Hetero-Onion-like, multilayered, core-Fe_3O_4|shell1-$MnFe_2O_4$|shell2-γ-Mn_2O_3 nanoparticles

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The interest in bi-magnetic core-shell nanoparticles is steadily increasing due to the possibility to obtain enhanced magnetic properties. Particularly, since the report on the use of exchange bias to overcome the superparamagnetic limit [1], the amount of experimental and theoretical work on passivated ferromagnetic (FM) nanoparticles coated with the corresponding antiferromagnetic (AFM) oxide layer has increased in the recent years [2]. Most of these systems are obtained by a simple chemical treatment of the core (e.g.,oxidation), thus both core and shell contain the same transition metal. The synthesis of new hetero-core-shell systems, composed of different transition metal materials, would lead to a new degree of freedom to control the magnetic properties [3] and is thus of great interest. In this work we present the study of tri-magnetic hetero-onion nanoparticles composed by core-Fe_3O_4(ferrimagnetic, FiM)|shell1-$MnFe_2O_4$(FiM)|shell2-γ-Mn_2O_3 (FiM).

The synthesis of the onion particles was carried out following a multi-step procedure where preformed iron oxide nanoparticles were used as seeds for the subsequent growth of manganese (II) oxide and its passivation to form γ-Mn_2O_3.[4] Briefly, the Fe_3O_4 seeds were prepared by thermolysis of the iron (III) oleate [5] leading to an average particle size of 6.5 ± 1 nm. The manganese oxide layers were laid on the iron oxide-based nanocubes modifying an earlier reported procedure used for the synthesis of MnO|γ-Mn_2O_3 nanoparticles [6], leading to an interface $MnFe_2O_4$ layer of roughly 2 nm and an outer γ-Mn_2O_3 shell of 1nm. The morphology and compositions were determined through X-ray diffraction, transmission electron microscopy (Fig. 1(a)) and electron energy loss spectroscopy (EELS). The quantitative analysis of the EELS spectra and the simulations of the dependence of the percentage of each element on the position along the particle diameter, shown in Fig. 1(b), were performed using the home-made software package MANGANITAS [7].

Magnetic measurements reveal that onion nanoparticles exhibit an extra transition at the known T_C of γ-Mn_2O_3 ($T_C \sim 40$ K) and an increase in T_B, where the latter is consistent with the creation of a Mn-ferrite interface layer. The results show that the coercivity increases significantly while M_S decreases compared with Fe_3O_4 seeds magnetic data. Both effects are consistent with the incorporation of γ-Mn_2O_3 which has a much larger anisotropy and smaller M_S than Fe_3O_4. Interestingly, the hysteresis loop the onion nanoparticles shows a two stage behavior, implying that the core and the shell switch independently. This is probably due to a spring-magnet [8] effect given the diameter-thickness of the constituents. Also, the core-shell nanoparticles show larger exchange bias than the seeds, which is expected since the seeds should only have surface effects while the core-shell should have FiM-FiM coupling [2].

References:

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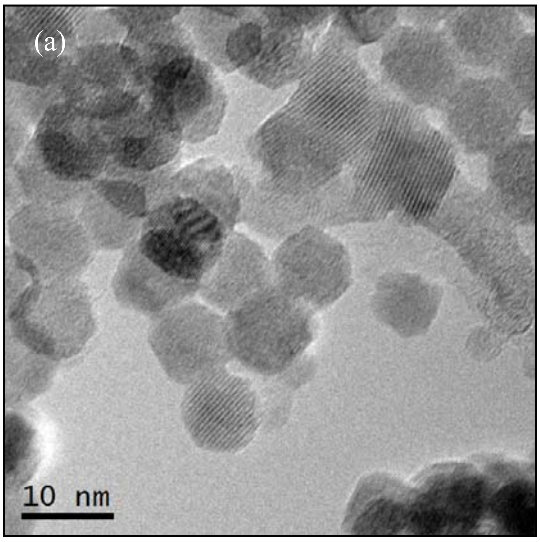
Figures:



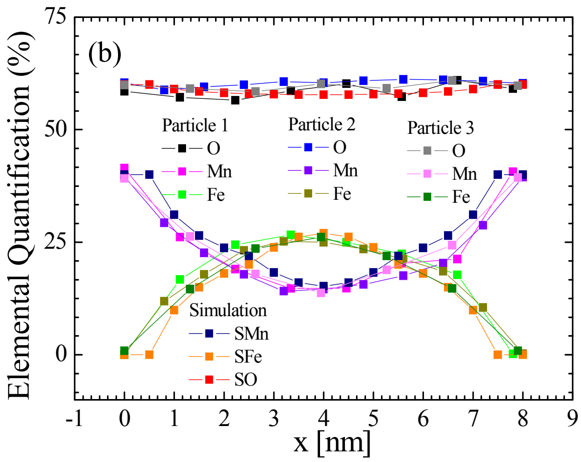


Figure. 1 (a) TEM Image of Fe_3O_4|$MnFe_2O_4$|γ-Mn_2O_3 hetero-core-shell nanoparticles. (b) Elemental quantification for three different core-shell particles and simulation considering a 1 nm Mn_2O_3/2 nm $MnFe_2O_4$/5 nm Fe_3O_4 core.