0.2})(acac) ₃	1.011(2)	0.206(1)	0.794(2)	-
Li(Ni _{0.5} Mn _{0.3} Co _{0.2})(acac) ₃	0.997(2)	0.194(1)	0.489(1)	0.317(1)
LiCoO ₂	0.990(2)	1.000(2)	-	-
LiNi _{0.8} Co _{0.2} O ₂	0.991(2)	0.209(1)	0.791(2)	-
LiNi _{0.5} Mn _{0.3} Co _{0.2} O ₂	0.964(2)	0.191(2)	0.493(1)	0.316(1)

Table S2. Refinement parameters of three precursors.

Precursors	LiCo(acac) ₃	Li(Ni _{0.8} Co _{0.2})(acac) ₃	Li(Ni _{0.5} Mn _{0.3} Co _{0.2})(acac) ₃
Space group	<i>R-3c</i>		
wRp	0.0139	0.0424	0.0318
Rp	0.0097	0.0297	0.0176
a (Å)	16.4222(11)	16.36783(87)	16.4365(19)
c (Å)	11.04747(74)	10.96088(77)	11.0148(16)
c/a	0.673	0.670	0.670

Table S3. Refinement parameters of three layered products.

Products	LiCoO ₂	LiNi _{0.8} Co _{0.2} O ₂	LiNi _{0.5} Mn _{0.3} Co _{0.2} O ₂
Space group	<i>R-3m</i>		
I(003)/I(104)	1.35	1.22	0.64
wRp	0.0244	0.0439	0.0140
Rp	0.0179	0.0331	0.0103
a (Å)	2.815627(56)	2.865944(37)	2.87945(30)
c (Å)	14.04893(27)	14.16518(24)	14.2441(14)
c/a	4.990	4.943	4.947
Ni(3b)	-	0.0394(31)	0.2133(53)
grain size (nm)	472(31)	519(64)	152(13)
preferred orientation of (003)	1.1949(74)	-	-

References.

1. V. Etacheri, R. Marom, R. Elazari, G. Salitra and D. Aurbach, *Energ Environ Sci*, 2011, **4**, 3243-3262.