



Same magnetic nanoparticles, different heating behavior: Influence of the arrangement and dispersive medium



Irene Andreu^a, Eva Natividad^{a,*}, Laura Solozábal^a, Olivier Roubeau^b

^a Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC-Universidad de Zaragoza, Campus Río Ebro, María de Luna, 3, 50018 Zaragoza, Spain

^b Instituto de Ciencia de Materiales de Aragón (ICMA), CSIC-Universidad de Zaragoza, Departamento de Física de la Materia Condensada, 50009 Zaragoza, Spain

ARTICLE INFO

Article history:

Received 30 June 2014

Received in revised form

23 October 2014

Accepted 25 October 2014

Available online 29 October 2014

Keywords:

Magnetic hyperthermia

Specific absorption rate

Iron oxide nanoparticles

Seeded growth synthesis

Linear response theory

Colloidal dispersions

ABSTRACT

The heating ability of the same magnetic nanoparticles (MNPs) dispersed in different media has been studied in the 170–310 K temperature range. For this purpose, the biggest non-twinned nanoparticles have been selected among a series of magnetite nanoparticles of increasing sizes synthesized *via* a seeded growth method. The sample with nanoparticles dispersed in n-tetracosane, thermally quenched from 100 °C and solid in the whole measuring range, follows the linear response theoretical behavior for non-interacting nanoparticles, and displays a remarkably large maximum specific absorption rate (SAR) value comparable to that of magnetosomes at the alternating magnetic fields used in the measurements. The other samples, with nanoparticles dispersed either in alkane solvents of sub-ambient melting temperatures or in epoxy resin, display different thermal behaviors and maximum SAR values ranging between 11 and 65% of that achieved for the sample with n-tetracosane as dispersive medium. These results highlight the importance of the MNPs environment and arrangement to maintain optimal SAR values, and may help to understand the disparity sometimes found between MNPs heating performance measured in a ferrofluid and after injection in an animal model, where MNP arrangement and environment are not the same.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The heating ability of magnetic nanoparticles (MNPs) for magnetic hyperthermia [1,2] is commonly quantified by means of the specific absorption rate (SAR) [3,4], also referred to as specific loss power (SLP). This heating ability is related to the magnetization reversal processes that occur when the MNPs are subjected to an alternating magnetic field. Accordingly, SAR values depend, like magnetic properties, on temperature.

Given that magnetic hyperthermia therapy involves temperatures from 36 up to about 50 °C, it is essential to evaluate SAR in this narrow temperature range, in function of the amplitude, H_0 , and frequency, f , of the applied magnetic field. Some materials may show a weak SAR variation in this range, making reasonable the use of average values for therapy planning. But in other cases, SAR values may change appreciably as temperature increases. An extreme case is found in self-regulating MNPs [5], in which the SAR drop at the temperature range of interest is the basis of their functionality.

Also, the determination of SAR in a wider temperature range may provide further information about the MNPs, needed for the feedback synthesis–characterization–application. For example, it is well-known that the thermal dependence of the out-of-phase ac magnetic susceptibility, χ'' , provides useful information of certain magnetic transitions. At low H_0 values, where the linear response theory [6] is fulfilled, SAR is linearly proportional to χ'' , thus providing similar information [7], but obtained with f and H_0 values more adequate for magnetic hyperthermia.

SAR(T) characterization may be also useful in the study of the behavior of MNPs in different dispersive media, where viscosity changes due to melting or pre-melting processes can allow orientation or free movement of MNPs. In this sense, the influence of the MNP colloidal environment on the temperature evolution of the magnetization, M , has been studied [8,9] under static magnetic fields, through zero-field-cooled (ZFC) and field cooled (FC) $M(T)$ measurements. Also, ac susceptibility studies have been performed on similar systems [10], using alternating magnetic fields with low amplitudes and frequencies.

In this work, we apply SAR(T) characterization to study the behavior of several systems composed of the same magnetic nanoparticles in different dispersive media and subjected to an alternating magnetic field suitable for magnetic hyperthermia. The

* Corresponding author.

E-mail address: evanat@unizar.es (E. Natividad).

different SAR(*T*) values and trends obtained demonstrate that, not only the intrinsic properties of the MNPs determine their heating ability, but also the spatial arrangement can enhance or reduce SAR values and shift the temperature at which the heating ability becomes maximal. Even though the experiments are not performed in physiological environment, the present findings certainly give a clue about the origin of the loss of performance of MNPs in *in-vivo* applications [11].

2. Experimental methods

2.1. Synthesis of magnetic nanoparticles

A series of magnetite nanoparticles of increasing sizes was synthesized following and adapting the original seeded growth method of Sun et al. [12,13] and a more recent study by Ern e et al. to obtain so-called “facets” and “twins” nanoparticles [14]. Thus ca. 6 nm Fe₃O₄ spherical nanoparticles seeds were obtained adding Fe(acac)₃ (2 mmol, > 99.9% trace metal basis), 1,2-hexadecanediol (10 mmol, 97%), oleic acid (6 mmol, 90%) and oleylamine (6 mmol, > 70%) to 20 mL benzyl ether (99%) under a flow of argon and first stirring magnetically at room temperature under Ar for 5 min. The mixture was then heated to 200 °C, maintained for 2 h at this temperature and heated to reflux (ca. 293 °C) for 1 h, under continuous stirring and flow of Ar. The rate of heating, a key parameter with respect to final nanoparticle size and shape, was the maximum attainable with our setup, at ca. 2.5 °C/min. The formed black dispersion was cooled to room temperature by removing the heat source, maintaining stirring. Once at room temperature, the reaction mixture was opened to air and ethanol (40 mL) was added, resulting in the precipitation of a black solid that was separated by centrifugation. This raw product was redispersed in n-hexane (40 mL, > 99%) in the presence of oleic acid (0.05 mL) and oleylamine (0.05 mL) with bath ultrasonication. After centrifugation to remove undispersed material, the product was then precipitated with ethanol (16 mL), centrifuged to remove the supernatant, and redispersed into n-hexane (16 mL) with bath ultrasonication. A first growth step was then done adding 84 mg of the obtained seeds dispersed in n-hexane to a mixture of Fe(acac)₃ (2 mmol), 1,2-hexadecanediol (10 mmol), oleic acid (2 mmol) and oleylamine (2 mmol) in 20 mL benzyl ether previously stirred for 5 min under a flow of Argon at room temperature. The mixture was then brought to 100 °C, temperature at which it was kept 30 min without condenser under Ar flow to evaporate the hexane. After fitting the condenser, the mixture was then warmed further and kept 1 h at 200 °C and finally refluxed 30 min, all under Ar flow. The exact same workup procedure as for the seeds was used. A total of 26 identical growth steps were then done using the exact same procedure except for the amount of nanoparticle seeds from the previous steps, now using 80 mg, and for the last seven growth steps reducing the amount of both oleic acid and oleylamine to 1 mmol. All reagents and solvents were purchased from Aldrich at the indicated purities and used without further purification.

2.2. Characterization of structure, morphology and size

The hydrodynamic size of MNPs was monitored after every five growth steps by Dynamic Light Scattering (DLS) using a Zetasizer Nano ZS from Malvern Instruments in backscatter mode using a 633 nm HeNe laser. The position of the maximum of the intensity distribution of particle sizes was used to check this size. For DLS experiments, the MNPs were suspended in hexane to reach a concentration of 0.03 mg/ml.

Complementary, given that the DLS intensity distribution does not reflect the precise size of MNPs, Transmission Electron

Table 1
Summary of samples prepared for SAR(*T*) measurements.

| Sample | Medium | <i>c</i> (mg/g) | <i>c</i> (mg/mL) |
|--------|---------------|-----------------|------------------|
| C6 | n-Hexane | 8.9 | 5.84 |
| C6-bis | n-Hexane | 15.3 | 10.10 |
| C12 | n-Dodecane | 9.0 | 6.90 |
| C16 | n-Hexadecane | 8.3 | 6.44 |
| C24 | n-Tetracosane | 9.0 | 7.08 |
| Epo | Epoxy resin | 84.3 | 62.7 |

Microscopy (TEM) images were taken after selected growth steps, in order to determine morphology and real size. Small quantities of diluted hexane ferrofluids were dropped onto carbon-coated copper grids and the solvent was left to evaporate. Observations were made on a JEOL 2000 FXII instrument working at an acceleration voltage of 200 kV.

The crystalline phase of selected nanoparticles was identified by X-ray powder diffraction (XRD). Experiments were performed with a Phillips X'per Pro diffractometer (Cu K α radiation) on MNP powder. Diffraction patterns were recorded in the 2 θ range 10–100° with a scan step of 0.03° (2 θ) for 3 s.

2.3. Preparation of samples for SAR(*T*) measurements

The MNPs obtained after the 20th growth step, selected for the study, were suspended in 4 different alkane solvents and in epoxy resin (Epofix™). A summary of the samples and their characteristics can be found in Table 1.

For the samples dispersed in n-hexane (C₆H₁₄), n-dodecane (C₁₂H₂₆) and n-hexadecane (C₁₆H₃₄), aliquots of the original ferrofluid (in n-hexane) were evaporated in weighted vials. Once the sample solid mass (MNPs+surfactant) was determined, the adequate volume of the selected organic solvent was added to reach the desired approximate concentration, and the vials were afterwards ultrasonicated in a water bath for 5 min at room temperature. Eventually, special purpose quartz containers were filled with these ferrofluids and sealed with adhesive to prevent leakages under the vacuum conditions required for the measurements.

The sample dispersed in tetracosane (C₂₄H₅₀) was prepared in a similar way but, due to the higher melting point of this alkane (48–54 °C), the dispersion was performed in a water bath at 100 °C under ultrasonication with a Hielscher UP200s working at 85% of its maximum power for 30 s using the S3 tip. After filling the quartz holder, the sample was thermally quenched in an ice-water bath and then sealed with the adhesive. Quenching provides a much more homogeneous final MNP distribution than slow cooling, based on visual inspection.

A last aliquot of the original ferrofluid was washed three times with dichloromethane and ethanol to remove as much surfactant as possible. The solid was then dispersed in epoxy resin in a high concentration, and the mixture was heated at 60 °C for resin curing.

2.4. Determination of sample concentration

The sample concentration, *c* (mass of magnetic material per mass or volume of sample), was determined combining elemental analysis with measurements of first magnetization curves, *M*(*H*). The Fe content was determined by Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES, Jobin Yvon 2000). *M*(*H*) curves were measured from 0 to 5 T at 300 K in a superconducting quantum interference device MPMS-XL from Quantum Design.

An additional sample of MNPs dispersed in tetracosane was prepared in the same way as sample C24. After recording its *M*(*H*) trend, this sample was digested in *aqua regia* at 90 °C and diluted

Download English Version:

<https://daneshyari.com/en/article/1798906>

Download Persian Version:

<https://daneshyari.com/article/1798906>

[Daneshyari.com](https://daneshyari.com)