Supplementary Information (SI) for Journal of Materials Chemistry C. This journal is © The Royal Society of Chemistry 2025

## **Supplementary Information**

## Effect of shell ratio on Mn/Co<sup>2+/3+</sup> cation distribution and exchange anisotropy behavior in spinel interphase supported Mn<sub>2</sub>O<sub>3</sub>-Co<sub>3</sub>O<sub>4</sub> nanostructures

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**Fig. SI-1.** SEM micrographs obtained for (a) Mn<sub>2</sub>O<sub>3</sub>, (b) S1, (c) S2, and (d) S3 along with the particle size distribution graph.

The acquired SEM micrographs in Fig. SI-1 unveiled the morphological distribution of  $Mn_2O_3-Co_3O_4$  nanostructures. The inset figures of Fig. SI-1 outline the mean particle size, with (a) representing pristine  $Mn_2O_3$  nanoparticles and (b-d) illustrating deposited  $Co_3O_4$  nanoparticles in S1, S2, and S3, respectively. The mean particle size for  $Mn_2O_3$  core particles is found to be approximately ~140 nm, while for  $Co_3O_4$  nanoparticles, the size is relatively small, nearly ~25 nm in each sample.



**Fig. SI-2.** TEM micrograph images with different magnifications (a, c) and (b, d) for samples S1 and S3, respectively. High-resolution images with calculated d-spacing (e, f) for  $Mn_2O_3$  and  $Co_3O_4$  phases. (g, h) SAED ring patterns of each sample with indexed rings of distinct phases.

Fig. SI-2 depicts TEM micrographs, high-resolution images, and selected area electron diffraction (SAED) patterns for samples S1 and S3. TEM micrographs in Fig. SI-2(a-d) represent the morphological arrangement in the sample, offering an explicit view of the coreshell type architecture. The lattice fringes for the  $Mn_2O_3$  and  $Co_3O_4$  phases can be clearly visualized in the high-resolution images shown in Fig. SI-2(e, f). These lattice fringes are utilized to calculate the interplanar distance (*d*) between the lattice planes via inverse Fourier transform. The calculated *d*-spacing values are 2.69 Å (222) and 2.71 Å (222) for  $Mn_2O_3$ , and 2.43 Å (311) and 2.43 Å (311) for  $Co_3O_4$  in samples S1 and S3, respectively. Fig. SI-2(g, h) demonstrates the SAED pattern rings for samples S1 and S3.



**Fig. SI-3.** TEM image for S1 specimen with EDS elemental analysis at different sites (i) focused on smaller  $Co_3O_4$  particles, (ii) in a denser region constituting  $Mn_2O_3$ - $Co_3O_4$  phase, and (iii) at the middle of  $Mn_2O_3$  core.

The EDS elemental analysis was performed to validate that the bigger particle is composed of  $Mn_2O_3$  while the smaller ones is of  $Co_3O_4$ . For that EDS was taken at specific locations of the TEM image as shown in Fig. SI-3. The recorded EDS spectrum primarily reflects the peaks for Mn, Co, and O. The other observed peaks are due to the coating of the oxide particles to ensure conductivity and prevent charge buildup. The EDS elemental results for the site (i) focused on the smaller particles showing the high Co concentration with negligible Mn content, and vice-versa for site (iii), suggesting the smaller particle constitutes of  $Co_3O_4$  and the bigger one is of  $Mn_2O_3$  phase as validated by the structural XRD results.

The different site-based elemental examination of the TEM image also helps in understanding the presence of the  $CoMn_2O_4$  phase in investigated samples. The acquired data reveals the atomic percentage of Mn and Co in the (i) and (iii) regions are not significant and can appear due to the system's focusing incapacity. But the presence of Mn and Co at the site (ii) is considerably high, again indicating the feasibility of  $CoMn_2O_4$  phase formation at the point of contact between the  $Mn_2O_3$  and  $Co_3O_4$  phase, rather than separately form within the AFM domain of  $Mn_2O_3$  and  $Co_3O_4$ .



Fig. SI-4. The core-level XPS spectra acquired for Mn<sub>2</sub>O<sub>3</sub> nanoparticles (a) Mn2p, (b) O1s.

To elucidate the origin of  $Mn^{4+}$  in the studied samples, we performed the room temperature core-level XPS measurement for the pristine  $Mn_2O_3$  nanoparticles, which is utilized as the seed to produce the  $Mn_2O_3$ -Co<sub>3</sub>O<sub>4</sub> nanocomposites. The acquired XPS spectra for Mn2p and O1s levels are illustrated in Fig. SI-4. The spectra are fitted using the Voigt function in combination with the Shirley background. The Mn2p spectrum in Fig. SI-4(a) demonstrates two major peaks corresponding to  $2p_{3/2}$  and  $2p_{1/2}$ , centered at 641.5 eV and 653.2 eV. Generally, the oxidation states of Mn are identified through the Mn  $2p_{3/2}$  energy level [1]. The Mn  $2p_{3/2}$  peak is further resolved in three distinct peaks attributed to  $Mn^{2+/3+/4+}$ . Whereas, Fig. SI-4(b) displays the oxygen O1s spectra for  $Mn_2O_3$ . The O1s peak is fitted with two components corresponding to the metal-oxygen bonds (O<sub>1</sub>), and oxygen vacancy (O<sub>11</sub>). The oxygen vacancy peak is frequently observed in the reported literature on Mn oxide [41, 42]. The ratio of the observed oxidation states is derived from the area under the deconvoluted curve and outcomes are tabulated in Table SI-1.

Table SI-1. The derived parameters from the fitted XPS spectrum for the Mn<sub>2</sub>O<sub>3</sub> nanoparticles.

Contents	Binding energy (eV)	Ratio (%)
Mn <sup>2+</sup> /Mn <sup>3+</sup> /Mn <sup>4+</sup>	640.9/642.0/643.9	20.1/61.1/18.8
Mn2p-ΔE (eV)	11.9	
OI	529.8	63.9
O <sub>II</sub>	531.3	36.1

 F. Wang, M. Xiao, X. Ma, S. Wu, M. Ge and X. Yu, Insights into the transformations of Mn species for peroxymonosulfate activation by tuning the Mn<sub>3</sub>O<sub>4</sub> shapes, Chem. Eng. J., 2021, 404, 127097.



**Fig. SI-5.** Magnetic hysteresis loops recorded under ZFC and FC (1T cooling field) conditions at different temperatures (60-100 K), column (a) for S1, column (b) for S2, and column (c) for S3.

Fig. SI-5 displays the M-H loops recorded at different temperatures (60, 70, 80, 90, 100 K) for specimens S1, S2, and S3. We can observe from the plotted hysteresis loops that with an increase in temperature, the coercivity of the samples is decreased as visualized by the diminished loop area. Herein, the shifting between ZFC-FC loops can be observed only up to a temperature of 80 K, and above that the ZFC and FC loops almost overlap due to the AFM to PM transition in the system above 86 K.