Controlling the Curie-temperature of Magnetic Nanoparticles for Hyperthermia

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ABSTRACT

The control of Curie temperature is very necessary in hyperthermia where cancerous cells are heated up to temperatures of 42-43°C using magnetic nanoparticles (NPs). In this paper we point out that surface spins have a major role in determining the Curie temperature of ferrite Mn₁₋ₓZnₓFe₂O₄ nanoparticles, where x = 0.5, 0.6, 0.8, and 1.0. The addition of Zn in Mn₁₋ₓZnₓFe₂O₄ is suggested to cause changes in the lattice distances. These changes are expected to be more pronounced near the surface of the NPs. Accordingly, surface disorder occurred which is surface spins. Our magnetization measurements revealed several trends. For each particular x value, the field cooled (FC) magnetization of the NPs remained nearly constant at temperatures below 50 K. Above this temperature, the magnetization either exhibited peaked regions or decreased sharply. The Curie temperature also increased up to x = 0.6, and then decreased for x = 0.8 and 1.0. The existence of the initial constant magnetization and the appearance of peak regions were considered to be signatures of surface spin-glass structures. A core-shell magnetization model of the ferromagnetic surface and the ferrimagnetic core was introduced to account for these results.

Keywords: hyperthermia, Mn-Zn ferrites, nanoparticles, surface spins

INTRODUCTION

Due to finite size effects, such as the high surface-to-volume atomic ratios and different crystal structures, magnetic NPs exhibit interesting and considerably different magnetic properties than those found in their corresponding bulk materials. These new properties prompted the implementation of this type of NPs in diverse fields. But the science of magnetic NPs is still evolving in three different directions. These are: the satisfactory understanding of their physics, the synthesizing of NPs in well-specified sizes with uniform distribution, and the expanding of the fields of their applications. All these directions are currently the subject of intense research activities around the world.

Hyperthermia using magnetic NPs has been gaining a lot of interest recently as a method for curing cancer (Hergt et al. 1998; Berry and Curtis 2003; Mornet et al. 2004; Hergt et al. 2006; Salloum et al. 2008). Hyperthermia involves heating of the cancerous cells up to temperatures of 42-43°C. If heated beyond this temperature range, the normal cells are damaged which is undesirable (Deger et al. 2002; Park et al. 2002; Hergt et al. 2008; Thiesen et al. 2008). The magnetic NPs are heated when subjected to oscillating magnetic field (Berry and Curtis 2003; Mornet et al. 2004; Aqil et al. 2008; Kline et al. 2009). But temperatures above the 42°C (315 K) may cause necrosis (Brusentsoy et al. 2002; Berry and Curtis 2003). A way to overcome this problem is to regulate the magnetic field and the time of exposure to this field i.e. to switch off the magnetic field as soon as the tissue temperature reaches the desired range. But since the NPs are spread around the tumor and lay at various depths inside the body, they are not uniformly heated. The NPs near the surface and closer to the source of the magnetic field have the maximum temperature whereas those located inside the body away from the source have low temperatures. Thus if the magnetic field is switched off when the surface of the NPs reach the optimum temperature range, the NPs inside the body are below this optimum temperature. Consequently the efficiency of the hyperthermia process is reduced. A solution to this problem is to use such NPs so that they stop heating up after they reach the threshold of 42°C (315 K). If the material of the magnetic NPs has a Curie temperature in the optimum heating range 42-43°C then if they are subjected to oscillating magnetic field the temperature of these will rise only up to its Curie temperature. If they are further subjected to the magnetic field of any intensity they will not be heated thereafter because beyond the Curie temperature the NPs become paramagnetic. This will also ensure a uniform heating because now the magnetic field can be kept on until all the NPs irrespective of their depth inside the body reach the optimum temperature which corresponds to their Curie temperature.

One major difficulty that underlies the use of NP therapy is the problem of getting the NPs to a particular site in the body. A potential benefit of using magnetic NPs is the use of localized magnetic field gradients to attract the particles to a chosen site, to hold them there until the therapy is complete and then to remove them. Various NPs were synthesized using physical as well as chemical methods. But since the application of NPs in vivo or ex vivo requires the NPs to be non-toxic, biocompatible and stable to the reticulo-endothelial system, the elements which are present in the human body naturally such as Fe, Ni, Mn, and Zn are preferred.

In this paper we discuss the factors that might play roles in making the ferrite Mn₁₋ₓZnₓFe₂O₄ NPs exhibit Curie temperature in the optimum range 42-43°C.
EXPERIMENTAL METHODS

All Mn-Zn-ferrite NPs used were obtained via chemical co-precipitation and fertilization (Patnaik 2004; Lu et al. 2007; Obaidat et al. 2009). First the metal salts are co-precipitated into hydroxides. This is done by addition of aqueous solution of metal salts in water to the co precipitating base (e.g. NaOH, CH3NH2OH, etc.). The reaction occurs as follows:

$$ (1-x)Mn^{x+} + xZn^{2+} + 2Fe^{3+} + 8OH^- $$

Then this precipitate is transformed into ferrite by heating in the precipitation alkaline solution (fertilization). The reaction for Mn-Zn ferrite NPs is as follows:

$$ (1-x)Mn(OH)_2 * xZn(OH)_2 * 2Fe(OH)_3 $$

This salt solution at 90°C was added to 8M NaOH solution at 90°C followed by vigorous stirring. The stirring and heating at 90°C continued for a minimum of 40 minutes. The product was then filtered, washed with distilled water and finally washed and dried with acetone. Four samples were made, they have the form Mn1-xZnxFe2O4 where x = 0, 0.5, 0.6, 0.8. The atomic composition was determined using X-ray powder diffraction (XRD). The magnetic measurements were conducted using Quantum Design SQUID. Field cooled (FC) magnetization measurements were conducted where a constant magnetic field of magnitude of 100 Oe was applied and the magnetic moment was measured as the temperature was varied from 0 K to 450 K.

RESULTS AND DISCUSSION

Fig. 1 shows the SEM picture for the Mn1-xZnxFe2O4 nanoparticles, with x = 0.5. All the other SEM pictures are typical to the one shown in Fig. 1. As can be seen, the nanoparticles are very agglomerated due to the fact that they are not coated. The size distribution was also considerably large with an average of 30 nm.

Fig. 2 displays the magnetization hysteresis (H-M) curves at 5 K and 300 K for the Mn1-xZnxFe2O4 nanoparticles, with x = 0.5. The other nanoparticles have a very similar behavior with very slight changes in the saturation and coercive fields at 5 K. We can see from figure 2 that at 300 K, the magnetization saturates soon at small magnetic field of value less than 1000 Oe. At 5 K, the magnetization does not saturate at the highest applied magnetic field value of 15,000 Oe. This non saturation of M at 5 K is attributed to large particle-particle magnetic interaction which is expected to occur for such agglomerated and non-coated particles.

Fig. 3 displays the temperature dependence of magnetization (M-T) for the ZnFe2O4 NPs. We can see a peculiar behavior of M-T. The magnetization, M remains nearly constant at M, as the temperature was increased from 0 K to nearly 50 K. As the temperature was increased further, we see a sudden and large increase in M that occurs at a particular temperature called the spin-glass temperature, Tg. It is clearly seen that M(T) forms a peaked region above Tg.

Fig. 4 shows that for x = 0.5, a similar behavior to the one presented in Figure 1 occurs. But for x = 0.6 and 0.8 the magnetization decreases sharply T = 90 K and 50 K, respectively. We believe that the peculiar M(T) results (for all x values) which are displayed in these two figures cannot be explained only using the magnetic changes that occur inside the bulk of these ferrite NPs. Due to finite size effects, these results are believed to be mainly due to factors related to the surface rather than the core of the NPs. We believe that the occurrence of a significant and sudden increase of magnetization at a particular temperature is a signature of a simultaneous rotation of many surface spins along the direction of the applied magnetic field (Obaidat et al. 2009). This means that many spins are locked together in a group with internal pinning forces such that they will be depinned toge-
The total magnetization of the NPs is the sum of the different kind of magnetization depending on several factors. Core of the NPs possesses the bulk magnetization of the material, where as the shell surrounding that core possesses a different surface magnetization due to surface effects. The atomic spin-glass structures experience internal exchange-coupling which is different than that of the bulk material. Fig. 5 displays the Curie temperature, $T_C$, as a function of the Zn concentration, $x$, for the Mn$_{1-x}$Zn$_x$Fe$_2$O$_4$ ferrite NPs. The Curie temperatures were calculated by extrapolation of the linear sections of the $M(T)$ curves. We can see that $T_C$ increases with the initial increase of $x$ and then decreases for concentration between $x = 0.6$ and $x = 1.0$. This increase and decrease of $T_C$ is believed to be due to the increase of surface disorder as the Zn concentration is changed. The increased surface disorder resulted in more surface spins which become more resistant to thermal energy due to the increased exchange-bias interaction between the ferromagnetic surface and the ferrimagnetic core. The exchange-bias interaction changes as volume of the ferrimagnetic core changes (Shannon 1976; Noguès et al. 2005b; Makhlof et al. 2008).

Since heating of the magnetic nanoparticles can be achieved by the magnetization hysteresis losses, it would be favorable for the hysteresis loop to be irreversible near the Curie temperature. We believe that by controlling surface morphology, the internal exchange-coupling of the spin-glass structures and the exchange-bias between the surface spins and the ferromagnetic core can be made to be significant at high temperatures, where an opening in the hysteresis loop would occur. Thus, using the core-shell model of magnetization of NPs and the existence of spin-glass structures with different orientations on the surface of the NPs, we were able to account for the behavior of the magnetization of these nanoparticles. Our model accounts for the observed constant magnetization below 50 K and the peaked-regions of magnetization above 50 K. The width of the peaked regions is suggested to depend on the internal pinning forces of the spin-glass structures and on the exchange-bias interaction between the ferromagnetic surface and the ferrimagnetic core of the NPs.

ACKNOWLEDGEMENTS

This work was financially supported by the Emirates Foundation under the Grant no. EF 29-2009/131 and by the Research Affairs at the UAE University under a contract no. 06-02-2-11/09.

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