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Failure Analysis of Hydrothermal Synthesis for Spinel Manganese-Cobalt Oxide

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Supplementary information

Table S1 EDS mapping quantitative analysis of Mn-Co-O precursor and sample.

Mn-Co-O	Weight content (wt%)			Atomic content (at%)			Atomic ratio	
	Mn	Co	O	Mn	Co	O	Mn/Co	Mn : Co
precursor	3.12	59.57	37.31	1.67	29.73	68.6	0.056	0.16 : 2.84
sample	3.64	73	23.36	2.4	44.8	52.8	0.054	0.15 : 2.85

Table S2 The lattice parameter and quantified ratio of pure Co_3O_4 and Mn-doped Co_3O_4 (Mn-Co_3O_4) phase through Rietveld refinements against synchrotron and laboratory XRD, respectively.

Sample	Phase	Crystal system	Space group	Lattice parameters a = b = c (Å)	Ratio (wt%)
Synchrotron XRD	Co_3O_4	Cubic	Fd-3m	8.10	73.9
	Mn-Co_3O_4			8.18	26.1
Laboratory XRD	Co_3O_4	Cubic	Fd-3m	8.11	22.2
	Mn-Co_3O_4			8.24	77.8

Table S3 The confirmed diffraction peaks positions and calculated inter-atomic spacing (d-spacing) through the Rietveld refinement against synchrotron XRD.

Phase	(h,k,l)	2θ (°)	d-spacing (Å)
Co_3O_4	111	8.45	4.68
	220	13.81	2.86
	311	16.21	2.44
	222	16.94	2.34
	400	19.58	2.03
	422	24.05	1.65
	511	25.53	1.56
	440	27.55	1.45
Mn-Co_3O_4	111	8.36	4.72
	220	13.68	2.89
	311	16.05	2.47
	222	16.77	2.36
	400	19.39	2.05
	422	23.80	1.70
	511	25.27	1.57
	440	27.83	1.43

Table S4 The refined lattice parameter and quantified ratio of Mn-Co-O sample using different molar feed ratio.

Sample	Phase	Crystal system	Space group	Lattice parameters			Ratio (wt%)
				a (Å)	b (Å)	c (Å)	
pure Co	Co_3O_4	Cubic	Fd-3m	8.10	8.10	8.10	100.0
Mn : Co = 1:1	Mn-Co_3O_4	Cubic	Fd-3m	8.13	8.13	8.13	92.9
	$CoMn_2O_4$	Tetragonal	I41/amd	5.73	5.73	9.31	7.1
Mn : Co = 2:1	Mn-Co_3O_4	Cubic	Fd-3m	8.20	8.20	8.20	49.0
	$CoMn_2O_4$	Tetragonal	I41/amd	5.73	5.73	9.31	51.0
pure Mn	Mn_2O_3	Cubic	I213	9.43	9.43	9.43	91.9
	γ-MnO_2	Monoclinic	C2/m	15.10	2.98	4.21	8.1

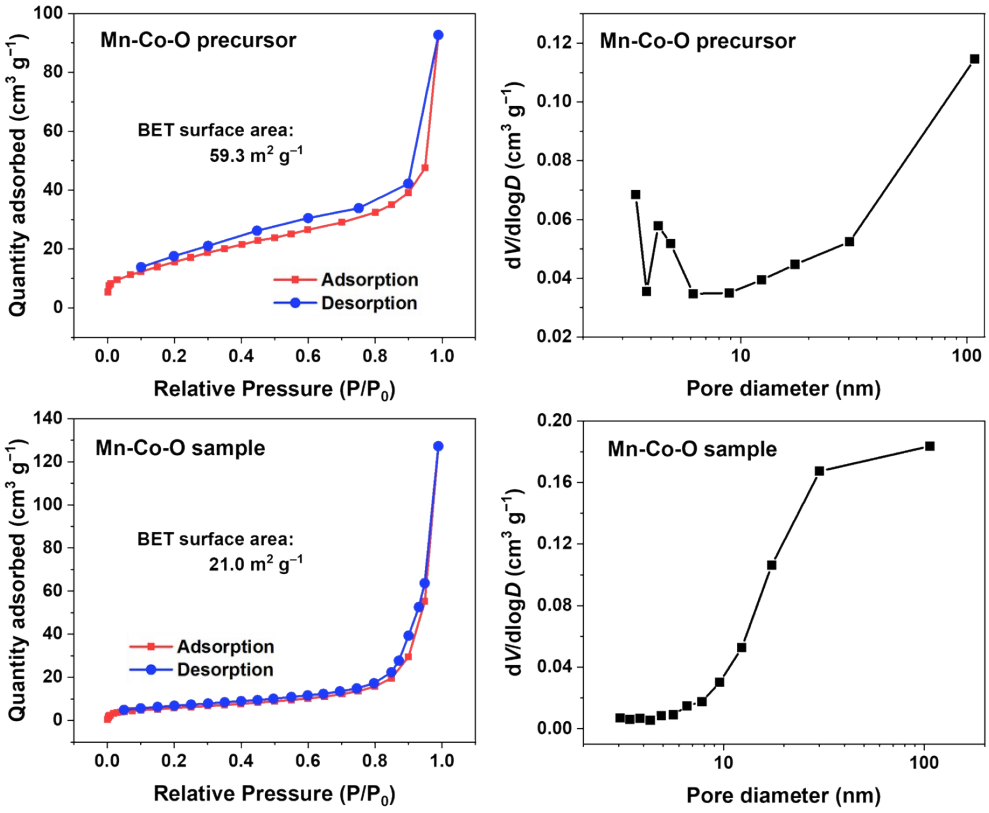

Fig. S1 The multipoint BET surface area and pore distribution of Mn-Co-O precursor and sample.

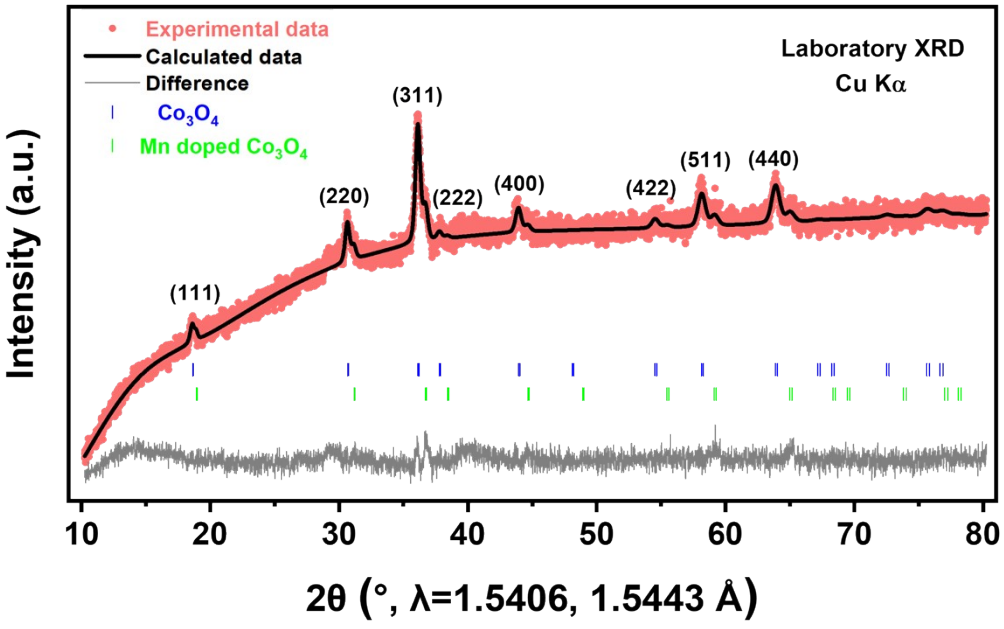

Fig. S2 The laboratory XRD data and Rietveld refinement of Mn-Co-O sample.

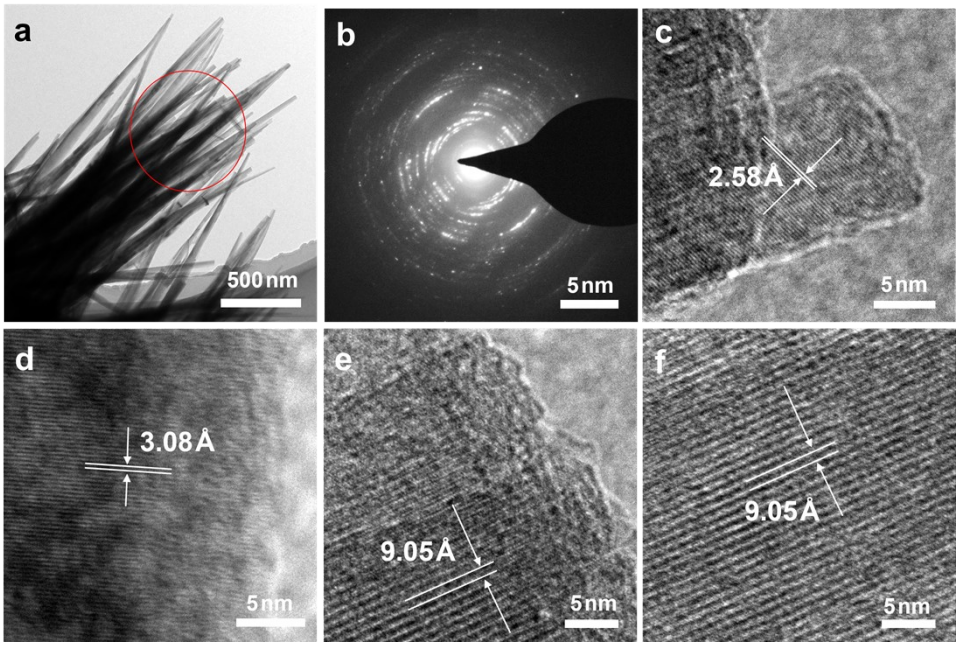

Fig. S3 Electron imaging and diffraction characterization of a microarea of Mn-Co-O precursor. (a) TEM, (b) SAED and (c-f) HRTEM images.

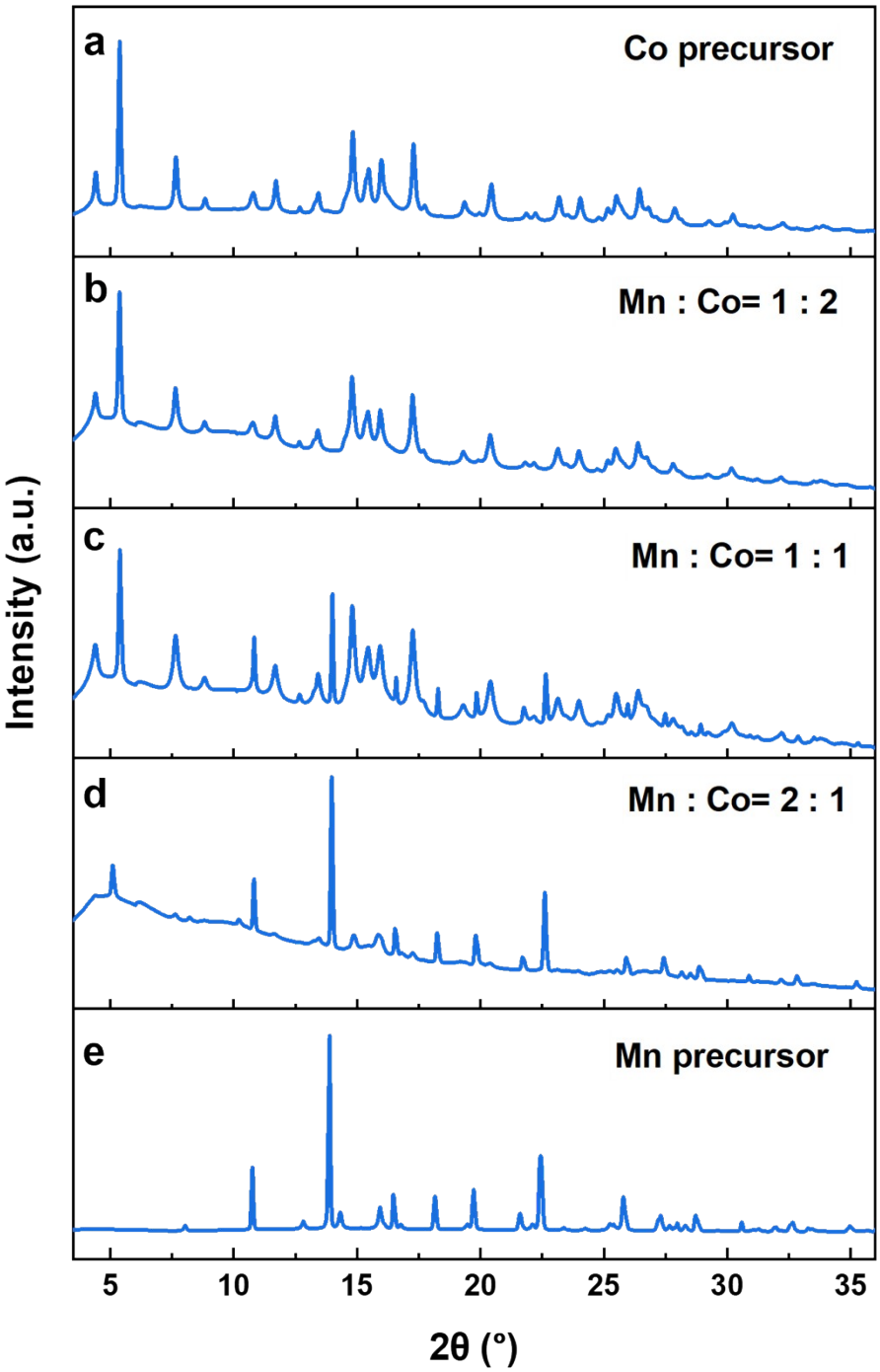

Fig. S4 Synchrotron radiation XRD patterns with Rietveld refinement of Mn-Co-O precursor at different molar feed ratio. (a) pure Co source, (b) Mn : Co = 1 : 2, (c) Mn : Co = 1 : 1, (d) Mn : Co = 2 : 1, (e) pure Mn source.

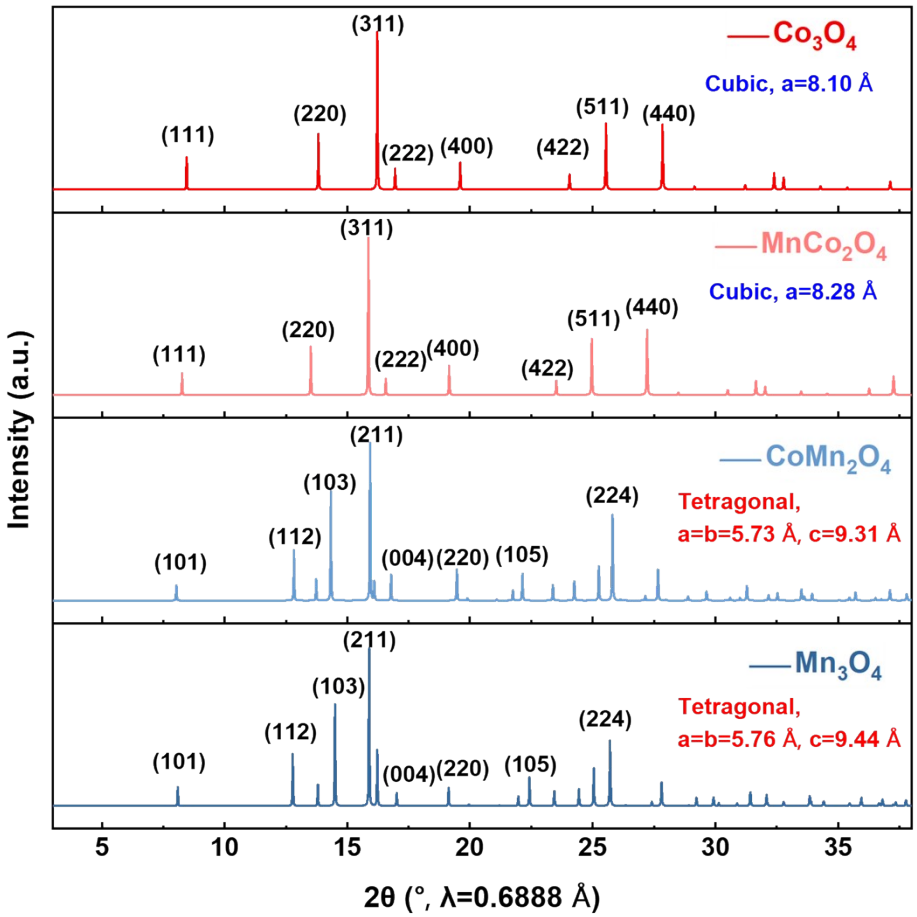

Fig. S5 The powder X-ray diffraction pattern of standard Co_3O_4, $MnCo_2O_4$, $CoMn_2O_4$ and Mn_3O_4 lattice structures, which are calculated and generated by Vesta 3.5.7 program.

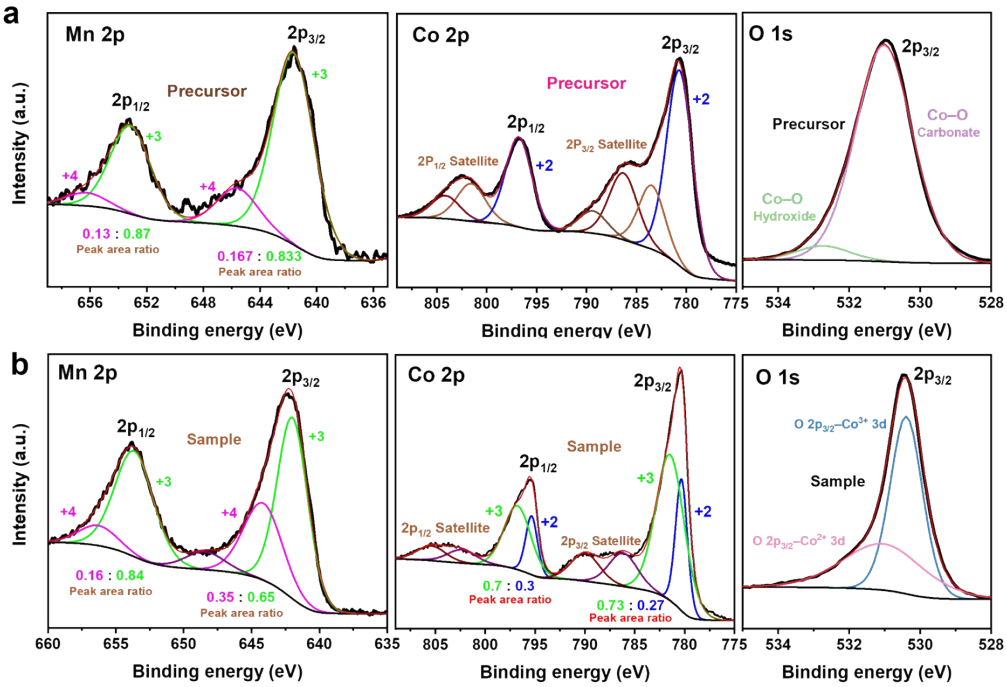

Fig. S6 The XPS of Mn-Co-O precursor (a) and sample(b) with Mn 2p, Co 2p and O 1s spectra, respectively.

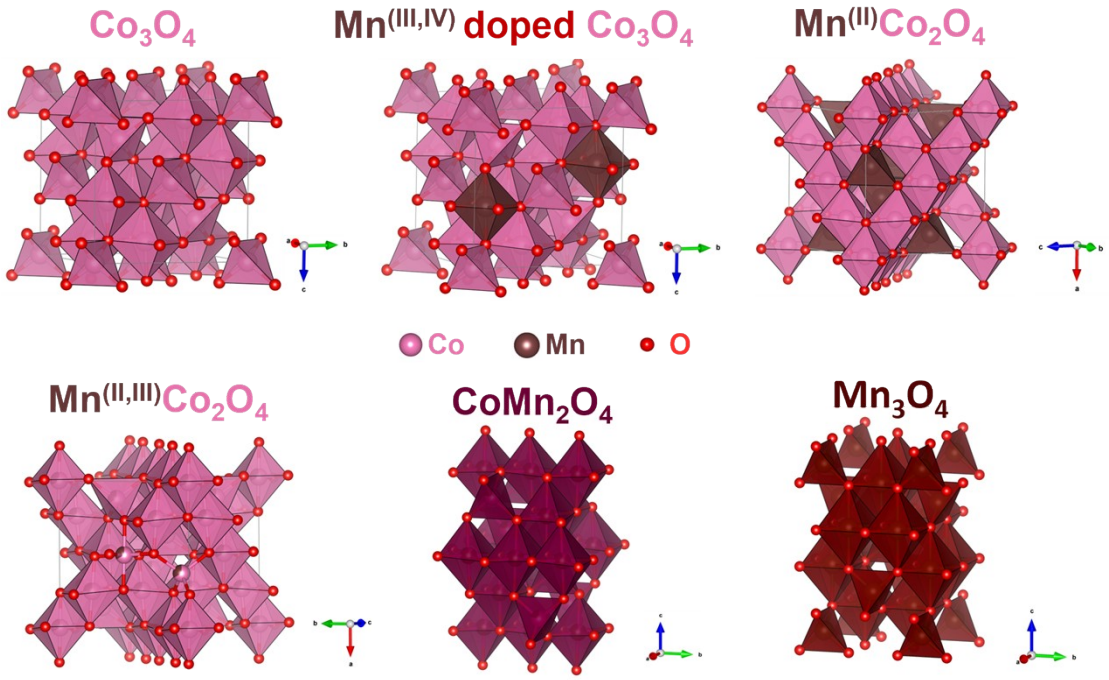

Fig. S7 The crystal lattice visualization of Co_3O_4, $Mn^{(III,\ IV)}$-doped Co_3O_4, $Mn^{(II)}Co_2O_4$, and $Mn^{(II,\ III)}Co_2O_4$, $CoMn_2O_4$ and Mn_3O_4.

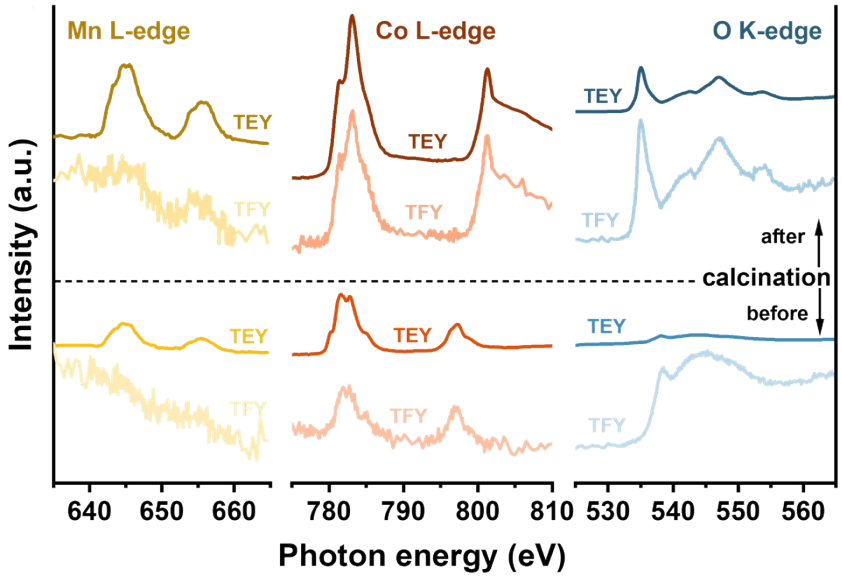

Fig. S8 The XAS plots with TEY and TFY mode of Mn L-edge, Co L-edge and O L-edge before and after calcination of Mn-Co-O precursor.

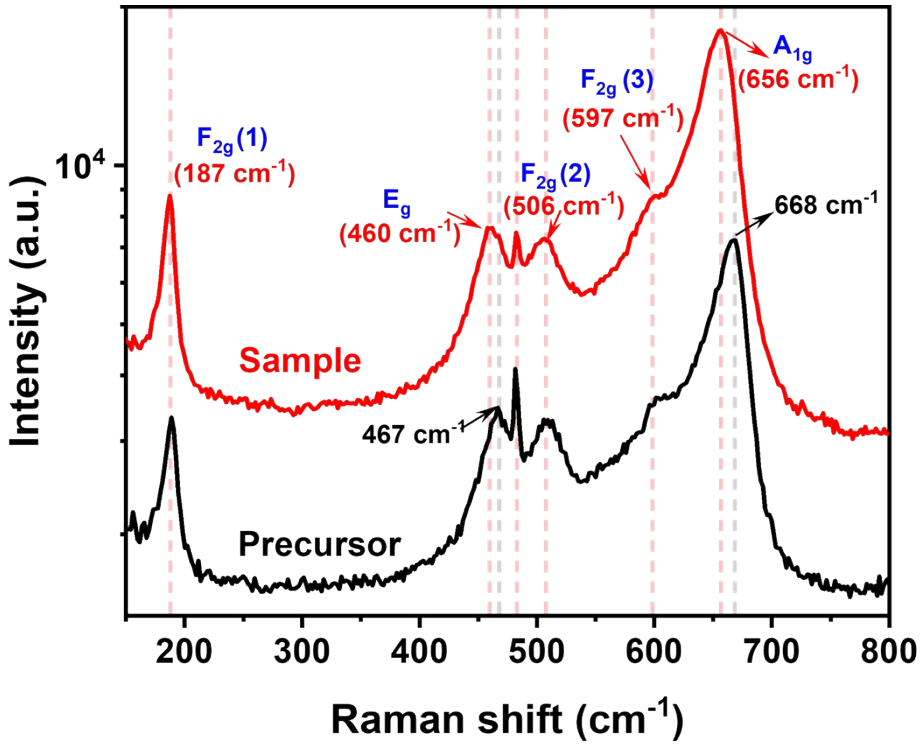

Fig. S9 Raman spectra of Mn-Co-O precursor and sample with x-axis transformed into log10-scale.