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New Insights into the Magnetic Properties of $CoFe_2O_4$@SiO_2@Au Magnetoplasmonic Nanoparticles

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Abstract: We report the successful synthesis and a complete magnetic characterization of $CoFe_2O_4$@SiO_2@Au magnetoplasmonic nanoparticles. The $CoFe_2O_4$ magnetic nanoparticles were prepared using the hydrothermal method. A subsequent SiO_2 shell followed by a plasmonic Au shell were deposited on the magnetic core creating magnetoplasmonic nanoparticles with a core–shell architecture. A spin-glass-type magnetism was shown at the surface of the $CoFe_2O_4$ nanograins. Depending on the external magnetic field, two types of spin-glass were identified and analyzed in correlation with the exchange field acting on octahedral and tetrahedral iron sites. The magnetization per formula unit of the $CoFe_2O_4$ core is not changed in the case of $CoFe_2O_4$@SiO_2@Au nanocomposites. The gold nanoparticles creating the plasmonic shell show a giant diamagnetic susceptibility, dependent on their crystallite sizes.

Keywords: core–shell nanoparticles; magnetoplasmonic nanoparticles; magnetic properties; spin-glass; exchange field

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1. Introduction

The flexibility of spinel ferrite $CoFe_2O_4$ or a $(Co_{1-x}Fe_x)_T(Co_xFe_{2-x})_OO_4$ structure, with a variable occupancy of tetrahedral (T) and octahedral sites (O), provides a wide range of physical properties and applications, particularly in their nanosized form. As a function of the inversion parameter, x, the structure changes from a normal spinel (x = 0) to an inverse spinel type (x = 1). In a bulk state, the $CoFe_2O_4$ ferrite has mainly an inverse-type spinel structure and crystallizes in an FCC-type lattice, space group $Fm\bar{3}m$. The ferrite is ferrimagnetically ordered, and the magnetic moments of the atoms situated in octahedral and tetrahedral sublattices, respectively, being antiparallelly aligned. According to the degree of inversion, a large range of magnetizations can be obtained. The superexchange parameters inside and between magnetic sublattices were determined in the bulk state, starting from a mean field model [1,2].

At the nanometer scale, the magnetic behavior of $CoFe_2O_4$ ferrite shows significant differences with respect to that of the bulk state. The crossover to a single domain behavior is 40 nm [3]. The system becomes superparamagnetic between 7 and 10 nm. A core–shell model was proposed for $CoFe_2O_4$ nanograins, in which a core of aligned spins is surrounded by a magnetically disordered shell [4]. The low-temperature magnetic behavior of ultra-small $CoFe_2O_4$ nanoparticles was also associated with a random freezing of surface