# Concentric MnFe$_2$O$_4$-rich core/Cr$_2$O$_3$-rich shell nanoparticles

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**Abstract.** Concentric MnFe$_2$O$_4$-rich core/Cr$_2$O$_3$-rich shell nanoparticles were obtained considering a postsynthetic modification of preformed MnFe$_2$O$_4$@Cr(OH)$_3$ units. The complex nanomaterials display an exchange bias (EB) effect likely due to the interface intermixing and possible cluster spin-glass phase and the presence in the same units of ferrimagnetic and antiferromagnetic-ferroelectric oxides. This particular case of transition metal oxides (TMO) heterostructures underlines the potential of chemical control in their final magnetic properties.

## 1. Introduction

A material is generally considered functional if it possesses a physical property that is usable in applications. Therefore considerable amount of research currently concentrates on multifunctional materials in which several physical properties could potentially be used simultaneously.[1] Multiferroics for example, represent a promising option because they simultaneously possess several ferroic orders such as ferromagnetism and ferroelectricity.[2] Such combination of functionalities can be exhibited by TMO in heterostructures,[3] bearing in mind the semilocalized character of their d electrons.[4] The correlation between chemical composition and structure in nanoscale systems particularly, considering ion and vacancy diffusion lengths, becomes a dynamical variable to control the final properties of nanocomposites. For example, changes in cationic valence state associated with changes in oxygen vacancy concentration profoundly affect magnetic, electronic and transport properties.[5] Accordingly, developments in synthesis to exploit and control the different mobility of cations and anions to engineer gradients in static and dynamic chemistry and carrier concentrations are required.[6] Herein we report concentric structured nanocomposites based on ferrimagnetic (FiM) MnFe$_2$O$_4$ and antiferromagnetic (AFM) and ferroelectric (FE) Cr$_2$O$_3$. The synthesis includes driving Cr(OH)$_3$ on the surface of clusters of MnFe$_2$O$_4$ nanoparticles, and a post-synthetic thermal treatment that renders the nanostructures Mn ferrite- and chromium oxide-rich at the core and shell, respectively, and offering concentric phases of Mn ferrite, iron and chromium oxides that determine the final magnetic behavior.
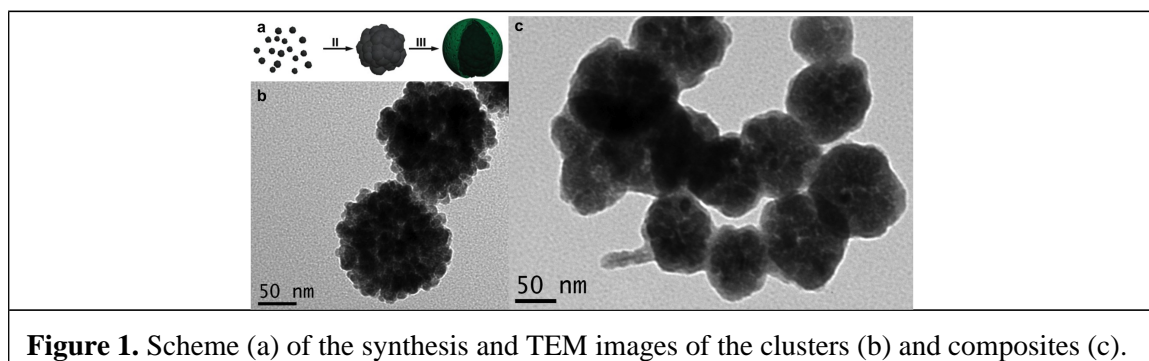
## 2. Experimental

MnFe$_2$O$_4$ clusters synthesis was carried out according to previous work.[7] FeCl$_3$ (5 mmol (Fluka) and MnCl$_2$ (2.5 mmol) were dissolved in ethylene glycol (40 mL (Aldrich)), followed by addition of NaAc

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(3.6 g (Aldrich)) and polyethylene glycol (1.0 g (Aldrich)). The mixture was stirred for 30 min and sealed in a teflonlined stainless-steel autoclave, heated to and maintained at 185 ºC for 8 h, and then allowed to cool down. The black products were washed and dispersed in aqueous solution. As a second step, 1 mL of $Cr(NO_3)_3$ (0.1 M (Aldrich)) and 4 mL of NaOH (0.075 M (Aldrich)) were added dropwise under mechanical stirring to 6 mL of $MnFe_2O_4$ clusters (1.55 mg/mL), keeping T at 25 ºC. After 10 min, the composites formed were centrifuged, dried and annealed at 650ºC during 2h in air.



**Figure 1.** Scheme (a) of the synthesis and TEM images of the clusters (b) and composites (c).

## 3. Results and Discussion

$MnFe_2O_4$ clusters were synthesized modifying the process reported by Li *et al.*[7] to have a suitable diameter ($108 \pm 10$ nm) for the process herein reported and schematically shown in fig. 1a. These cores (see fig. 1b) once in aqueous solution permit a controlled deposition of $Cr(OH)_3$ in basic medium onto their surface,[8] such that the hydroxide precipitates and evolves into a thin layer surrounding them to form core-shell nanostructures. Once the core-shell structures were formed, they were centrifuged, washed and annealed at 650ºC in air to promote the formation of the outer $Cr_2O_3$ shell. The TEM analysis (fig. 1c) reveals the core-shell structured attained, with a clear variation in the contrast up to the surface of the nanoparticles and likely with the chromium oxide ($< 8$ nm thick) surrounding each Mn ferrite-based multiple core. The XRD pattern of the sample (fig. 2a) corresponds to a mixture of several phases including the expected chromium oxide ($Cr_2O_3$, (JPCDS-ICDD card 38-1479)) as the main component (indexed) and Mn ferrite ($MnFe_2O_4$, (JPCDS-ICDD card 10-0319)) with the lower percentage in the sample. The thermal treatment promotes an intermixing process favoring the formation of hematite ($Fe_2O_3$, (JPCDS-ICDD card 24-0072)) and chromium-iron oxide ($Cr_{2-x}Fe_xO_3$). Indeed, kinetic factors become key in determining the feasibility of an ion exchange reaction, especially at the nanoscale at which limits on long-range solid-state ion diffusion are significantly relaxed by the large surface-to-volume ratios.[9] These results were confirmed by Raman spectroscopy (fig. 2b) which also demonstrated the intermixing of phases in the initial cores.
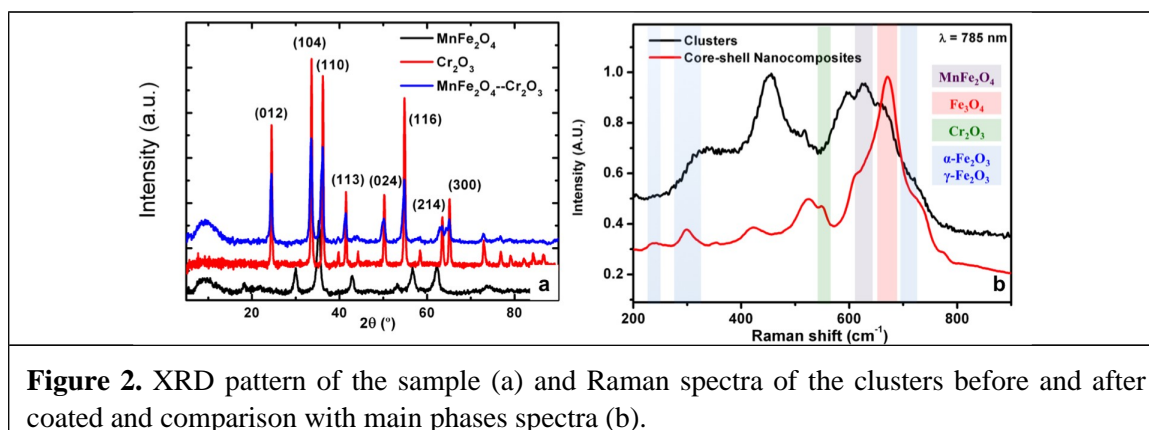


**Figure 2.** XRD pattern of the sample (a) and Raman spectra of the clusters before and after coated and comparison with main phases spectra (b).

The hysteresis loops registered at 10 K (fig. 3a) show an important decrease in the net value of the magnetization per mass of sample as shifting from $MnFe_2O_4$ (calcinated) clusters to the nanocomposites. A characteristic superparamagnetic behavior with low values of $H_C$, which decrease notably as the temperature increase, is observed in both cases. This feature underlines the presence of small magnetic units interacting in the samples, even after the annealing process. Fig. 3b includes the temperature dependence of magnetization (ZFC-FC (100 Oe)) and in both cases the curves split around T=300 K, which can also be associated with a strongly interacting system.
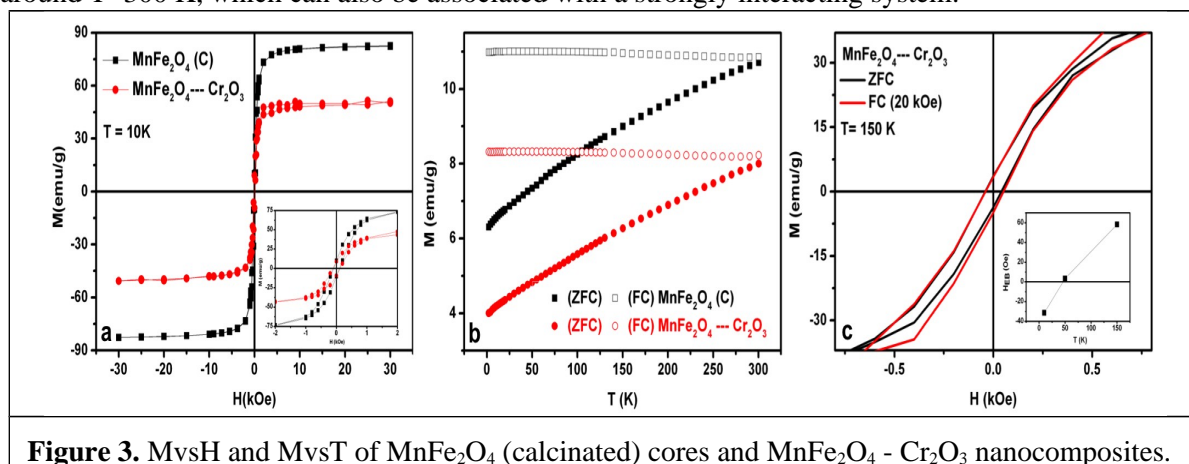


**Figure 3.** MvsH and MvsT of $MnFe_2O_4$ (calcinated) cores and $MnFe_2O_4$ - $Cr_2O_3$ nanocomposites.

The difference in the magnetic behavior of both samples can be related to the coupling between the FiM ($MnFe_2O_4$ and $Cr_{2-x}Fe_xO_3$[10]) and the AFM (hematite ($T_N = 956$ K) and $Cr_2O_3$ ($T_N = 310$ K)) phases taking place in the heterostructures. The hysteresis loops (fig. 3c) at 150 K (ZFC and FC (20 kOe)) reflect a subtle increase in $H_C$, around 100 Oe, and shift in the second case (likely due to averaging effects as having a 3D connectivity pattern between the FiM-AFM interfaces), which are generally attributed to an EB effect.[11] Though the interfacial interaction between the FiM-AFM phases may be blurred by the intermixing, it appears to be the main source of EB. The EB field ($H_{EB} = (H_{C+}+H_{C-})/2$) varies with temperature It also exhibits a temperature-driven sign reversal related to a change in the magnetic order at the interface and likely due to a spin-glass interaction at low temperatures, favored by the polycrystalline nature of the strong interacting units in the sample (see inset in fig. 3c).[12,13]

## 4. Conclusion

Concentric structured nanoparticles of FiM $MnFe_2O_4$ and AFM and FE $Cr_2O_3$ with a mixed interface based on hematite and chromium iron oxide were prepared. These complex nanomaterials display an exchange bias effect likely due to the mentioned interface and possible cluster spin-glass phase.

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