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Surface effects in uncoated and amorphous SiO_2 coated cobalt ferrite nanoparticles

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ABSTRACT

Surface effects in uncoated and amorphous silica (SiO_2) coated cobalt ferrite nanoparticles have been studied by using dc magnetization. Both uncoated and SiO_2 coated nanoparticle samples were synthesized by using sol–gel method. SiO_2 coated nanoparticles exhibit smaller average crystallite size as compared to uncoated nanoparticles. Saturation magnetization (M_s) revealed decreasing trend at low temperatures for uncoated nanoparticles as compared to coated nanoparticles which may be due to magnetically dead nanoparticle's surface layer for uncoated nanoparticles. A step-like behavior near remanent field was observed for both the samples but more pronounced for SiO_2 coated nanoparticles. This fast magnetic relaxation near remanent field in coated nanoparticles is due to lesser dipolar (interparticle) interactions among nanoparticles. Bloch's law shows a good fit for coated nanoparticles. SiO_2 coated nanoparticles showed larger values of coercivity at low temperatures due to their enhanced surface anisotropy as compared to uncoated nanoparticles. Kneller's law for temperature dependent coercivity shows a good fit for SiO_2 coated nanoparticles and is attributed to lesser dipolar interactions among coated nanoparticles as compared to uncoated nanoparticles. The exchange bias phenomenon was also observed for both the samples, which signify the presence of core–shell interactions. However, SiO_2 coated nanoparticles exhibit larger values of exchange bias at low temperatures due to their strong surface anisotropy as compared to uncoated nanoparticles. The presence of exchange bias in uncoated nanoparticles indicates that their surface layer is not totally magnetically dead. In summary, (i) the SiO_2 coated nanoparticles have lesser dipolar interactions due to SiO_2 coating and (ii) surface layer in uncoated nanoparticles is not magnetically dead but may have different preferred ordering at low temperatures as compared to SiO_2 coated nanoparticles.

1. Introduction

Cobalt ferrite ($CoFe_2O_4$) is a ferrimagnetic material with inverse spinel structure [1]. Nanoscale $CoFe_2O_4$ has moderate saturation magnetization, high magnetic anisotropy, high coercivity and mechanical hardness as required in many applications e.g., data storage, magnetic resonance imaging (MRI), drug delivery, cancer treatment, ferro-fluids material and optical devices [2–5]. In spinel ferrite structure, there are two types of lattice sites for divalent metal ions such as octahedral and tetrahedral [6]. The unit cell of a spinel ferrite consists of 32 oxygen, 16 trivalent iron and 8 divalent metal ions. In inverse spinel structure, divalent metal ions prefer octahedral lattice sites. The magnetic moments on the octahedral and tetrahedral lattice sites are antiparallel to each other.

In nanoparticles, the most important thing is to control their surface functionalization for different applications [7]. The surface to volume ratio becomes high in nanoparticles which can affect their physical properties [8]. Ferrite nanoparticles exhibit core–shell structure with ferrimagnetically aligned core and disordered surface shell [9]. The ferrimagnetically aligned core spins combine together to form a huge core spin. The magnetic reversal in single-domain nanoparticles is due to physical coherent rotation of the huge core spin while in multi-domain particles it is due to domain wall motion [10,11]. On the other hand, the surface spins are disordered and frustrated due to defects created by broken surface bonds [8]. Due to these broken bonds, anisotropy of the surface spins is different from the core spins. Therefore magnetic core anisotropy gets different preferential direction as it approaches the nanoparticle's surface. The surface spins also experience different exchange interactions as compared to core spins. The disordered surface spins are also responsible for reduced magnetization in nanoparticles as compared to their counter bulk material [12]. There can also be interactions among the core and surface spins known as core–shell interactions [13–15]. The core–shell interactions along with surface anisotropy can alter the magnetic reversal of the huge core spin [16]. At low temperatures, the surface effects are usually more pronounced due to random frozen surface spins [17,18].

For magnetic based applications, the surface spins get importance in controlling the individual nanoparticle's magnetic moment. The surface magnetic response, anisotropy, core–shell interactions, and ordering

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can be controlled by using different surface coatings [19,20]. The surface spin response depends upon their magnetic state, anisotropy, surface layer thickness, disorder, and also surrounding environment such as coating. In coated nanoparticles, the coated material can either enhance or diminish the surface magnetization. Therefore the magnetization state of the surface spins is important for determining the net magnetization of nanoparticles. In this article, we will study the surface effects in uncoated and SiO_2 coated $CoFe_2O_4$ nanoparticles by using temperature dependent magnetic properties.

2. Experiment

Uncoated and SiO_2 coated $CoFe_2O_4$ nanoparticles were synthesized by using sol–gel method [21]. Cobalt nitrate ($Co(NO_3)_2.6H_2O$) and iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) were mixed in ethanol with respective stoichiometry to prepare solution 1. Another solution 2 was prepared containing citric acid and distilled water in a molar ratio of 1:4. Then solution 2 was mixed drop-wise in solution 1 under constant stirring and heating at 80 °C. After mixing both solutions, tetraethyl orthosilicate (TEOS, 60% of the weight of total nitrates) was added drop-wise which acts as a precursor for SiO_2. Now ammonia was added to adjust the pH value to 5. The combined solution was kept at 80 °C until the formation of gel. The gel is dried overnight at 100 °C to remove water and ethanol contents. The dried gel was then crushed into fine powder and annealed at 900 °C for 2 h to form the required SiO_2 coated $CoFe_2O_4$ nanoparticles. For uncoated $CoFe_2O_4$ nanoparticles, TEOS was not added to the solution [22]. The initial structural characterization was done by X-ray diffraction (XRD) (Bruker D8 Advance instrument) using Cu-$K\alpha$ ($\lambda =$ 0.154 nm) radiation at ambient temperature and transmission electron microscopy (TEM). The magnetic measurements were done by using a superconducting quantum interference device (SQUID)-magnetometer (Quantum Design, MPMS-XL-7).

3. Results and discussion

X-ray diffraction (XRD) is one of the vital measurement techniques to characterize the structural properties. Fig. 1(a) shows the XRD diffraction patterns of uncoated and SiO_2 coated cobalt ferrite ($CoFe_2O_4$) nanoparticles. XRD patterns were compared with standard peaks given in the literature (see Fig. 1(b)) which confirms the inverse cubic spinel structure of $CoFe_2O_4$. The average crystallite size was calculated according to Debye–Scherer's formula which is $\tau = 0.9\lambda / \beta\cos\theta$. The calculated average crystallite size for uncoated and SiO_2 coated $CoFe_2O_4$ nanoparticles are 31 and 25 nm, respectively. The average crystallite size is deceased for SiO_2 coated nanoparticles due to the larger number of nucleation sites in a SiO_2 matrix for the formation of nanoparticles and these sites restrict the growth of the nanoparticles [23].

Fig. 2 shows the transmission electron microscopy image of SiO_2 coated $CoFe_2O_4$ nanoparticles at a 100 nm scale. It is observed that more nanoparticles are nearly spherical with less agglomeration and also elongated irregular in shape.

Fig. 3 (a) and (b) shows the 5 T field cooled M–H loops of uncoated and SiO_2 coated $CoFe_2O_4$ nanoparticles with maximum applied field of ± 5 T at different temperatures T = 4.2, 50, 100, and 300 K.

It is observed that the magnetic moments of uncoated nanoparticles are more saturated due to their larger average crystallite size as compared to coated nanoparticles. For both the samples, a step-like behavior of magnetization is observed but more pronounced for the SiO_2 coated nanoparticles. The step-like magnetization vanishes at a higher temperature e.g. T = 300 K. The cause of this magnetization step is the faster relaxation of the magnetic moments near the switching field (from positive to negative or vice versa). The possible reason for the different step-like behaviors in uncoated and coated nanoparticles could be the different surface magnetization and core–shell interactions [24]. Another cause can be lesser dipolar interactions among the SiO_2 coated nanoparticles [20]. Therefore SiO_2 coating can change the surface magnetization due to its interaction with the atoms at the nanoparticle's surface [25]. On the other hand, in the case of uncoated nanoparticle, the surface spins have coordination bonds only on the inner side with core spins. Therefore the surface SiO_2 coating can significantly affect the magnetization reversal of the nanoparticle's huge core spin [26].

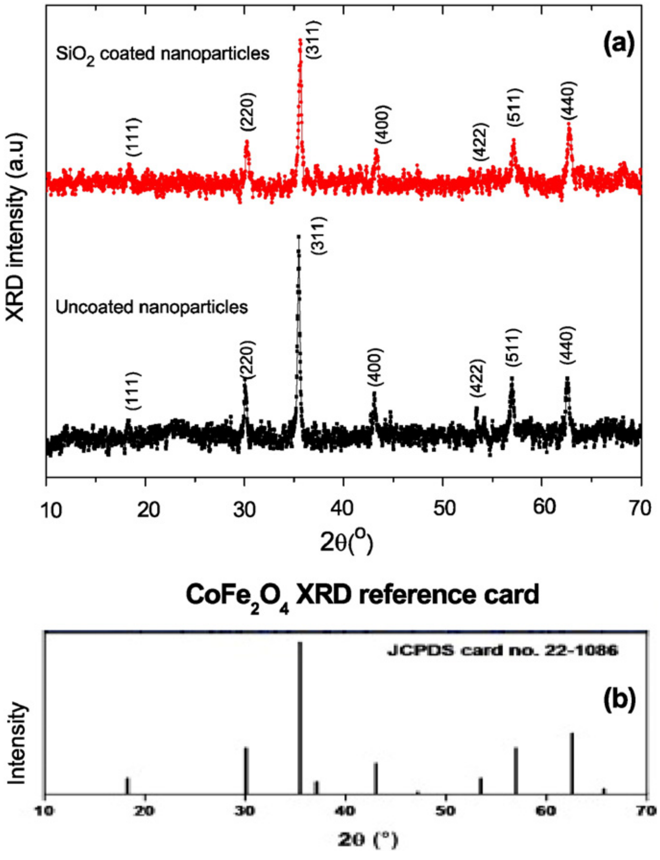

Fig. 1. (a) XRD patterns of uncoated and SiO_2 coated $CoFe_2O_4$ nanoparticles, and (b) XRD reference PDF card of $CoFe_2O_4$.

Fig. 4(a) shows the temperature dependence of saturation magnetization (M_s) for both the samples. For SiO_2 coated nanoparticles, M_s increases with decreasing temperature whereas uncoated nanoparticles show non-monotonous behavior. The increase of M_s with decreasing temperature can be explained by using the Neel–Arrhenius relation for nanoparticle spin-flip [27,28],

$$\tau = \tau_0 \exp(E_A/k_BT) \tag{1}$$

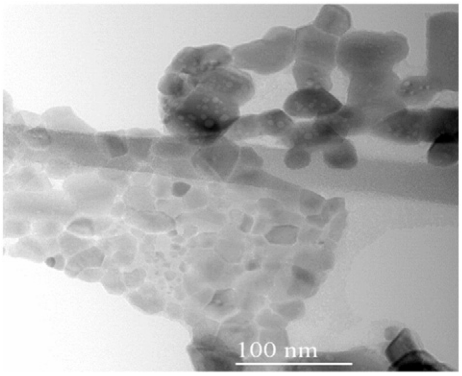

Fig. 2. Transmission electron microscopy of SiO_2 coated $CoFe_2O_4$ nanoparticles at 100 nm scale.