Characterization of Fe_3O_4 nanoparticles by Electron Magnetic Resonance Spectroscopy: Relation between synthetic parameters and magnetic behaviour

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Magnetic nanoparticles have attracted importance in the biological area due to different applications such as contrast agents for magnetic resonance imaging [1], magnetic carriers for drug delivery [2] or hyperthermia [3]. Among the myriad of materials with high magnetic response, magnetite has been widely used because of its active surface chemical functionality, biocompatibility and low cost. Nevertheless for medical purposes it is necessary to control not only the size and the size distribution, but also the synthesis method must also provide a way to avoid particle aggregation and protect the surface from oxidation. In this sense, we present a comparative study of the synthetic parameters that affect the size and the content of matter surrounding magnetite nanoparticles smaller than 7 nm. What's more, in this kind of magnetic nanoparticles, different effects like surface effects or aggregations yield contradictory results for the same kind of nanoparticles. In order to discriminate these contributions, electron magnetic resonance spectroscopy has been employed.

For the preparation of Fe_3O_4 nanoparticles, reduction of iron(III) acetylacetonate by hexadecanediol in the presence of oleylamine and oleic acid was performed. Variations in the concentrations of the reagent and the stirring method yielded monodisperse nanoparticles between 3.5(5) to 7.1(9) nm. The content of organic ligands attached to the surface was calculated from thermogravimetric measurements. The weight loss was associated to oleic acid and differs remarkably among studied samples, ranging from 16.1 % to 40.9 %. Although the higher organic content corresponds to samples with smallest particle size, it has been observed that reagents concentrations also affect the organic content.

Electron magnetic resonance spectra of solid nanoparticles show an intense and slightly asymmetric line. The position of the main resonance field, H_r,, as well as the peak to peak linewidth, ΔH_{pp}, vary depending on the sample. The signal broads and shifts to the left from the position at g_{efec} = 2.0, corresponding to samples with ideal superparamagnetic behaviour, with decreasing organic content. Nevertheless, it was verified a dependence of the shape and position of the signal with the sample handling in the RPE experiments. In this sense, a measurement method has been optimized in order to get reproducible results, that is the samples were either embedded in a piece of paper or deposited in a polymer film forming a monolayer. The angular dependence of the signal on these deposited nanoparticles was studied when the sample was placed in the perpendicular (θ = 90º) and parallel (θ = 0º) orientations. It has been observed that the shifting between 0 and 90º (Δg_{efec}) is more related with the organic content surrounding the NP than with the diameter in the studied size range. Finally, the thermal evolution of the resonance signal was also measured for two samples with two different Δg_{efec} values related to superparamagnetic and ferromagnetic behaviours, respectively.

References

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