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Improving the magnetic heating by disaggregating nanoparticles

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ABSTRACT

Recently, potential applications of the magnetic heating for heterogeneous catalysis or organic synthesis have been reported. As these new applications are not limited by biocompatibility requirements, a wide range of possibilities for non-aqueous colloidal nanoparticles with enhanced magnetic properties is open. In this work, manganese and cobalt ferrite nanoparticles are synthesized by co-precipitation method with average particle size around 12 nm. The particles are either coated with tetramethylammonium hydroxide (TMAOH) and dispersed in water or with oleic acid (OA) and dispersed in hexane to produce aggregated or disaggregated nanoparticles, respectively. It is observed that the particle disaggregation improves significantly the heating efficiency from 12 to 96 W/g in the case of cobalt ferrite, and from 120 to 413 W/g for the manganese ferrite. The main responsible for this improvement is the reduction of hydrodynamic volume that allows a faster Brownian relaxation. This work also discusses the relevance of the size distribution.

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1. Introduction

The heating efficiency of magnetic nanoparticle is nowadays intensively investigated because the applications to magnetic cancer therapy [1–6]. However, the potential applications for heterogeneous catalysis has been recently reported [7]. Additionally, there are recent evidences that different chemical reactions in liquid media can be triggered using heating induced by iron oxide nanoparticles [8]. These new concepts consist in taking advantage of the heating efficiency of the nanoparticles under alternating magnetic field to produce in-situ catalysis or to induce organic synthesis. This opens a new and wide range of possibilities in the area of heating efficiency of nanoparticles. First of all, biocompatibility is no more a requirement, thus, any kind of metals or metal alloys (Fe, Co, Ni, FeCo, etc) or any magnetic oxide with enhanced magnetic properties can be used [7,9–13]. Second, the dispersion media can be organic or inorganic; this provides different magnetic properties to the nanoparticles compared to the aqueous colloids [9,14]. Finally, new frequency and amplitude field ranges can be explored because no limitation in the product $Hf < 5 \times 10^9$ A/ms [see Ref. [15]] is necessary for a catalytic process.

At present, ferrite nanoparticles are the most common material for hyperthermia because the low toxicity, good magnetic properties and straightforward synthesis by ecofriendly routes, where the spinel structures can be obtained with high crystallinity degree. Thus, the heating efficiency in aqueous colloids of these materials is well established [16–21].

It is know that for an assembly of interacting particles which are at the limit of superparamagnetic to ferromagnetic behavior, the role of dipolar interactions on the heating efficiency is to diminish the effective field acting on a particle, i.e., for isolated non-interacting particles, the heating is more effective than in the case of interacting particles [22–27]. At very low concentrations, the state of interacting or non-interacting particles depends on aggregation degree. Nanoparticles dispersed in water form aggregates, therefore, the particles are interacting independently of the concentration [14,16]. On the other hand, particles synthesized in organic media are disaggregated and the interactions depend then on concentration; thus, the heating efficiency can be improved significantly by disaggregating the particles [14].

In addition, the aggregation degree also plays a significant role

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for those particles whose heating mechanism is mainly given by Brownian relaxation. Specially, this is the case for the magnetic nanoparticles with high magnetic anisotropy, as the cobalt ferrite. In the case of aggregates, large hydrodynamic sizes slow down the Brownian relaxation diminishing the heating efficiency; the particles must be disaggregated in order to get faster relaxations. On the other hand, manganese ferrites are soft materials which main relaxation mechanism in given by Neel although Brownian relaxation cannot be discarded at all.

This work discusses the influence of aggregation degree and size distribution on the SAR for the case of cobalt and manganese ferrites. We show that the disaggregation of nanoparticles improves significantly the heating efficiency because the release of the Brownian relaxations.

2. Experimental methods

2.1. Materials

Manganese (II) chloride tetrahydrate (99%) is purchased from Alfa Aesar. Iron (III) chloride hexahydrate (97%), cobalt (II) hexahydrate (98%), tetramethylammonium hydroxide solution (10%wt), hexane (95%), hydrochloric acid (37%) and oleic acid are purchased from Sigma Aldrich. Sodium hydroxide (analytical grade) is purchased from Merck. All reagents are used without further purification.

2.2. Synthesis of $MnFe_2O_4$ and $CoFe_2O_4$

To synthesize the nanoparticles, 2.5 mmol of $MCl_2 \cdot nH_2O$ ($n = 6$ for $M = Co$ and $n = 4$ for $M = Mn$) is dissolved in 250 μL of HCl (37%) and 4 mL of water is added. On the other hand, 5 mmol of $FeCl_3 \cdot 6H_2O$ is dissolved in 10 ml of water. Both solutions are heated at 50 °C, mixed and added to a solution of 50 ml NaOH (3 M) at 100 °C. The stirring is adjusted to 600 rpm, and a black precipitate is formed immediately. The synthesis temperature is kept constant at 100 °C with different reaction times t at 15, 30 and 60 min, in order to get different particle sizes. The samples are called M-t, with $M = Mn$, Co and $t = 15$, 30, 60, indicating the corresponding ferrite and the reaction time of the synthesis. After that, the mixture is cooled down to room temperature and magnetically separated, washed several times with distilled water under sonication. Finally, the precipitate is dispersed in 0.1 M TMAOH [28]. All samples are fractioned by centrifugation in order to select the smallest particle sizes [29,30].

2.3. Oleic acid coating (OA)

To reduce particle agglomeration and produce a non-polar stable ferrofluid, 3 ml of dispersed NPs are magnetically separated from the TMAOH solution and then mixed with 500 μL of OA and 2 mL of hexane under vigorous stirring during 10 min [31].

2.4. Structural and colloidal characterization

X-ray diffraction (XRD) patterns are measured by a multipurpose PANalytical X'pert MPD with Cu-K_α source. The X-ray patterns are collected between 10° and 70° in 2θ. The average crystallite size (D_{XRD}) is calculated using the Scherrer equation with the full-width-half-maximum (FWHM) of the (311) peak.

The size and shape of the particles are measured by transmission electron microscopy (TEM) using a JEOL-2000FXII at 200 kV, and a high-resolution transmission electron microscope (HRTEM) with XEDS detector JEOL JEM 3000F operated at 300 kV. The samples are prepared by diluting the nanoparticles in ethanol, a droplet of diluted sample is placed on a carbon coated copper grid and the solvent is evaporated at room temperature. The mean particle size and distribution are evaluated by measuring more than 100 particles by means of Digital Micrograph™. Afterwards, data are fitted to a Gaussian distribution to obtain the mean particle size (d_{NP}) and standard deviation (σ). The polydispersity degree is calculated as σ/d_{NP}, and is considered to be representative of the homogeneity of the particle sizes. In addition, an elemental analysis by energy dispersive spectroscopy (EDS) is performed in each sample.

Colloidal properties are studied in a Zetasizer Nano S, from Malvern Instruments. Hydrodynamic sizes of the particles in suspension, d_h, are measured by Dynamic Light Scattering (DLS) with the samples dispersed in water and hexane. Each hydrodynamic value is the result of three different measurements at different dilutions to avoid errors coming from multiple scattering; the scattering index for the solvent of the colloid, water or hexane, is used. The d_h is measured by DLS in volume because the presence of some few large aggregates could overestimates d_h when are obtained from the intensity data.

The Fe concentration is measured with an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES) Perkin Elmer Optima 2100 DV. For this purpose samples are digested with nitric acid to oxidize the organic coating and then, with hydrochloric acid to dissolve the particles.

2.5. Magnetic characterization

Static magnetic measurements are carried out on powder samples by means of a Quantum Design vibrating sample magnetometer. Magnetization curves are measured up to 5 T at 5 K and 300 K. Zero field-cooled and field-cooled curves (ZFC-FC) are obtained from 5 to 300 K at 100 Oe applied magnetic field.

Heating capacities of the nanoparticles are measured with a commercial system Magnetherm 1.5 (Nanotherics) with a close circuit of water maintained at 16 °C that cools the coils. Additionally, the samples are placed inside a Dewar to avoid heat loss by convection or conduction. The samples are characterized under radiofrequency field with 110 kHz and 200 Oe field frequency and amplitude, respectively.

The temperature of the colloids is measured with a fiber optical thermometer and registered with a computer. Prior to turning the magnetic field on, the sample temperature is recorded for about 30 s in order to ensure thermal stability and to have a baseline for the calculation of SAR. As the field is turned on, the temperature rise is measured either during 300 s or up to 80 °C for aqueous colloids and 40 °C for hexane colloids, well below the corresponding boiling temperatures 100 °C and 69 °C, respectively. By performing a linear fit of data (temperature versus time) in the initial time interval, the slope $\Delta T/\Delta t$ can be obtained. As the measurements are performed in non-adiabatic conditions, the curve slopes $\Delta T/\Delta t$ are fitted only in the first few seconds after turning the magnetic field on. The time range is selected such as the slope is maximum, typically during the first 30 s.[32] Previously to any measurement, a blank sample containing only water is measured under the same conditions to ensure that there is no heating transfer from the coils.

Since the Fe concentrations are in the range 1–10 wt%, the SAR values can be calculated as $SAR = \frac{C_{liq}}{c_{Fe}} \frac{\Delta T}{\Delta t}$, where C_{liq} is the specific heat capacity of water (4.185 J/gK) or hexane (2.28 J/gK) and c_{Fe} is the Fe weight concentration in the colloid [18]. Then, the SAR values are obtained by fitting the experimental heating curves and normalizing to the iron mass (W/g_{Fe}).

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