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Surface spins disorder in uncoated and SiO_2 coated maghemite nanoparticles

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ABSTRACT

We studied the surface spins disorder in uncoated and silica (SiO_2) coated maghemite (γ-Fe_2O_3) nanoparticles using temperature and time dependent magnetization. The average crystallite size for SiO_2 coated and uncoated nanoparticles was about 12 and 29 nm, respectively. Scanning electron microscopy (SEM) showed that the nanoparticles are spherical in shape and well separated. Temperature scans of zero field cooled (ZFC)/field cooled (FC) magnetization measurements showed lower average blocking temperature (T_B) for SiO_2 coated maghemite nanoparticles as compared to uncoated nanoparticles. The saturation magnetization (M_s) of SiO_2 coated maghemite nanoparticles was also lower than the uncoated nanoparticles and is attributed to smaller average crystallite size of SiO_2 coated nanoparticles. For saturation magnetization vs. temperature data, Bloch's law ($M(T)= M(0).(1- BT^b)$) was fitted well for both uncoated and SiO_2 coated nanoparticles and yields: $B=3\times10^{-7}\ K^{-b}$, b=2.22 and $B=0.0127\ K^{-b}$, b=0.57 for uncoated and SiO_2 coated nanoparticles, respectively. Higher value of B for SiO_2 coated nanoparticles depicts decrease in exchange coupling due to enhanced surface spins disorder (broken surface bonds) as compared to uncoated nanoparticles. The Bloch's exponent b was decreased for SiO_2 coated nanoparticles which is due to their smaller average crystallite size or finite size effects. Furthermore, a sharp increase of coercivity at low temperatures (< 25 K) was observed for SiO_2 coated nanoparticles which is also due to contribution of increased surface anisotropy or frozen surface spins in these smaller nanoparticles. The FC magnetic relaxation data was fitted to stretched exponential law which revealed slower magnetic relaxation for SiO_2 coated nanoparticles. All these measurements revealed smaller average crystallite size and enhanced surface spins disorder in SiO_2 coated nanoparticles than in uncoated γ-Fe_2O_3 nanoparticles.

1. Introduction

Iron oxide nanoparticles have been extensively studied over the last few decades and continue to maintain interest due to their potential use in wide range of disciplines including magnetic fluids, catalysis, biotechnology, biomedicine, magnetic resonance imaging, magneto optical devices, data storage, and environmental remediation [1,2]. Among the three main oxides of iron namely maghemite (γ-Fe_2O_3), magnetite (Fe_3O_4) and hematite (α-Fe_2O_3), γ-Fe_2O_3 nanoparticles (NPs) have become one of the most promising candidates for many applications due to their non-toxicity, biocompatibility, eco-friendly performance, relatively low cost thermal and chemical stability. Their properties depend upon configuration, annealing temperature, particle size, and doped materials. Bulk γ-Fe_2O_3 is a ferrimagnetic material at room temperature with a Curie temperature (T_c) of 928 K and has spinel structure similar to magnetite but with vacancies in the cation sublattice. Two-thirds of the sites are filled with Fe (III) ions arranged regularly, with two filled sites being followed by one vacant site [3–7]. Haneda and Morrish [8] found that the degree of vacancy ordering decreases with decreasing particle size, with no vacancy ordering in maghemite nanoparticles smaller than about 20 nm. Maghemite nanoparticles also exhibits spin-glass state due to the presence of vacancies, interactions among spins located on tetrahedral and octahedral sites and broken bonds on the nanoparticle's surface [9].

Iron oxide nanoparticles have high surface energy as a result they tend to aggregate so as to minimize the surface energy. Therefore providing proper surface coating and developing some effective protection strategy to keep the stability of magnetic iron oxide nanoparticles is very important for practical applications. It includes coating with surfactants, polymers, and biomolecules, or coating with an inorganic

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layer, such as non-magnetic SiO_2. Practically in many cases, the protecting shells not only stabilize the magnetic nanoparticles, but can also be used for further surface functionalization [10]. Azhdarzadeh et al. [11] prepared Theranostic MUC-1 aptamer targeted gold coated superparamagnetic iron oxide nanoparticles for magnetic resonance imaging and photothermal therapy of colon cancer and concluded that gold coating can reduced their cytotoxicity. Ashtari et al. [12] reported an effective method for recovery of target ssDNA using amino-modified SiO_2-coated Fe_3O_4 nanoparticles. Here we use non-magnetic SiO_2 for coating γ-Fe_2O_3 nanoparticles because it is chemically inert and strongly stable against agglomeration as well as under aqueous conditions [13]. It also affects the average crystallite size of nanoparticles and gives a functionalized chemical surface for practical applications. In this article, we studied the surface spin disorder in uncoated and SiO_2 coated γ-Fe_2O_3 nanoparticles by using temperature and time dependent magnetic measurements.

2. Experimental

Uncoated and SiO_2 coated (60 wt% of total nitrates) γ-Fe_2O_3 nanoparticles were synthesized by using sol-gel method as reported elsewhere [14]. The samples were annealed at 250 °C for 4 h to get the single-phase γ-Fe_2O_3 nanoparticles. The initial structural characterization was done by X-ray diffraction (XRD) (Rigaku D/MAX-Ultima III) using Cu-Kα (λ=0.154 nm) radiations at ambient temperature. The surface morphology and size of both uncoated and SiO_2 coated γ-Fe_2O_3 nanoparticles were investigated by scanning electron microscopy (SEM). The magnetic measurements were done by using a superconducting quantum interference device (SQUID) (MPMS-XL-7, Quantum Design) magnetometer.

3. Results and discussion

X-ray diffraction is one of the vital measurement techniques to characterize the structural properties. Fig. 1 shows the XRD diffraction patterns of uncoated and SiO_2 coated γ-Fe_2O_3 nanoparticles. The position of γ-Fe_2O_3 peaks remain almost similar for SiO_2 coated nanoparticles, however the relative intensities of the peaks got diminished as compared to uncoated nanoparticles. The average crystallite size was calculated according to Debye-Scherrer's formula which is $\tau=0.9\lambda/\beta\cos\theta$. The calculated average crystallite size (using most intense peak (311)) was 12 nm and 29 nm for SiO_2 coated and uncoated γ-Fe_2O_3 nanoparticles, respectively. The average crystallite size decreases for SiO_2 coated nanoparticles due to formation of large number of nucleation sites during synthesis procoess, which finally

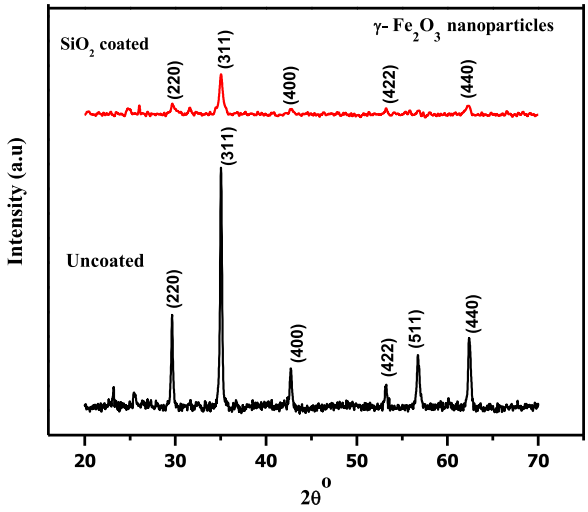

Fig. 1. XRD patterns of uncoated and SiO_2 coated γ-Fe_2O_3 nanoparticles.

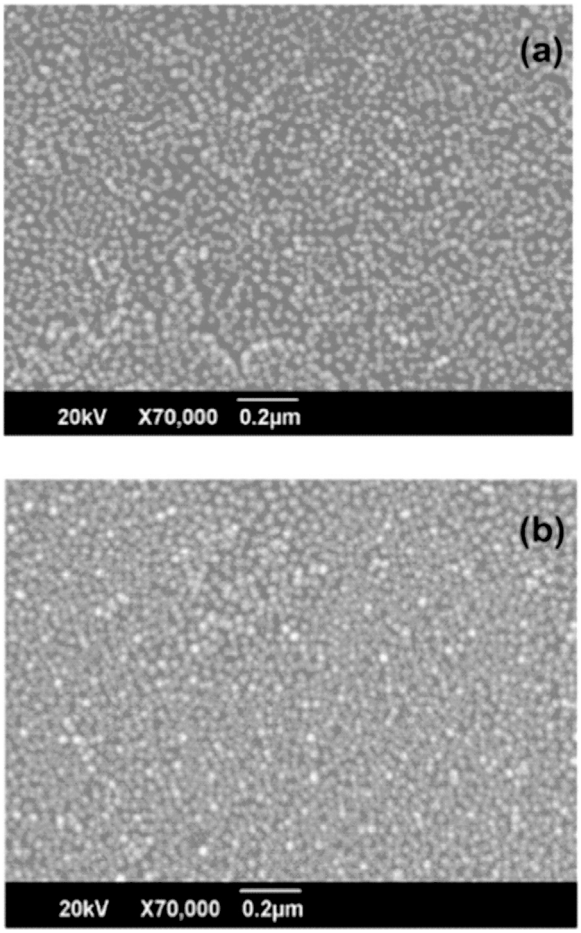

Fig. 2. (a) SEM image of uncoated γ-Fe_2O_3 nanoparticles at 0.2 μm scale and x=70,000 magnification, (b) SEM image of SiO_2 coated γ-Fe_2O_3 nanoparticles at 0.2 μm scale and x=70,000 magnification.

restricts the growth of nanoparticles [14,15]. No peaks were found for SiO_2 due to its amorphous nature.

The surface morphology and size of both uncoated and SiO_2 coated γ-Fe_2O_3 nanoparticles were investigated by using scanning electron microscopy (SEM). Fig. 2(a) and (b) shows the SEM images of uncoated and SiO_2 coated nanoparticles at scale 0.2 μm and magnification x=70,000.

SEM image of SiO_2 coated γ-Fe_2O_3 nanoparticles shows that the nanoparticles are smaller in size as compared to uncoated nanoparticles. SiO_2 has ability to control the particle size and avoids agglomeration due to its non-magnetic nature [16].

The temperature dependences of magnetization for uncoated and SiO_2 coated γ-Fe_2O_3 nanoparticles were recorded in the zero field cooled (ZFC) and field cooled (FC) protocols under 100 Oe as shown in Fig. 3(a) and (b), respectively. For ZFC curve, the sample is first cool down to 4.2 K in zero applied field and then magnetization is recorded by increasing temperature with the application of 100 Oe magnetic field to obtain ZFC curve. For FC curve, the sample is field cooled from 300 K under the same 100 Oe applied field and magnetization is measured with decreasing temperature to obtain FC curve. Average blocking temperature (T_B) of the nanoparticles was obtained by taking the peak value of ZFC curve.

For SiO_2 coated nanoparticles, ZFC curve shows a broad T_B peak at T=90 K, while there is no such peak observed for uncoated nanoparticles up to 300 K. The broad blocking peak in coated nanoparticles does not mean the exact T_B of all the nanoparticles because bigger particles are still blocked up to 300 K [17–20]. The coated nanoparticles also show hysteresis in M-H loop at 300 K, which confirms the