Heating efficiency dependency on size and morphology of magnetite nanoparticles

Parekh, Kinnari; Parmar, Harshida; Sharma, Vinay; Ramanujan, Raju V.

2018

Parekh, K., Parmar, H., Sharma, V., & Ramanujan, R. V. (2018). Heating efficiency dependency on size and morphology of magnetite nanoparticles. AIP Conference Proceedings, 1942(1), 050022-. doi:10.1063/1.5028653

<https://hdl.handle.net/10356/88669>

<https://doi.org/10.1063/1.5028653>

© 2018 The Author(s) (Published by AIP). This paper was published in AIP Conference Proceedings and is made available as an electronic reprint (preprint) with permission of The Author(s) (Published by AIP). The published version is available at: [<http://dx.doi.org/10.1063/1.5028653>]. One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper is prohibited and is subject to penalties under law.

Downloaded on 26 Apr 2023 19:55:09 SGT

Heating Efficiency Dependency on Size and Morphology of Magnetite Nanoparticles

Kinnari Parekh,^{1, a)} Harshida Parmar² Vinay Sharma³ and R. V. Ramanujan²

¹*K C Patel R & D Centre, Charotar University of Science & Technology, Changa-388421, Gujarat, India*

²*Rolls-Royce@NTU Corporate Lab, Nanyang Technological University, 639798, Singapore*

³*School of Materials Science and Engineering, Nanyang Technological University, 639798, Singapore*

^{a)}Corresponding author: kinnariparekh.rnd@charusat.ac.in

Abstract. Different size magnetite nanoparticles ranging from superparamagnetic (9 nm) to single domain (27 nm) and multi domain (53 nm) were synthesized using chemical route. Morphology of these particles as seen from TEM images indicates shape change from spherical to cubic with the growth of particles. The saturation magnetization (σ_s) and Specific Loss Power (SLP) showed maximum for single domain size, 72 emu/g and 102 W/g, respectively then those of multi domain size particles. These samples show higher SLP at relatively low concentration, low frequency and low amplitude compared to samples prepared by other routes.

INTRODUCTION

Magnetic Fluid Hyperthermia (MFH) is one of the applications of nanotechnology in medicine in which tumor cells are heated and destroyed by magnetic nanoparticles (MNPs) injected into the body and targeted to the tumor site. Application of an external alternating magnetic field (AMF) causes heating of the nanoparticles. For successful magnetic hyperthermia therapy, one of the requirements is efficient heating of MNPs which is usually accomplished by measuring specific loss power (SLP) under controlled conditions. SLP is a function of the physico-chemical properties of MNPs, its concentration, and the parameters of AMF (frequency and amplitude). The physico-chemical properties of MNPs are crucial to determine pharmacokinetics, toxicity and biodistribution of MNPs [1]. Higher SLP can be used to lower particle concentration in the tumor. In addition, the frequency and amplitude of the applied alternating magnetic field has to be adapted to the magnetic properties of the MNPs to optimize heat generation.

For MFH, the theoretical ideal magnetic particle core diameter for heat generation is in the range of 10-20 nm which is lower than the ideal size required for magnetic drug targeting. Particles smaller than 10 nm are ideal for tumor penetration, but are rapidly cleared by renal filtration and extravasation. Hence, particles in the 10-50 nm size range with appropriate coatings provide a good balance of circulation times, ability to be manipulated by an external magnetic field and heat generation by hyperthermia. Particles with sizes around the mono domain–multi domain transition, i.e. particles below 50 nm in diameter are preferred since they are expected to produce the maximum SLP. The SLP of 35 nm magnetite particles is more than twice as high as that of 10 nm particles. There are very few reports on the size variation from single domain to multi domain using chemical methods [2-3]. A correlation between physico-chemical properties of particles with SLP value was reported earlier in the particle range of superparamagnetic to single domain [4-5]. We report a chemical technique to produce the magnetic nanoparticles in different size ranges (superparamagnetic-SP, single domain-SD and multi domain-MD), different shapes (spherical and cubic). The aim is to produce these particles using an oxidation method; the oxidation rate will be controlled by changing Me/OH ratio, which is expected to vary average particle size. The study is focused to attain maximum heating response at relatively low frequency and magnetic field.

EXPERIMENTAL

Three different size magnetite (Fe_3O_4) nanoparticles samples were synthesized using the chemical method where the samples from superparamagnetic (SP), single domain (SD) and multi domain (MD) size was prepared using only Fe^{2+} ion as precursors [2]. As the reduction potential of KNO_3 (+0.81 V) is similar to the required oxidation potential of Fe^{2+} (-0.77 V), KNO_3 (0.25 M) is used as the oxidizing agent. Precipitates obtained during synthesis were washed 5 times with warm demineralized water and then acetone washed 4 times. The washed slurries were dried at ambient temperature to obtain the nanoparticles.

RESULTS & DISCUSSION

X-Ray Diffractometer (XRD)

Bruker powder X-ray diffractometer model table-top D2 PHASER with $\text{Cu K}\alpha$ wavelength 0.154056 nm was used to measure structural parameters in the 2θ angle from 10° to 80° with 0.02° step. The characteristic peaks in XRD pattern (Figure 1a) corresponds to that of the spinel structure of $\text{Fd}3\text{m}$ space group. All the samples possess single phase spinel structure even though only Fe^{2+} ion was used in the synthesis. There is no impurity phase present in any of the samples. The broadening of most intense peak corresponding to (311) plane and Scherrer's formula is used to calculate the crystallite size (D_x). The calculated size is 7, 27 and 53 nm respectively for SP, SD and MD particles. XRD result reveals that larger magnetite nanoparticles were obtained via oxidation method. The lattice parameter (a) for the present samples varies from 0.8397 to 0.8414 nm. It is interesting to note that the lattice parameter for the bulk Fe_3O_4 is reported as 0.8396 nm [6].

FIGURE 1. (a) X-ray diffraction pattern, (b) magnetic response of powder samples of different size and (c) Temperature change as a function of heating time at 475 kHz frequency, 4 kA/m field strength for 3 % by weight Fe_3O_4 in glycerol.

In the present system KNO_3 mixed with NaOH solution was used to oxidize Fe^{2+} to Fe^{3+} . The slow addition of base ions will nucleate particles and the formed nuclei will be surrounded by metal ions present in the system. As oxidation of Fe^{2+} takes place slowly with the addition of base ions, the precipitation of extra Me^{2+} ions will take place on already nucleated particles. At the same time, fresh nuclei will also form. Thus, simultaneous process of nucleation and growth resulted in higher particle growth due to Ostwald ripening process.

Magnetic Characterization

Lake Shore Vibrating Sample Magnetometer (VSM), Model 7404 was used to measure magnetic response at room temperature. The field dependent magnetization of the samples is shown in Figure 1b. The saturation magnetization (σ_s) is found maximum for SD followed by that of SP and MD. For SP particles, the magnetization loop (σ versus H) shows the absence of hysteresis, i.e., zero remanence and zero coercivity, which indicate the presence of superparamagnetic magnetite samples. However, as particle size increases, the loop starts to open up near the origin indicating the onset of coercivity with increasing crystallite size. The value of coercivity (H_c) is found as 260 and 212 Oe respectively for SD and MD particles. The saturation magnetization of particles was determined from extrapolation of the M versus $1/H$ data in the field range of 1.0 to 1.2 T. The σ_s is the maximum for SD particles (72 emu/g), followed by that of SP (64 emu/g) and MD (55 emu/g). In all cases the σ_s observed at 300 K is less than the reported bulk value, 92 emu/g due to the finite size effect [6].

Hyperthermia measurement

The thermal response was studied at 475 kHz frequency and intensity of 4.0 kA/m. The dispersion of MNPs (3 wt. %) in glycerol was placed within a water-cooled 5-loop copper induction coil energized by an AC generator (Inductelec, UK). The temperature was directly measured inside the sample by an optical fiber probe fluoroptic thermometer (m600, Luxtron). The heating power of MNPs measured by specific loss power (SLP) is affected by particle size, shape, concentration, dipolar interaction, etc. SLP is defined as the absorbed power, normalized by the mass of MNPs, under an applied AMF of certain frequency and intensity H_0 and defined as

$$SLP = \frac{1}{m} \left(\frac{dT}{dt} \right) C = \frac{1}{m} \left(\frac{dT}{dt} \right) \sum_{i=1}^n x_i m_i$$

Where, m is the mass of MNPs in the glycerol dispersion; dT/dt is the initial slope of temperature rise in time curve; and C [$J \cdot K^{-1}$] is the heat capacity of a sample in the form of the dispersion consisting of n components, x_i [$J/g \cdot K$] is the specific heat capacity of a component and m_i [g] is the mass of a component of the sample. The following values were used in the calculations: x (glycerol) $2.434 J/g \cdot K$; x (magnetite) $= 0.67 J/g \cdot K$. Figure 1c shows the temperature evolution curves for the samples of magnetite at 475 kHz frequency with 4 kA/m intensity. The calculated value of SLP is 40, 102 and 20 W/g respectively for SP, SD and MD particles. According to the results obtained, only 27 nm size Fe_3O_4 sample shows significant heating effect of 102 W/g SLP. The superparamagnetic sample has slower heating rate whereas multi domain size particles has very little heating effect. The heating characteristics of particles are a complex function of the properties of individual nanoparticles and their collective magnetic behavior. The effect of inter-particle interactions on SLP is still not understood. However, the morphology of these nanoparticles helps to understand heating behavior.

Microscopy: TEM

Bright field Transmission Electron Microscopic (TEM) images were obtained from JEOL, JEM 2100 operated at 200 KV. Figure 2 shows well separated and evenly distributed nanoparticles. Image shows that SP is spherical while SD is faceted cubic shape. MD sample possess both types of morphology, a mixture of spherical shape as well as faceted cubic shape particles. Similar change in morphology of the particles from sphere to cube was observed [3] when concentration of Fe^{2+} changes and it related to excess in Fe^{2+} or OH^- in the initial reaction media. Verges et al [7] has reported larger spherical particles of 300 nm in diameter for excess of Fe^{2+} but as the concentration of OH^- excess became greater, the particles became cubic and size decreased from 169 nm to 33 nm. In our case, excess of Fe^{2+} in SD and MD leads to cube shape particles which upon changing excess of OH^- tends to produce spherical 8 nm size particles which agrees with the results of Verges et al.

The inset image of SP and SD shows the high resolution TEM (HRTEM) image and selected area electron diffraction (SAED) pattern of particles. The HRTEM demonstrates well developed lattice fringes confirming the crystalline nature of the particles. A ring pattern with spots reveals a large number of randomly oriented crystalline particles. The lattice spacing attributed to the inverse spinel ferrite structure of magnetite. This result is in agreement with the results obtained from XRD measurement. The diameter / edge length of the particles is measured at different areas of the grid and is 8 ± 0.3 nm for SP, 27 ± 3 nm for SD and 200 ± 10 nm for cube shape particles and 10 nm for spherical particles for MD, respectively. The particle size obtained from TEM agrees well with the crystallite size obtained from XRD measurements especially for SP and SD samples. Whereas, the size obtained for MD sample does not match with the calculated crystallite size using XRD measurement. This is because of the limitations of Scherrer's formula which calculate crystallite size if particles are small (< 50 nm) and not overlapping of crystal boundaries.

It is seen that the heating response of the sample is high when the particles are cubic (SD). Purushotham et al [8] has reported the influence of particle size where they find increasing SLP (22.4 to 42.8 W/g) with increasing particle size from 14 to 43 nm for 10 mg/ml concentration in Milli Q water. The maximum SLP obtained by them for 43 nm size particles is much lower than the value we found in our experiment. Tumor temperatures (41-47 °C) can also be increasing by increasing MNPs concentration. The concentration used in the present experiment is much lower than ~ 120 mg/ml (of Fe) used for clinical trials [9]. Similarly, it is reported that cube shape particles [10] shows higher SLP than the spherical shape particles. Our results match

with this observation. Ma et al [11] have found 75.6 W/g (80 kHz, 32.5 kA/m) for 46 nm size particles prepared using oxidation method. In our case, we are getting 102 W/g (475 kHz, 4 kA/m) SLP for 3 mg/ml concentration of Fe_3O_4 particles in glycerole. Moreover, the particles are not dispersed in water or saline media, which will further enhance the SLP value due to better dispersibility of particles [12]. From all the above reported results it can be said that the higher heating rate is found when the samples are prepared by oxidation method than it is prepared by other method.

FIGURE 2. TEM images of Fe_3O_4 samples. Inset figure shows the HRTEM image and electron diffraction pattern.

CONCLUSION

Magnetite particles from superparamagnetic, single domain and multi domain were synthesized using oxidation method by changing Me/OH ratio from 0.375 to 0.6. TEM image shows spherical shape for SP particles whereas cube shape for SD and MD particles. The saturation magnetization (72 emu/g) and SLP (102 W/g) is found maximum for SD particles and minimum for multi domain size particles. Also, for Fe_3O_4 particles a significant high value of SLP is observed at relatively low concentration, low frequency and amplitude of applicator.

ACKNOWLEDGMENTS

One of the authors (KP) thanks DST, Govt. of India for financial support received through Project grant no. DST/SERB/2016/001000.

REFERENCES

1. C. C. Berry, *J. Mater. Chem.*, **15**, 543-547 (2005).
2. S. Upadhyay, K. Parekh, and B. Pandey, *J. Alloys Comp.*, **678**, 478-485 (2016).
3. T. Sugimoto and E. Matijević, *J. Colloid Interface Sci.*, **74**, 227-243 (1980).
4. S. Smolkova, N. E. Kazantseva, V. Babayan, P. Smolka, H. Parmar, J. Vilcakova, O. Schneeweiss and N. Pizurova, *J. Magn. Magn. Mater.*, **374**, 508-515 (2015).
5. X. L. Liu, E. S. G. Choo, A. S. Ahmed, L. Y. Zhao, Y. Yang, R. V. Ramanujan, J. M. Xue, D. D. Fan, H. M. Fan and J. Ding, *J. Mater. Chem. B*, **2**, 120-128 (2014).
6. J. Smit and H. P. J. Wijn, *Ferrites*, (Wiley, New York, 1959), p.158.
7. M. A. Vergés, R. Costo, A. G. Roca, J. F. Marco, G. F. Goya, C. J. Serna and M. P. Morales, *J. Phys. D: Appl. Phys.*, **41**, 134003 (10pp) (2008).
8. S. Purushotham, P. E. J. Chang, H. Rumpel, I. H. C. Kee, R. T. H. Ng, P. K. H. Chow, C. K. Tan and R. V. Ramanujan, *Nanotechnology*, **20**, 305101 (11pp) (2009).
9. M. Johannsen, U. Gneveckow, K. Taymorian, B. Thiesen, N. Waldöfner, R. Scholz, K. Jung, A. Jordan, P. Wust and S. A. Loening, *Int. J. Hyperthermia*, **23**(3), 315-323 (2007).
10. H. Khurshid, J. Alonso, Z. Nemat, M. H. Phan, P. Mukherjee, M. L. Fdez-Gubieda, J. M. Barandiaran and H. Srikanth, *J. Appl. Phys.*, **117**, 17A337 (4 pages) (2015).
11. M. Ma, Y. Wu, J. Zhou, Y. Sun, Y. Zhang and N. Gu, *J. Magn. Magn. Mater.*, **268**, 33-39 (2004).
12. I. S. Smolkova, N. E. Kazantseva, V. Babayan, P. Smolka, H. Parmar, J. Vilcakova, O. Schneeweiss, N. Pizurova, *J. Magn. Magn. Mater.*, **74**, 508-515 (2015).