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Reduced surface spin disorder in ZrO_2 coated γ-Fe_2O_3 nanoparticles

F. Zeb[a], M. Shoaib Khan[a], K. Nadeem[a,*], M. Kamran[a], H. Abbas[a], H. Krenn[b], D.V. Szabo[c,d]

[a] Nanoscience and Technology Laboratory, International Islamic University, Islamabad 44000, Pakistan
[b] Institute of Physics, Karl-Franzens University, Universitätsplatz 5, A-8010 Graz, Austria
[c] Institute for Applied Materials, Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany
[d] Karlsruhe Nano Micro Facility (KNMF), Karlsruhe Institute of Technology (KIT), D-76344 Eggenstein-Leopoldshafen, Germany

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ABSTRACT

Surface spin disorder in microwave plasma synthesized zirconium dioxide (ZrO_2) coated maghemite (γ-Fe_2O_3) nanoparticles have been studied by using AC and DC magnetic measurements. The inverse spinel structure of γ-Fe_2O_3 was confirmed by X-ray diffraction. The calculated average crystallite size of γ-Fe_2O_3 and ZrO_2 phase was about 13 and 6 nm, respectively. Zero field cooled/field cooled measurements revealed average blocking temperature at 65 K. The fitted value of K_{eff} deduced from simulation was higher than that of bulk γ-Fe_2O_3 magneto-crystalline anisotropy which is mainly due to surface spin disorder. However, it was lower than the reported value for uncoated γ-Fe_2O_3 nanoparticles, which is due to reduction in surface effects and interparticle interactions in ZrO_2 coated nanoparticles. Below 25 K, a sharp increase in saturation magnetization was observed which is due to extra contribution of frozen surface spins to magnetism at low temperatures. The coercivity also showed a sharp increase below 25 K, which is due to presence of strong core-surface interactions at low temperatures. For AC susceptibility, Arrhenius law fit revealed weak interactions among the nanoparticles which were not strong enough to create a spin-glass state. In summary, ZrO_2 coated γ-Fe_2O_3 nanoparticles showed reduced surface spin disorder and weak interparticle interactions which is due to non-magnetic ZrO_2 coating.

1. Introduction

Magnetic nanoparticles exhibit different magnetic properties as compared to their bulk materials which depend upon the size, shape and preparation technique/chemistry of the materials [1]. In fine magnetic nanoparticles, large surface to volume ratio creates disordered surface spins, which alter their magnetic properties. The surface spin disorder arises due to broken super-exchange interactions at the nanoparticle's surface that produces magnetic disorder and exchange frustration at the nanoparticle's surface. The nanoparticle's surface with deficient oxygen also leads to the broken exchange bonds [2] that can produce a spin-glass like state with high anisotropy [3–5]. A spin-glass is a magnetically disordered state which exhibits high magnetic frustration in which each electron/atom spin freezes in a random direction below a spin-glass freezing temperature [6,7].

Among different oxides of iron, maghemite (γ-Fe_2O_3) is one of the most important oxide due to its diverse and remarable properties like high Cuire temperature, non-toxity, and chemical stability which makes it promising candidate for many applications such as in ferro-fluids, biomedical, data storage, and magnetic tunneling-barrier [8,9]. At nano-scale, the existence of surface spin disoder caused by finite size effects usually influences the physical properties of the γ-Fe_2O_3 nanoparticles. Millan et al. [10] reported decreased magnetization in uncoated γ-Fe_2O_3 nanoparticles due to the presence of magnetically disordered surface layer. Parker et al. [11] observed a spin-glass state in uncoated γ-Fe_2O_3 nanoparticles and attributed it to the strong interparticle interactions. Martinez et al. [12] also reported spin-glass behavior in γ-Fe_2O_3 nanoparticles at low temperatures and attributed it to pinning effect of the frozen spins at the nanoparticle's surface.

Uncoated γ-Fe_2O_3 nanoparticles usually show agglomeration which is the effect of accumulative forces among the nanoparticles [13]. Therefore, certain specific surface protection strategies are needed to attain the stability of these nanoparticles by using suitable surface coating with specific materials either by polymers, magnetic or non-magnetic material. Non-magnetic coating can reduce/enhanced the magnetization or spin glass behavior and avoid agglomeration of nanoparticles [14]. Therefore, it is important to coat the nanoparticles with suitable material to minimize the surface energy of the nanoparticles and weaken the strength of interactions among nanoparticles. Novotná et al. [15] prepared oleic acid coated γ-Fe_2O_3 nanoparticles and reported that oleic acid reduces the interparticle magnetic interactions. Girija et al. [16] proposed that ZrO_2 coating not only protects

* Corresponding author.
E-mail address: kashif.nadeem@iiu.edu.pk (K. Nadeem).

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the magnetic nanoparticles from possible oxidation in surrounding environment but also reduces the interparticle dipolar interactions.

In this article, we have chosen a non-magnetic material zirconium dioxide (ZrO_2) for coating because it has interesting properties including low toxity and high thermal stability. It also acts as a good insulating material that can reduced the agglomeration of nanoparticles. It can exist in three phases which are strongly temperature dependent, these phases are monoclinic, cubic and tetragonal [17–19]. Our prime emphasis was to study the surface spin disorder in ZrO_2 coated γ-Fe_2O_3 nanoparticles by using AC and DC magnetization measurements.

2. Experimental

Microwave plasma synthesis technique has been used to synthesized ZrO_2 coated γ-Fe_2O_3 nanoparticles. The complete synthesis process is explained elsewhere [20]. Structural analysis of ZrO_2 coated γ-Fe_2O_3 nanoparticles was studied by using X-ray powder diffraction (XRD) done by Bruker D8 Advance instrument by using $Cu - K\alpha$ ($\lambda = 0.154\ nm$) radiation. Transmission electron microscopy (TEM) was used for the imaging of nanoparticles. Magnetic measurements (AC and DC) were done by using superconducting quantum interface device (SQUID from Quantum Design, MPMS-XL-7) magnetometry. The percentage of non-magnetic ZrO_2 and magnetic γ-Fe_2O_3 phase was calculated from XRD relative intensities, and the contribution of ZrO_2 phase was subtracted from all the magnetization measurements.

3. Results and discussion

X-ray diffraction (XRD) is an important technique for finding the phase and average crystallite size of the nanoparticles. Fig. 1 (a) shows the XRD scan of ZrO_2 coated γ-Fe_2O_3 nanoparticles. We have used aluminum substrate for XRD measurement. The XRD peaks at (111), (220), (311), (511) and (440) correspond to γ-Fe_2O_3 nanoparticles phase as confirmed by JCPDS card # 39-1346. A peak at 26.1° (211) is observed which is referred to magnetite [21]. The XRD peaks at (101), (100), (112) and (202) shows the presence of *t*-ZrO_2 phase [22] as confirmed by JCPDS card # 80-0965. The miller indices (111), (200) and (220) correspond to the out-of-scale peaks at angles 38.5°, 45° and 65°, respectively are specific for aluminum substrate. The percentage of γ-Fe_2O_3 and ZrO_2 phase has been estimated by XRD relative intensities, which comes out 32 and 68% for γ-Fe_2O_3 and ZrO_2, respectively. The average crystallite size was about 13 and 6 nm for γ-Fe_2O_3 and ZrO_2 phases, respectively as calculated by using Debye Scherrer's formula as given below,

$$D = \frac{0.9\,\lambda}{\beta \cos\theta} \tag{1}$$

Transmission electron microscopy (TEM) is a useful technique to study of shape and size of the nanoparticles. TEM image of ZrO_2 coated γ-Fe_2O_3 nanoparticles at the scale of 20 nm is shown in Fig. 1 (c). It shows that the nanoparticles are nearly spherical and less agglomerated. The particle size distribution is calculated from TEM images by using a software ImagJ and fitted with Gaussian distribution function as illustrated in Fig. 1 (d). The best fit of Gaussian best fit gives the average particle size of about 10.16 ± 0.16 nm.

Fig. 2 shows the experimental and simulated temperature dependent zerofieldcooled (ZFC)/fieldcooled (FC) dc magnetization curves under the applied field of 50 Oe.

For measuring ZFC curve, the sample is ZFC to 5 K in zero applied field and then magnetization is measured on increasing temperature after an application of 50 Oe magnetic field. For FC curve, the sample is field cooled from 300 K under the same applied field and magnetization is measured on decreasing temperature. The ZFC curve shows a maximum around 65 K, which is the average blocking temperature (T_B) of the nanoparticles. The magnetic nanoparticles become thermally unstable for $T > T_B$ and show superparamagnetic behavior [23]. We have done simulation of ZFC/FC curves by adopting a Néel-Brown relaxation model of uniaxial anisotropy. The log-normal distribution function $f(V)$

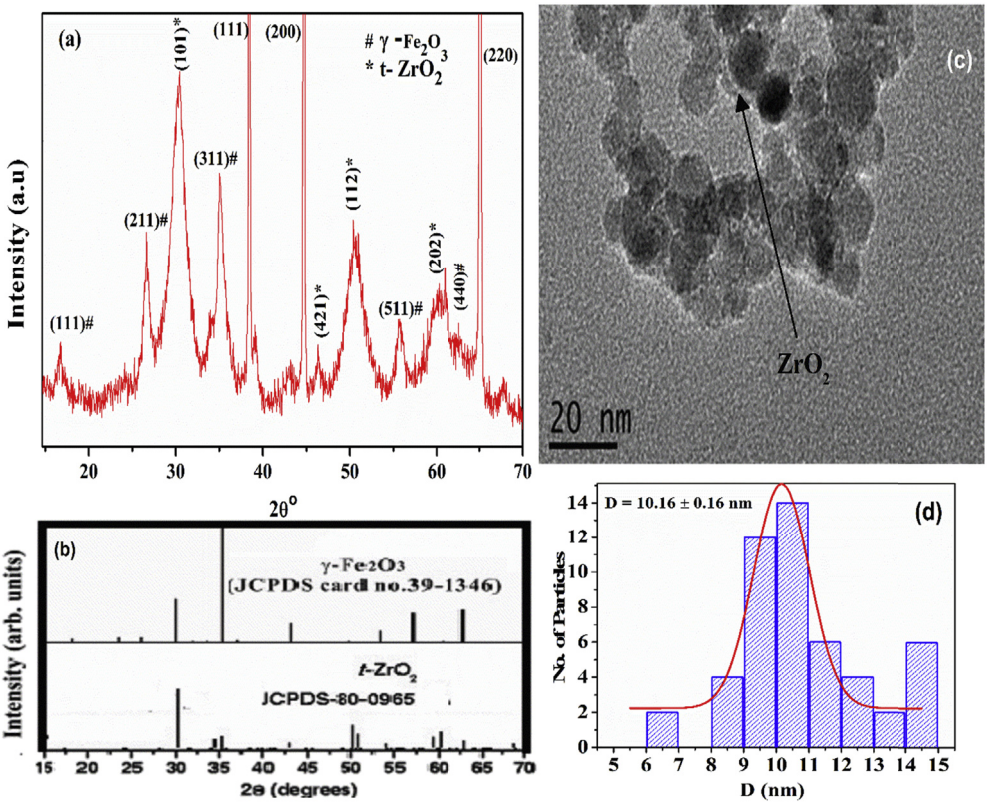

Fig. 1. (a) XRD scan of ZrO_2 coated γ-Fe_2O_3 nanoparticles, **(b)** JCPDS cards for γ-Fe_2O_3 and ZrO_2, **(c)** TEM image of ZrO_2 coated γ-Fe_2O_3 nanoparticles at 20 nm scale and **(d)** particle size distribution from TEM images fitted with Gaussian distribution (red line). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)