Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
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X-ray emission spectroscopy: an effective route to extract site occupation of cations

Electronic Supplementary Information (ESI)

A. As-synthesized Co-Mn metal nanoparticles

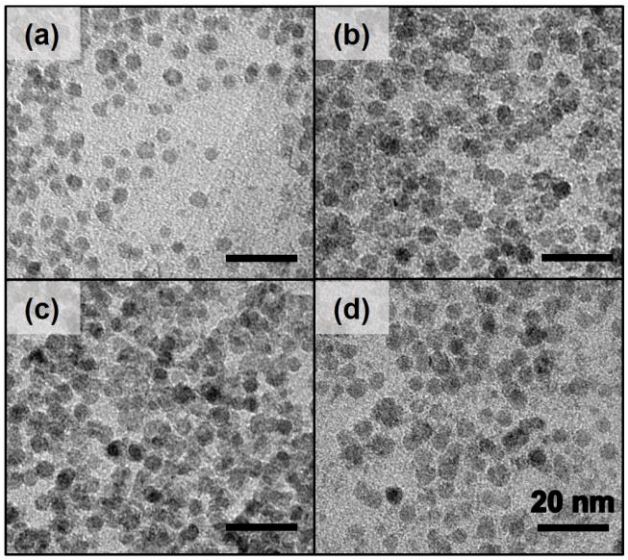

Figure S1. TEM images of unoxidized Co-Mn metal NPs synthesized using hot injection method with varying Co/Mn precursor ratios. The size for the metal NPs before oxidation are 4.25 ± 0.55 nm, 3.75 ± 0.41 nm, 4.75 ± 0.56 nm, and 4.84 ± 0.69 nm, which after oxidation correspond to 'x' = 1.00, 1.13, 1.20, and 1.31, respectively, in the formula $Co_xMn_{3-x}O_4{\cdot}(CoO)_y$.

B. XRD of NPs oxidized in air at 200 ^{O}C for 90 mins

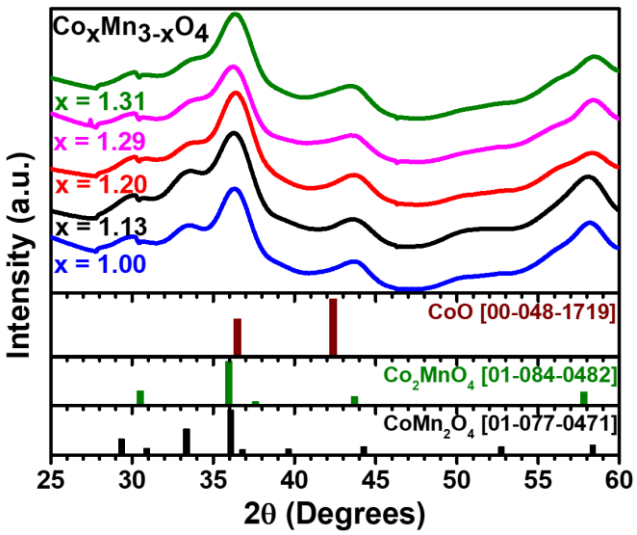

Figure S2. XRD patterns of $Co_xMn_{3-x}O_4$ NPs oxidized in air at 200 ^{o}C for 90 mins for 'x' values varying between 1 and 1.31. The bar patterns show the reference XRD patterns for CoO (JCPDS: 00-48-1719), Co_2MnO_4 (JCPDS: 01-084-0482), and $CoMn_2O_4$ (JCPDS: 01-077-0471). The XRD peaks for the samples correspond to the spinel phase, however, no specific trend is observed as a function of stoichiometry.

C. Determination of concentration of Co^{2+}_{CoO} and Co^{2+}_{Oh} cation species

CoO present as impurities in the NPs consists of Co^{2+} octahedrally bonded to oxygen atoms. Since it has similar coordination environment and ligand geometry as Co^{2+} present at O_h sites of the spinel (Co^{2+}_{Oh}), the contribution from the bulk CoO standard needs to be deconvoluted to separate the contribution of Co^{2+}_{CoO} and Co^{2+}_{Oh} cation species to the Co-K$\beta_{1,3}$ spectras of the samples.

The oxidized NPs having a mixture of spinel and CoO phase can be written as:

$$Co_xMn_{3-x}O_Z \equiv (Co_tMn_{1-t})[Co_{(y-t)}Mn_{2-(y-t)}]O_4 \cdot (CoO)_z$$

- $Co_{Oh} = y - t + z$
- $Co_{Td} = t$
- $Co_{total} = y + z$
- $Mn_{Oh} = 2 - y + t$
- $Mn_{Td} = 1 - t$
- $Mn_{total} = 3 - y$

Constraints: $0 < x < 3$, $Z > 0$, $0 < t < 1$, $y < 2 + t$, $z > 0$

The 3 variables t, y, and z can be solved using the 3 equations:

1. $\frac{Co_{total}}{Mn_{total}} = \frac{x}{3-x} = \frac{y+z}{3-y}$; where value of 'x' is known from ICP
2. $\frac{Co_{Oh}}{Co_{total}} = \frac{y-t+z}{y+z}$
3. $\frac{Mn_{Oh}}{Mn_{total}} = \frac{2-y+t}{3-y}$

The values of $\frac{Co_{Oh}}{Co_{total}}$ and $\frac{Mn_{Oh}}{Mn_{total}}$ are known from linear combination fitting of the XES spectra:

$\frac{Co_{Oh}}{Co_{total}} = \frac{CoO+ZnCo_2O_4}{CoCr_2O_4+CoO+ZnCo_2O_4}$ and $\frac{Mn_{Oh}}{Mn_{total}} = \frac{MnO+ZnMn_2O_4}{MnAl_2O_4+MnO+ZnMn_2O_4}$

$Co^{2+}_{CoO} = z$ and $Co^{2+}_{Oh} = Co^{2+}_{Oh,Total} - z$

Therefore, the concentrations of Co^{2+}_{CoO} and Co^{2+}_{Oh} can be determined for each stoichiometry.

D. Exclusion of Mn^{4+} species in $Co_xMn_{3-x}O_4$ NPs

Higher error when Mn^{4+} specie is included in the fitting of the Mn $K\beta_{1,3}$ XES data. Furthermore, based on the calculations discussed in the section C of ESI, unrealistic values of concentration of different species of cations (t,y < 0 or > 2) were obtained. Therefore, MnO_2 standard is not included in the fitting.

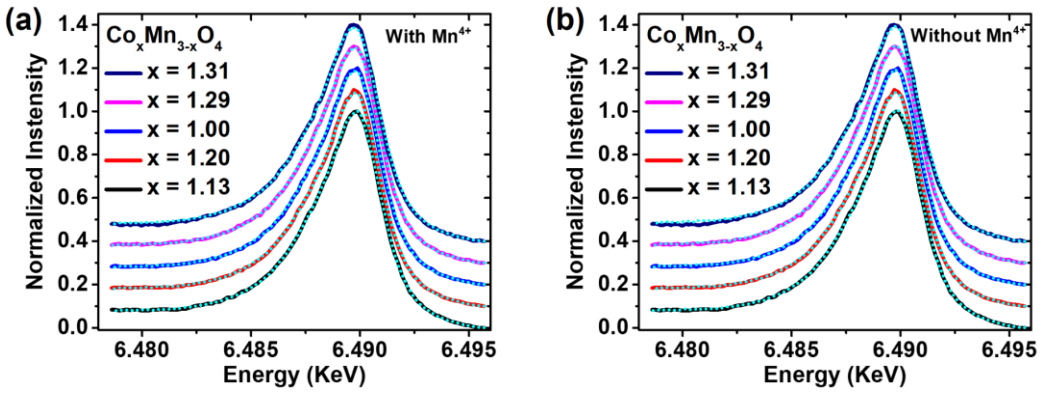

Figure S3. Confirmation of absence of Mn^{4+} specie in the $Co_xMn_{3-x}O_4$ NPs. Figure shows the fits of Mn $K\beta_{1,3}$ XES spectras (a) with, and (b) without the MnO_2 standard. Fits show higher error on inclusion of MnO_2 standard (Table S1).

Table S1. Error numbers for fit of Mn $K\beta_{1,3}$ XES spectras with and without the MnO_2 standards.

x in $Co_xMn_{3-x}O_4$	Fit Statistics (Mn^{4+} included)		Fit Statistics (Mn^{4+} not included)	
	Reduced χ^2	Adj. R-Square	Reduced χ^2	Adj. R-Square
1.00	3.10E-05	0.99962	2.76E-05	0.99966
1.13	1.89E-05	0.99977	1.57E-05	0.99981
1.20	2.31E-05	0.99972	2.31E-05	0.99972
1.29	2.78E-05	0.99967	2.09E-05	0.99975
1.31	8.56E-05	0.99898	6.74E-05	0.9992

E. Site occupation using EXAFS and XES, and the associated errors

EXAFS										
x in $Co_xMn_{3-x}O_4$	**% Mn at Oh sites**	**% Error**	**% Mn at Td sites**	**% Error**	**% Co at Oh sites**	**% Error**	**% Co at Td sites**	**% Error**	**% CoO**	**% Error**
1.13	82.03	13.70	17.98	13.70	24.25	14.35	75.75	14.35	0.00	0.00
1.20	78.98	22.25	21.03	22.25	0.00	0.00	86.98	27.98	13.02	27.98
1.00	100.00	2.45	0.00	2.45	0.00	0.00	46.70	27.36	53.30	27.36
1.29	100.00	1.39	0.00	1.39	0.00	0.00	72.45	33.91	27.55	33.91
1.31	100.00	3.36	0.00	3.36	0.00	0.00	53.33	21.01	46.68	21.01
Average % error		**8.63**		**8.63**		**14.35**		**24.92**		**22.05**

Total average % error **15.72**

XES										
x in $Co_xMn_{3-x}O_4$	**% Mn at O_h sites**	**% Error**	**% Mn at T_d sites**	**% Error**	**% Co at O_h sites**	**% Error**	**% Co at T_d sites**	**% Error**	**% CoO**	**% Error**
1.13	81.41	4.08	18.59	4.08	40.37	1.28	55.26	1.28	4.36	0.00
1.20	95.61	5.74	4.39	5.74	13.75	0.00	45.89	0.86	40.36	0.86
1.00	100.00	6.97	0.00	6.97	0.00	0.00	42.59	1.38	57.41	1.38
1.29	100.00	6.55	0.00	6.55	13.49	0.00	45.50	0.56	41.00	0.56
1.31	100.00	11.59	0.00	11.59	10.34	0.00	35.39	1.70	54.27	1.70
Average % error		**6.99**		**6.99**		**1.28**		**1.16**		**0.90**

Total average % error **3.46**