Size-dependent magnetic anisotropy of PEG coated Fe₃O₄ nanoparticles; comparing two magnetization methods

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Abstract: Understanding the size dependent magnetic anisotropy of iron oxide nanoparticles is essential for the successful application of these nanoparticles in several technological and medical fields. PEG-coated iron oxide (Fe₃O₄) nanoparticles with core diameters of 12 nm, 15 nm, and 16 nm were synthesized by the usual co-precipitation method. The morphology and structure of the nanoparticles were investigated using transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), and X-ray diffraction (XRD). Magnetic measurements were conducted using a SQUID. The effective magnetic anisotropy was calculated using two methods from the magnetization measurements. In the first method the zero-field-cooled magnetization versus temperature measurements were used at several applied magnetic fields. In the second method we used the temperature-dependent coercivity curves obtained from the zero-field-cooled magnetization versus magnetic field hysteresis loops. The role of the applied magnetic field on the effective magnetic anisotropy, calculated from the zero-field-cooled magnetization versus temperature measurements, was revealed. The size dependence of the effective magnetic anisotropy constant \( K_{eff} \) obtained by the two methods are compared and discussed.

Keywords: Magnetization, Nanoparticles, Magnetic anisotropy, Coercivity.

1. Introduction

In magnetic nanoparticles (MNPs), magnetic anisotropy employs a direct impact on the magnetization, remanence, reversal and relaxation. Magnetic anisotropy is therefore a crucial parameter in the preparation of magnetic nanoparticles designed for high-density data storage applications and for medical applications [1–8]. For this reason, a controlled modulation of the magnetic anisotropy for a given size of crystals is one of the most efficient ways which improves and tunes their magnetic properties. The anisotropy of the magnetic material is utilized to control the critical applied magnetic field required to switch the magnetization of the element between its two magnetic stable states, thus creating a binary barcode. The suspension of MNPs in biomedical application may be delivered to the site of application by intravenously or by direct localized injection method. These methods require agglomeration-free MNPs which cannot inhibit their own distribution and can be achieved either by reducing the size of the NP or by modifying their surface chemistry. The modification of the surface of nanoparticles is done by using various biocompatible and biodegradable high molecular weight polymers [9,10]. The coating also can provide the colloidal stability of the particles against aggregation and gravitational settling by reducing the inter-particle dipole-dipole interactions [11-16]. The most commonly available coatings are; derivatives of dextran [17,18], polyvinyl alcohol (PVA), Polyethylene glycol (PEG) [19], and some nonpolymeric coatings etc. [20].
As mentioned, the MNPs have attracted a lot of interest in the field of biomedical applications, [21–24] such in magnetically induced hyperthermia (MIH), [25,26] magnetic resonance imaging, [27] targeting drug delivery, [28] and radioisotope-labeled targets [29]. The MIH is one of the most promising techniques for cancer treatment [30] where localized MNPs are heated by an applied alternating magnetic field. The heated MNPs kill only tumor cells and thus reduce injuries to the surrounding healthy tissues. In addition, enhancing the particles’ magnetic anisotropy results in an increase in the relaxation time and allows for the use of lower frequencies of the alternating magnetic field. Because of their low toxicity, high saturation magnetic moment at room temperature, and highest ordering temperatures among spinel ferrites [31], both the magnetite (Fe$_3$O$_4$) and maghemite (γ-Fe$_2$O$_3$) MNPs are considered very suitable MNPs for the use in MIH. Both types of MNPs were approved by the food and drug administration (FDA) as the biocompatible magnetic materials for MIH in humans [32]. Increasing heating efficiency of these iron oxide nanoparticles will allow for the reduction of the amount of nanoparticles delivered to the targeted organ and thus will minimize negative side effects. Improving the heating capability of these MNPs can be achieved by controlling the particle size and some special magnetic properties. Possible ways to increase this heating rates are by increasing the magnetic anisotropy of the MNPs. Pure Fe$_3$O$_4$ MNPs have some physical limits of magnetically induced heat generation [33]. In the last few years, the magnetic anisotropies of MNPs were tuned by mutual coupling of magnetic hard and/or soft components for enhancing the heating power to therapeutic efficacy [26]. Hence, there is a direct relation between magnetic anisotropy and the magnetic induction performance.

Using magnetic nanoparticles in magnetic recording depends on their magnetic thermal stability which directly correlated with the magnetic energy barrier of the nanoparticles [34–35]. The magnetic energy barrier depends on both the size of the nanoparticle and on its magnetic anisotropy. Hence, the knowledge of the size-dependent magnetic anisotropy in nanoparticles is essential in their applications in data storage devices.

In this paper, we have studied the role of particle size on the effective magnetic anisotropy, $K_{eff}$ of PEG coated Fe$_3$O$_4$ nanoparticles. This was done by calculating the $K_{eff}$ using two methods that are based on magnetic measurements.

2. Experimental details

The PEG functional iron oxide (Fe$_3$O$_4$) nanoparticles were synthesized by the usual co-precipitation method. The FeCl$_3$.6H$_2$O (0.1M) and FeCl$_2$.4H$_2$O (0.05M) were used as precursor materials. They were dissolved in deionized water separately and mixed at 300 K. The 25% ammonium hydroxide solution was promptly added to the mixture and a 25% NH$_4$OH solution continuously mixed drop by drop until pH became 10. The final solution was then stirred for 30 minutes. The reaction time was varied from 1 h to 5 h to get nanoparticles with different sizes. Finally, the Fe$_3$O$_4$ nanoparticles were collected by magnetic field separation and washed properly. The collected precipitation was dried at 40°C in vacuum. The PEG solutions with the proportionate concentration were prepared by dissolving PEG powder in distilled water. Particular amount of water and Fe$_3$O$_4$ nanoparticles were vigorously stirred for 15 minutes. Afterwards, the PEG-solution was mixed to the suspension and stirred for about 30 min. The mixture was then centrifuged at 6000 rpm to obtain the ferrofluid. Finally, the precipitated ferrofluid was collected and dried overnight in vacuum condition. The sample which were made with a reaction time of 1 h, 2 h, and 5 h were assigned as S1, S2, and S3, respectively. The morphology of the nanoparticles were confirmed by several microscopic tools such as high resolution transmission electron microscopy (HRTEM), and selected area electron diffraction (SAED). Structure and phase analysis was conducted by X-ray diffraction (XRD) using SHI-MADZU Lab X-XRD-6100 with CuKα ($\lambda =1.5418$ Å) diffractometer. The dc magnetic measurements were done using SQUID from quantum design. Magnetization ($M$) versus applied field ($H$) up to ±3 T was measured for all the samples at several temperatures under zero field-cooling (ZFC) condition. ZFC and field-cooled (FC) magnetization versus temperature ($M$-$T$) measurements were
conducted at several applied magnetic fields (20, 50, 100, 200, and 500 Oe) in the temperature range of 2 – 300 K.

3. Result and discussions

Figure 1 displays the X-ray diffraction plots of the PEG-coated magnetite (Fe₃O₄) nanoparticles. The corresponding diffraction peaks were attributed to Fe₃O₄ confirming the phase purity of the samples.

![Figure 1. The XRD patterns for sample (a) S1, (b) S2, and (c) S3.](image)

The XRD data was plotted for 2θ ranging from 20° to 70°. The characteristic diffraction peaks at 2θ = 30.1°, 35.4°, 43.3°, 53.6°, 57.2°, and 62.7°, were attributed to (220), (311), (400), (422), (511), and (440) Bragg reflection of Fe₃O₄. The preponderance of amorphous phase of PEG clarified that the crystalline nature of Fe₃O₄ was suppressed due to the presence of PEG. Note that the diffraction peaks of Fe₃O₄ nanoparticles were matched with cubic spinel structure. The average particle sizes were calculated from the XRD by using Scherrer formula; 

$$D_p = \frac{0.94\lambda}{\beta\cos\theta},$$

where $D_p$ is the average crystallite size, $\lambda$ is the x-ray wavelength, $\beta$ is the full width of half maximum (FWHM) of the XRD line, and $\theta$ is the Brag’s angle. The average particle sizes calculated were 12 nm, 15 nm, and 16 nm, respectively.

The morphology of the nanoparticles were confirmed by several microscopic tools such as transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), and selected area electron diffraction (SAED). Figure 2 (a) shows the TEM image of particles in sample S1. The particles are observed to be almost spherical in shape. The histogram for sample S1 is shown in the inset of figure 2 (a) where it confirms the narrow size distribution of the nanoparticles. The average diameter of the core of the Fe₃O₄ particles is 12 nm and the average coating thickness is around 2 nm. The circular rings shown in the SAED pattern in the inset of figure 2 (b) confirms the polycrystalline nature of the sample. The TEM and HRTEM images of the other samples are typical to those shown in figure 2 but with different core sizes.
The average Fe$_3$O$_4$ particle diameters calculated from the TEM images for samples S2, and S3 are 15 nm, and 16 nm, respectively. The shell thickness is 2 nm for all samples.

![TEM and HRTEM images](image)

**Figure 2.** (a) TEM image and (b) HRTEM image of sample S1. The inset of (a) represents the size histogram for the corresponding sample. The inset of (b) is the SAED pattern confirming the polycrystalline nature of the sample.

Magnetic anisotropy is defined as the directional dependence of a material's magnetic properties. The magnetic moment of magnetically anisotropic materials will like to align with an "easy axis", which is an energetically favorable direction of spontaneous magnetization. There are different experimental methods that could be used to obtain the effective anisotropy constant, $K_{\text{eff}}$ [36]. Some of these include obtaining $K_{\text{eff}}$ from Mössbauer spectra, the coercive field, and the ac magnetic susceptibility. One other method to obtain $K_{\text{eff}}$ is from the zero-field-cooled (ZFC) magnetization versus temperature measurements. In this study, $K_{\text{eff}}$ was calculated using two methods from the magnetization measurements. In the first method, $K_{\text{eff}}$ was calculated from the temperature-dependent coercivity curves which were obtained from ZFC magnetization versus magnetic field ($M-H$) hysteresis loops at several temperatures. In the second method, $K_{\text{eff}}$ was calculated from the ZFC magnetization versus temperature ($M-T$) measurements at several applied magnetic fields.

In the ZFC $M-H$ measurements, the temperature of the sample was cooled down from room temperature to a lowest available temperature (2 K) in the absence of any applied magnetic field. After that, a magnetic field was applied and the magnetic moment was recorded. The magnetic moment was measured while the applied magnetic field varied between -3 T and +3 T. The $M-H$ hysteresis loops under ZFC measured at $T = 2$ K, for samples S1, S2, and S3 were shown in figure 3. Similar hysteresis loops were obtained at 50 K and 100 K.
Figure 3. Magnetization versus magnetic field measured at $T = 2$ K for all samples. The inset shows an enlarged portion around the center of the loop.

It is worth mentioning that the real values of magnetization for these coated nanoparticles are larger than the reported values here. The magnetization is the magnetic moment measured by the SQUID divided by the measured mass of the sample. But this mass is composed of both the mass of the PEG coating and the mass of the iron oxide core. The PEG coating does not contribute to the measured magnetization. The reported magnetization values should include the iron oxide core only. Hence, the measured values should be multiplied by the ratio of the total mass of the particle to the mass of the core ($m_{\text{total}}/m_{\text{core}}$) to obtain the real magnetization values. We calculated the average sizes of the core and the shell in each sample from the HRTEM images. Then by using a density of 5 g/cm$^3$ for the Fe$_3$O$_4$ core and 1.13 g/cm$^3$ for the PEG coating, the calculated mass ratios ($m_{\text{total}}/m_{\text{core}}$) are calculated to be 1.13, 1.11, 1.097 for samples S1, S2, and S3, respectively. Thus to obtain the real magnetization values, the reported values should be multiplied by 1.13, 1.11, and 1.097 for samples S1, S2, and S3, respectively.

The coercive field, $H_C$ was inferred by taking the average of the values between negative and positive field axes of the hysteresis loop where magnetization is zero ($H_C = \frac{|H_{\text{cl}}|+|H_{\text{cd}}|}{2}$). It should be noted that any experimental sample containing large numbers of NPs with various sizes, shapes, surface effects, and inter-particle interactions has $K_{\text{eff}}$ with the superposition of all these effects. Figure 4 shows the coercive field as a function of temperature under ZFC protocol for all samples. The coercivity was obtained from the $M$-$H$ hysteresis loops which were obtained at $T = 2$, 50 K, and 100 K. The role of the size distribution on the magnetic properties of nanocrystalline PEG-coated Fe$_3$O$_4$ is better understood through $T$-dependence of the coercive field. Generally, for an assembly of identical and non-interacting magnetic nanoparticles, the temperature dependence of coercive field can be studied on the basis of Néel relaxation and the Bean-Livingston approaches. Temperature dependence of $H_C$ can be written as [37]:

$$H_C = 0.96 \frac{K_{\text{eff}}}{M_S} \left[1 - \left(\frac{T}{T_B}\right)^{\alpha K}\right] \ldots \ldots (1)$$
Here $\alpha_K$ is called the Kneller exponent, $K_{\text{eff}}$ is the effective anisotropy constant for spherical particles, $M_S$ is the saturation magnetization, $T_B$ is the mean blocking temperature, and $H_0 = 0.96 \frac{K_{\text{eff}}}{M_S}$ …… (2).

![Figure 4](image)

**Figure 4.** The temperature dependent coercivity for sample (a) S1, (b) S2, and (c) S3. The solid lines represent the fittings of the measured data to $H_C$ that is expressed in equation 1.

For non-interacting particles with similar sizes, $\alpha_K = \frac{1}{2}$. In fact the real nanoparticles systems can present large size distribution and significant interparticle interactions once magnetic measurements are generally carried out at powder samples. The $K_{\text{eff}}$ values were calculated by fitting the experimental data of the temperature dependence $H_C$ as expressed in equation 1. The $M_S$ values were taken from the magnetic hysteresis loops at the corresponding temperatures.

It should be noted that this approach is in agreement with experimental results only in the low temperature region when most of the particles are blocked. Figure 5 displays the calculated $K_{\text{eff}}$ values as function of the size of particles.
The effective anisotropy, $K_{\text{eff}}$ as function of (a) the particle diameter, and (b) the inverse of the particle diameter. The solid line in (a) is a guide to eyes, and the dashed line in (b) is the best fit for the data points.

These values of the effective anisotropy are very close to the values reported for Fe$_3$O$_4$ nanoparticle in other studies [38]. These values are larger than the bulk value for Fe$_3$O$_4$ which is $K_{\text{eff}} = 1.1 \times 10^4$ J/m$^3$ [39]. This larger value could be attributed to the large contribution of surface spin effects which result in surface anisotropy. The nanoparticles exhibit a variation in values of $K_{\text{eff}}$ when different molecules are chemisorbed on the particles [40, 41]. This indicates that surface anisotropy gives crucial contribution to $K_{\text{eff}}$. In addition, deviations from a perfect spherical shape should also have influence on these anisotropy values. The effective anisotropy can be regarded as a result of volume (core) anisotropy and surface anisotropy. It is not an easy task to separate the parameters that control the effective anisotropy in nanoparticles. However, by considering several nanoparticle samples with different core dimensions, the difference in effective anisotropy can be suggested to be due to contributions of different surface to core ratios. When using this method, it is assumed that other parameters controlling the effective anisotropy remain unchanged by changing the sample. We have analyzed $K_{\text{eff}}$ on the basis of a model [42] in which the total energy barrier is given by:

$$
\Delta E = K_{\text{eff}}V = K_V V + K_S S \ldots \ldots \ldots (3)
$$

Where $K_V$ and $K_S$ are the volume and surface anisotropy energy constants, respectively. Considering that the particles are spherical with average diameter $d$, Eq. 3 can be written as

$$
K_{\text{eff}} = K_V + \frac{6}{d} K_S \ldots \ldots \ldots (4)
$$

The size dependence of $K_{\text{eff}}$ is in agreement with Eq. 4. As can be seen in figure 5 (a), at all temperatures (2, 50, 100 K), $K_{\text{eff}}$ increases as the size of NPs decreases. This behaviour could be attributed to the enhancement of the surface anisotropy with decreasing the size of NPs. The straight-line fits for $K_{\text{eff}}$ versus...
data which is shown in figure 5 (b), yield the values $K_V$ and $K_S$. According to Eq.4, the slope of the straight line $= 6 K_S$ and the intercept of the extrapolated straight line with the $K_{eff}$ axis is $K_V$.

There are several factors that could influence surface magnetization and hence, the surface magnetic anisotropy. For example, the complex redistributions of the spin-polarized electronic density, which results from the reduced coordination of atoms at the surface of the nanoparticles, lead to changes in the spin-orbit energy and hence in the magnetic anisotropy energy [43]. In addition, expansion or contraction of the lattice structure [44-45], and the breaking of the crystallographic symmetry at the surface [46, 47] could also contribute towards the surface anisotropy of nanoparticles.

The second method that was used to calculate $K_{eff}$ is based on ZFC and FC magnetization versus temperature ($M$-$T$) measurements. For the typical time window of SQUID or VSM measurements, the following equation will be used to calculate the effective anisotropy.

$$K_{eff} < V > \approx 25 k_B < T_B > \ldots \ldots (5)$$

Which is obtained from:

$$< T_B > = \frac{K_{eff} < V >}{ln(\tau_{SQUID}/k_B)} = \frac{K_{eff} < V >}{25 k_B} \ldots \ldots (6)$$

Here $K_{eff}$ is the effective magnetic-anisotropy energy per unit volume, $\tau_{SQUID}$ is the characteristic measuring time of the instrument (~10 s) and $\tau_0$ is related to the natural frequency of the gyromagnetic precession (~$10^{-9}$–$10^{-13}$ s). $< V >$ is the average volume of the nanoparticles obtained either from the HRTEM images or the XRD patterns. $< T_B >$ is the average blocking temperature of the nanoparticles.

The blocking temperatures was obtained directly from ZFC and FC $M$-$T$ magnetization curves. Figure 6 displays the ZFC and FC magnetization versus temperature curves for sample S1 obtained at 200 Oe. Similar curves were obtained at several other fields for all samples.

![Figure 6](image_url)

**Figure 6.** The ZFC and FC magnetization versus temperature curves for sample S1 obtained at the applied filed of 200 Oe.

In the ZFC $M$-$T$ magnetization measurements, the sample was initially cooled from room temperature to 2 K. A small magnetic field (50-500 Oe) was applied to the sample and the magnetization was measured as the temperature was being raised to 300 K. For the FC $M$-$T$ measurements, the magnetization was recorded again while the temperature was lowered down to 2 K under the application of the same magnetic field.
The $K_{eff}$ values were calculated using Eq. 5 where the particle volume was calculated using the diameters obtained from the TEM images. Figure 7 displays the calculated $K_{eff}$ values as function of the particle diameter at several applied fields. As can be seen in this figure, $K_{eff}$ values display a similar behavior to the obtained from the first method where $K_{eff}$ increases with the decrease of the size of the particle. However, the magnitudes of $K_{eff}$ obtained using the second method are considerably larger. We can see that as the applied field increase, the values of $K_{eff}$ obtained in the second approach those obtained in the first method. The volume and surface contributions to $K_{eff}$ were obtained using Eq. 4 at all the applied fields and the results are displayed in figure 8. Both contributions increase with decreasing the size of the particles.

![Figure 7](image1.png)

**Figure 7.** $K_{eff}$ values as function of the particle diameter at several applied fields.

![Figure 8](image2.png)

**Figure 8.** The volume, $K_V$ and surface $K_S$ contributions to $K_{eff}$ at several applied fields.
The difference in magnitude and in the behavior of effective anisotropy with size of the nanoparticles can be understood based on the different mechanisms of two magnetization protocols. In the $M-T$ ZFC measurements, the magnetic moment of each one of the nanoparticles is thermally activated and thus it always oscillate between the two easy axis directions which are the lowest two energy states of magnetization. The applied magnetic field has a small magnitude and thus less influence on the orientation of the magnetic moments of the nanoparticles. In the $M-H$ ZFC measurements, magnetic moment each nanoparticle is being forced to rotate along the magnetic applied field direction.

4. Conclusions:

The morphology, structure, and effective anisotropy of PEG-coated iron oxide ($\text{Fe}_3\text{O}_4$) nanoparticles were investigated. The TEM, HRTEM, and SAED images show the crystalline nature of the nanoparticles with nearly spherical shape with narrow size distributions. Using magnetic measurements, the size dependence of the effective magnetic anisotropy constant $K_{eff}$ of the nanoparticles were obtained using two dc magnetization methods. In both methods, $K_{eff}$ was found to decrease significantly and almost linearly with increasing the size of particles. However, the magnitudes of $K_{eff}$ were considerably different.

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