



# Particle size effect on phase and magnetic properties of polymer-coated magnetic nanoparticles

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## ARTICLE INFO

### Article history:

Received 1 February 2008

Received in revised form

24 July 2008

Available online 14 August 2008

### PACS:

73.63.Bd

74.25.Ha

75.50.Bb

75.50.Tt

### Keywords:

Magnetic nanoparticles

Polymer coating

Hyperthermia

Particle size distribution

Dark-field microscopy

## ABSTRACT

Polymer-coated magnetic nanoparticles are hi-tech materials with ample applications in the field of biomedicine for the treatment of cancer and targeted drug delivery. In this study, magnetic nanoparticles were synthesized by chemical reduction of  $\text{FeCl}_2$  solution with sodium borohydride and coated with amine-terminated polyethylene glycol (aPEG). By varying the concentration of the reactants, the particle size and the crystallinity of the particles were varied. The particle size was found to increase from 6 to 20 nm and the structure becomes amorphous-like with increase in the molar concentration of the reactant. The magnetization at 1 T field ( $M_{1T}$ ) for all samples is  $> 45$  emu/g while the coercivity is in the range of 100–350 Oe. When the ethanol-suspended particles are subjected to an alternating magnetic field of 4 Oe at 500 kHz, the temperature is increased to a maximum normalized temperature ( $3.8^\circ\text{C}/\text{mg}$ ) with decreasing particle size.

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## 1. Introduction

The effective use of magnetic nanoparticles for biomedical applications [1] such as targeted drug delivery [2], magnetic resonance imaging (MRI) contrast enhancement [3] and hyperthermia treatment of cancer [4] depends on a number of factors related to the size and magnetism of the biocompatible nanoparticles. Increasing the magnetization is advantageous to facilitate manipulation in drug delivery schemes [5]. By maximizing magnetization, the strength of stray magnetic fields emanating from the nanoparticles is more effective for higher MRI contrast applications due to interactions with the proton moment of the local environment [5]. The nanoparticles must be small so that they can be super-paramagnetic in order to avoid agglomeration and to remain in circulation without being removed by the body's natural filters such as the liver or the immune system [1]. In this study, we look at the effect of concentration of the reacting solutions on the particle size and magnetic properties of the chemically synthesized nanoparticles.

## 2. Experiment

All the chemicals used are of reagent grade and deionized water was used throughout the reaction. The reaction was carried out by the reduction of the metal salt with sodium borohydride [6,7]. A mass of 2 g of  $\text{FeCl}_2$  purchased from Alfa Aesar was dissolved in ethyl alcohol and 1 g of  $\text{NaBH}_4$  from Alfa Aesar was dissolved in deionized water. The concentration of the reagents was varied by keeping the solute mass constant and varying the solution volume. The molar concentrations of  $\text{NaBH}_4$  solution was varied from 1.75 to 0.26 M as summarized in Table 1. The reaction was carried out by mixing the two reagents through a Y-tube in a pressurized system [6,7]. The system was pressurized using nitrogen gas to pump out the reagents and mixed through a Y-tube (1.6 mm ID) before falling into the coating solution. The latter contains a compensated mass of amine-terminated polyethylene glycol (aPEG; Aldrich CAS #: 34901-14-9) dissolved in 25 ml of ethanol so as to maintain a constant concentration of approximately 0.6 M. The collected solution was then washed three times with ethyl alcohol to remove the water, the excess reagents and the reaction by-products such as NaCl. The washed product is then stored in a vial in ethyl alcohol for further measurements. All the samples were characterized structurally and magnetically to understand the effects of the synthesis

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**Table 1**  
Sample name, synthesis recipes for preparation of different sample

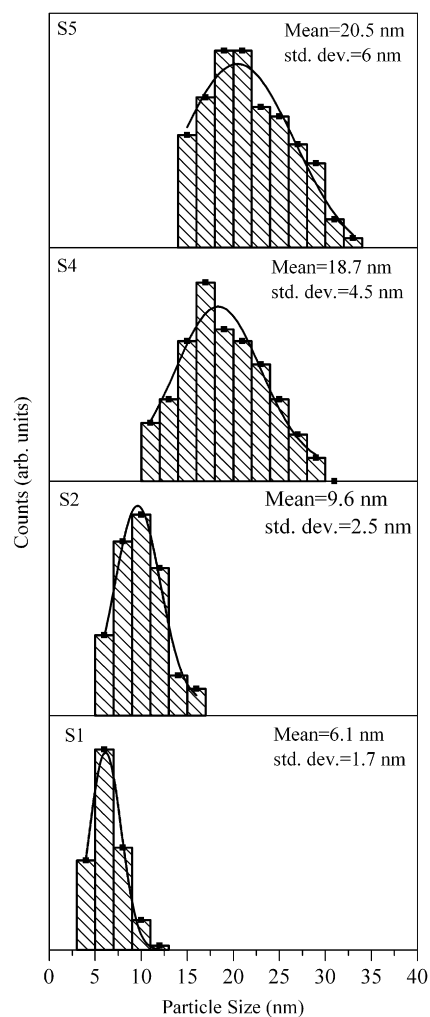
Sample name	Vol. of solvents (ml)	Conc. FeCl <sub>2</sub> (M)	Conc. NaBH <sub>4</sub> (M)	Mass aPEG (mg)	Conc. aPEG solution (M)
S1	15	1.05	1.75	53.8	0.60
S2	25	0.63	1.05	71.24	0.58
S3	50	0.32	0.53	111.28	0.55
S4	75	0.21	0.35	193.78	0.68
S5	100	0.16	0.26	206.07	0.56

parameters. The samples were dried under ambient conditions before measurement. Structural measurements included phase determination using X-ray diffraction (Philips XRD) with CuK<sub>α</sub> radiation. The X-ray fits were analyzed using XFIT [8] software by de-convoluting the original data and fitting them with amorphous and crystalline components. By calculating the area under these peaks we can approximately determine the percentage of phases that constitute the sample. A small amount of sample was then pressed into pellet to study the thermal behavior during heating and cooling cycle using a Perkin Elmer thermogravimetric/differential thermal analyzer (TG/DTA). Transmission electron microscopy (JEOL JEM 3010) was used for particle size determination and microstructure characterization. The hysteresis loops were measured using a vibrating sample magnetometer (LakeShore VSM) at room temperature with a maximum field of 1.0 T on the dried sample, which was packed on a sheet of paper and covered with a Mylar tape. Heating characteristics were studied by applying a 4 Oe, 500 kHz AC magnetic field to a sample dispersed in ethyl alcohol in a test tube seated in a ten-turn water-cooled copper coil. Temperature measurements were made with an infrared temperature sensor connected to a digital thermometer located at the opening of the test tube. The temperature was normalized per unit mass of metal nanoparticles for comparison of samples.

### 3. Results and discussion

Fig. 1 shows the particle size distribution of samples S5, S4, S2 and S1 synthesized with different NaBH<sub>4</sub> concentrations; the concentration of FeCl<sub>2</sub> changes proportionally as shown in Table 1. The mean particle sizes of the nanoparticles are 6.1, 9.6, 18.7 and 20.5 nm for samples S1, S2, S4 and S5, respectively. The percentage ratio of the standard deviation to the mean size of the particle distribution is constant around 27% considering finite error in the statistical distribution of the particle sizes. The size distribution indicates the reduction in mean particle diameter with increasing reactant concentration. When considering the development of phases, the particle size decreases with a concurrent increase in the oxide volume fraction, which concurs with the increase in the oxide phase as shown in Fig. 2, as small particles tend to oxidize more due to larger surface-to-volume ratio [11].

The X-ray powder diffraction pattern shown in Fig. 3 was measured at room temperature for all the samples. The XRD patterns are similar and consist of sharp peaks superimposed on broad peaks near 44.6° and a small shoulder near 35°. The fits to the X-ray patterns are composed of three phases as seen in Fig. 3 for sample S4. The sharp component around 45° is attributed to the crystalline bcc  $\alpha$ -Fe phase, the broad peak to an amorphous phase [9] and the shoulder around which is centered on 35° is due to an iron (Fe) oxide phase. The XRD pattern of samples S1 and S2 are typical for an amorphous substance as evidenced by the complete absence of sharp crystalline peaks. Thus we can confirm that there is no long-range crystalline order as expected for an amorphous compound. Broad peaks are also apparent in samples



**Fig. 1.** Particle size distribution for different reactant concentrations.

S4 and S5 with the additional presence of a sharper peak superimposed on the broad Fe peak. The incorporation of boron during the synthesis of Fe may be the origin of the amorphous phase seen in Fig. 1 [10]. The evolution of the crystalline, amorphous and oxide components with concentration are shown in Fig. 2. The volume fraction of crystalline Fe phase decreases with increase in molarity of NaBH<sub>4</sub> as more boron is incorporated into the Fe crystal lattice. The amorphous phase initially increases slightly and then decreases as the smaller particles oxidize more; finally, the oxide phase steadily increases as the surface oxidation increases with the increase in surface-to-volume ratio of particles. The presence of a broad peak in XRD measurement (Fig. 3) may be due to amorphous nature or the nanocrystalline nature of the sample. This was confirmed by measuring the heat exchange involved during heating and cooling cycle for samples S1 and S5.

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