Effects of Organic Coating on Hyperthermic Efficiencies

An Exploration of Role of Coating on Hyperthermic Properties

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Abstract

In the last years magnetic heating has been widely investigated for several applications in biomedicine (in particular for magnetic fluid hyperthermia, MFH, and controlled drug release) and catalysis. MFH works by means of injection of magnetic nanoparticles (MNPs) and subsequent application of an alternating magnetic field (AMF) of frequency f and amplitude H, which determines heat generation. The estimation of MNPs heat transfer efficacy is given by the specific loss power (SLP). Naked MNPs when used for biomedical applications need to be covered with an appropriate biocompatible coating, that ensures chemical and biological stability. Their heating efficiency is affected by the amplitude and frequency of the applied AC field, and by the microscopic parameters as the core size, the kind of magnetic ion and the NPs core shape. These variables can reduce or increase the heat release and therefore it appears crucial to determine what is the best combination of chemico-physical characteristics to have an optimal system for applications in medical area[1]. In the current investigation we studied the effect of different biocompatible coatings on the hyperthermic efficiency of novel MNPs.

Introduction

In the present study, spinel iron oxide nanoparticles of Maghemite ($\gamma - Fe_2O_3$) were synthesized by using chemical coprecipitation, the most used method in the case of NPs intended for biomedicine, due to low cost, simplicity and high yield of the reaction. The different biocompatible coatings chosen for this study were: polyethylene glycol with oleic acid (PEG-OA), double-oleic acid (OA-OA), polyacrylic acid (PAA) and polyglycolic acid (PGA).

Materials and Methods

The magnetic properties and the stability of the five magnetic nanostructures were investigated by TEM, DLS, AFM, SQUID and calorimetry (for MFH) to have a complete information about magnetic and structural features.

MNPs Heating Mechanisms

The dominant mechanisms for heat production for superparamagnetic MNPs are the Néel and Brown relaxation. The respective typical relaxation times are expressed as:

$$\tau_N = \tau_0 e^{\left(\frac{KV}{k_B T}\right)} \qquad \tau_B = \frac{3\eta V_h}{k_B T} \tag{1}$$

The effective relaxation time τ_{eff} is a combination of Néel and Brown times $1/\tau_{eff} = 1/\tau_N + 1/\tau_B$. The quantity useful for expressing the efficiency of heat release in MFH is the SLP, which is affected by shape, size, crystal structure, saturation magnetization and magnetic susceptibility, as well as by field strength (H) and frequency (f) of the alternating magnetic field. The SLP, in the Linear Response Theory model, is given by::

$$SLP = \pi \mu_0 \chi_0 H_0^2 f \frac{2\pi f \tau_{eff}}{1 + (2\pi f \tau_{eff})^2} \frac{1}{\rho} \tag{2}$$

In the magnetic hyperthermic measurements, the ferrofluid samples were positioned at the center of the coil of an alternating magnetic field generator (by Nanoscale Biomagnetics S.L.). The experiments started from room temperature $\sim 20°C$, and were performed as a function of frequency (between 252 and 808 kHz, at constant magnetic field of 200 Oe) or as a function of field (at 252, 397 and 728 kHz and the field strength was varied in the range 50-300 Oe). The SLP values were calculated according to [2]:

$$SLP = \frac{c_{MNP} m_{MNP} + c_{H_2O} m_{H_2O}}{m_{MNP}} \frac{\Delta T}{\Delta t} \tag{3}$$

Results

The particles present a diameter below the superparamagnetic limit (~20 nm), as confirmed by the very narrow hysteresis loops. The ZFC-FC curves show low value of blocking temperature (T_B ~63 K) for the naked particles and around 95÷100 K for the coated MNPs. The magnetic saturation values vary between 73.5 emu/g (@PAA) and 57.6 emu/g (@PEG-OA), and present an intermediate value for bare MNPs. The coercive field is around 300 Oe.

Sample	d_{TEM} (nm)	d_{AFM} (nm)	T_B (K)	M_S (emu/g)	H_C (Oe)	K_{eff} $(\cdot 10^4 J/m^3)$	χ_d $(\cdot 10^{-5} emu/g)$
MNP	7.4(2)	/	63.0	71.6(1)	320	2.87(5)	2.0(3)
@PAA	8.9(2)	9.2(6)	98.8	73.5(2)	361	4.72(5)	6.0(8)
@PGA	8.8(2)	9.0(7)	94.6	76.5(1)	320	5.04(1)	8.5(2)
@PEG-OA	8.5(2)	10.4(1)	97.8	57.6(2)	335	2.88(7)	3.4(6)
@OA-OA	8.2(2)	11.6(1)	97.3	60.3(6)	351	3.27(6)	3.6(5)

Table 1: Dimensional and magnetic quantities of naked and coated MNPs

The samples present values of anisotropy K_{eff} comparable to the one of pure bulk magnetite (1.3 10^4). From Figure 1 we can note a superparamagnetic behavior for all MNPs and in the bottom inset the peaks of demagnetizing magnetostatic (dipolar) interactions for three samples are reported: the dipolar interactions are dominant over the exchange interactions.

The χ_d value, which denote the existence of non-collinear spins in the magnetic structure, are different for the samples: for @PAA and @PGA are higher than the other three samples (bare, @OA-OA and @PEG-OA). χ_d values are about 10^{-5} for the coated samples, while the typical value for bulk particles is in the order of 10^{-6} emu/g. This suggests that the coating does not erase completely the surface spin disorder; the superexchange interactions are partially suppressed by coating and consequently these spins near the surface are not collinear, but rather subtend a certain angle with the magnetization easy axis.

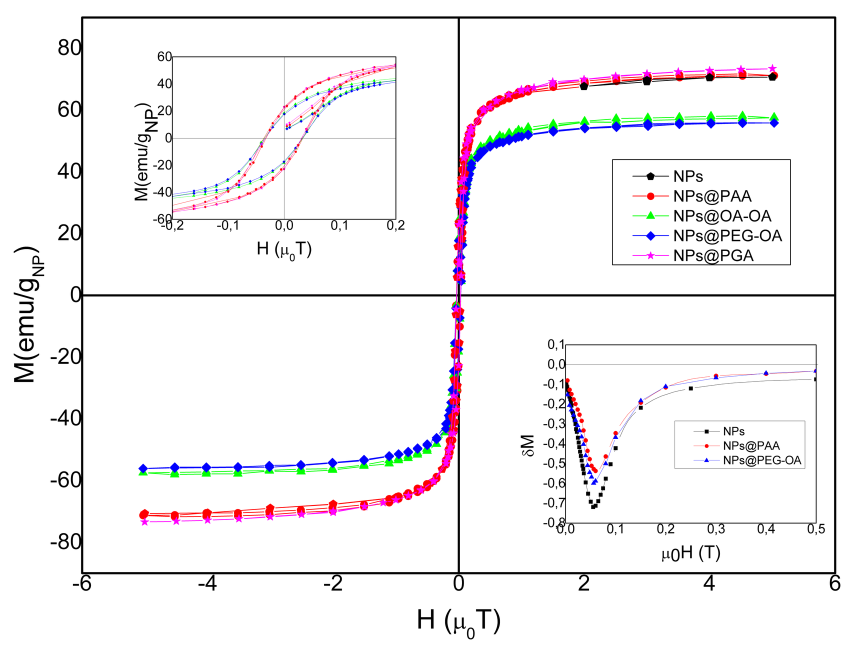

Figure 1: Hysteresis curves at 2.5 K.Top inset: zoom at low field to show hysteresis loops. Bottom inset: Henkel δm curves, where its clear the dominant effect of dipolar interaction.

Sample	$SLP_{max}(W/g_{\gamma-Fe_2O_3})$	$\tau_N(ns)$	$\tau_B(10^{-4}s)$
MNP	196(20)	46(2)	3.8(2)
@PAA	220(22)	290(7)	11(3)
@PGA	217(22)	600(10)	19(1)
@PEG-OA	154(15)	39(6)	7.7(3)
@OA-OA	142(14)	60(6)	6.1(1)

Table 2: Maximum values of SLP for each sample and the Néel and Brown relaxation times evaluated by magnetic and structural measurements.

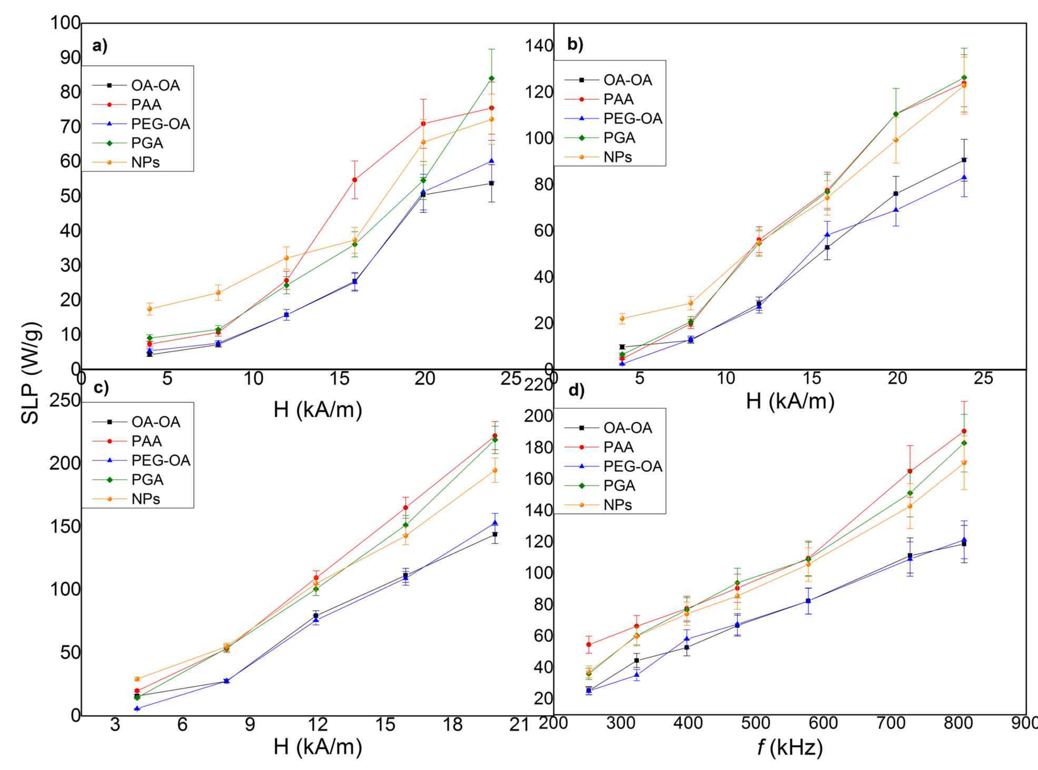

Figure 2: The SLP values for the sample with different coatings at 252 kHz (a), 397 kHz (b) and 728 kHz (c). In (d) SLP as a function of frequency at 200 Oe is shown.

The maximum values of SLP are observed (at 728 KHz and H=21 kA/m) for PAA@MNP (220 W/g) and PGA@MNP (217 W/g) whereas the naked particles have an SLP of 196 W/g at 728 kHz. The differences in SLP among samples with different coatings are contained within the error bars. As a consequence, we can assert that the coatings @PAA and @PGA give the same hyperthermic efficiency.

Conclusions

- The coating, as well as size and shape, of MNPs plays a fundamental role to determine the hyperthermic efficiency.
- The chemical characteristics (as the coating) influence the saturation magnetization, as seen by the comparison of $M(H)$ curves obtained for compounds with the same magnetic core diameter.
- The coating modifies the topology of the surface spins of MNPs, reducing the disorder and consequently the spins are not collinear.
- The best coatings to reach high hyperthermic efficiency are @PAA, @PGA and @PEGMA (compared with naked nanoparticles) which are good candidates for biomedical use.

Bibliography

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