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Organization dependent collective magnetic properties of secondary nanostructures with differential spatial ordering and magnetic easy axis orientation

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ABSTRACT

Achieving control on the formation of different organization states of magnetic nanoparticles is crucial to harness their organization dependent physical properties in desired ways. In this study, three organization states of iron oxide nanoparticles (γ-Fe_2O_3), defining as (i) assembly (ii) network aggregate and (iii) cluster, have been developed by simply changing the solvent evaporation conditions. All three systems have retained the same phase and polydispersity of primary particles. Magnetic measurements show that the partial alignment of the easy axes of the particles in the network system due to the stacking aggregation morphology can result in significant enhancement of the coercivity and remanence values, while the opposite is obtained for the cluster system due to the random orientation of easy axes. Partial alignment in the aggregate system also results in noticeable non-monotonic field dependence of ZFC peak temperature (T_{peak}). The lowest value of the blocking temperature (T_B) for the cluster system is related to the lowering of the effective anisotropy due to the strongest demagnetizing effect. FC (Field cooled) memory effect was observed to be decreasing with the increasing strength of dipolar interaction of organization states. Therefore, the stacking aggregation and the cluster formation are two interesting ways of magnetic nanoparticles organization for modulating collective magnetic properties significantly, which can have renewed application potentials from recording devices to biomedicine.

1. Introduction

Magnetic nanoparticles with superparamagnetic property have attracted considerable research attentions due to their anomalous characteristics and technological applications. Magnetic nanoparticles below the single-domain state show this unusual property, where spins of individual particle act as giant spin, called super-spin, can randomly flip direction at room temperature [1–3]. According to Neel–Brown model of magnetization reversal of superparamagnetic particles, the mean time between two flips is given by Neel–Arrhenius equation $\tau = \tau_0 \exp(\frac{KV}{K_B T})$, where τ_0 is attempt time and of the order of 10^{-10}–10^{-13} s, K is the effective anisotropy constant, V is the volume of the particle, T is the measurement temperature and K_B is the Boltzmann constant. Thus, for a particular magnetic material theoretical superparamegnteic relaxation should be achieved below a critical size [4]. However, it is not fully realized as a key factor dipolar interaction among the particles also plays the crucial role on the relaxation dynamics [5].

Modification in the moment relaxation dynamics due to the influence of dipolar interaction is still a controversial issue. Dormann–Bessais–Fiorani (DBF) model is an acceptable model which showed the slowing of moment relaxation time with the increasing strength of dipolar interaction [6,7]. Most of the experimental data were well explained by this model [8–11]. Their assumption was based on the effect of a dynamic interaction field, where the particles' blocked and unblocked states were assumed in the experimental time window. Later DBF model was reconfirmed by the Monte Carlo based simulation, where it was observed that the effective anisotropy energy barrier increases due to the formation of an increasing number of small energy barriers caused by the reduction of anisotropy barriers as the local dipolar fields increase [12]. In contrast, Mørup model showed faster relaxation time due to interparticle interaction, while explaining the Mossbauer spectroscopy data on weakly interacting γ-Fe_2O_3 nanoparticles [13]. DBF model was modified with an interaction dependent phenomenological damping parameter, η, included in the expression for τ_0, which could explain this finding [14]. Mørup model put forward a “flip” process, where, it was assumed that the magnetic moment of a particle spends most of the time close to its

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easy direction. But, this assumption is not acceptable at high temperature, i.e. in the unblocked state, because in the unblocked state the probability of finding magnetic spins outside of the minima is appreciable. It is worth mentionable that both of these phenomenological models have considered only the random distribution of the magnetic easy axes, but not any partial alignment of easy axes or particular geometry of the assemblies. Influence of partial alignment of magnetic easy axes on the modification of magnetic properties like, coercivity and remanence was shown [15,16]. However, these studies have not shown the effect of easy axes alignment on relaxation dynamics or on blocking temperature. It is very much possible that the alignment of magnetic easy axes can affect on blocking temperature too through variation in the self-produced demagnetizing field.

Demagnetizing field is a homogeneous field originating from the dipolar interaction, whose strength depends on the average ensemble magnetization and sample shape. In an arbitrarily shaped organization demagnetizing field depends on the particles positions relative to the sample boundaries [17]. Along with, the partial alignment of the magnetic easy axes is another factor for influencing the strength of demagnetizing field. For instance, organization of single-domain magnetic nanoparticles with aligned easy axes will hardly show demagnetizing effect rather than showing magnetizing effect. Therefore, in the calculation for relaxation time for interacting magnetic nanoparticles, the contribution of demagnetizing field along with the dynamic dipolar field has to be considered to have an acceptable solution of this problem. This approach was attempted by theoretical approach, but so far we know no reports showing this through experimental data.

Many reports are there, where the dipolar interaction among magnetic nanoparticles was tuned using non-magnetic capping molecules or isolating nanoparticles inside some non-magnetic cages [18]. There are also some other routes, where, volume fraction of magnetic nanoparticles is varied in non-magnetic matrices for controlling interparticle spacing [19]. However, in such systems it is not feasible to control spatial ordering and easy axes orientation at the same time. Based on the clusters' size or magnetic volume fraction on non-magnetic matrix, only some tentative measurement of interparticle spacing can be estimated which is related to the observed magnetic properties.

In contrast, this work has considered the effect of spatial arrangement and orientation of magnetic easy axes of iron oxide nanoparticles together on demagnetizing interaction and hence on the observed collective magnetic properties. In this regard, three systems have been developed, namely, (i) IO_{NPs}@OA; an assembly of iron oxide nanoparticles, where, nanoparticles are separated by a measureable spacing, (ii) IO_{agg}@CTAB; an network aggregation of the same nanoparticles, where, particles are situated side by side at the closest distance from each other and (iii) IO_{NPCs}@PAA; identical clusters of the same nanoparticles, where the particles are at some measurable separation, but much smaller than in the assembly system. Based on the preparation strategies of these three systems and the intrinsic magnetic nature of the nanoparticles, different ground state of magnetic spin structures have been achieved, which have been related to the collective magnetic properties. Since, all the three systems have been developed from the same batch of primitive nanoparticles, the effect of size distribution is not considered in the study.

2. Analysis and characterizations techniques

High resolution transmission electron micrographs (HRTEM) were recorded on a JEOL 2100 electron microscope operating at an accelerating voltage of 200 kV. For this, the colloidal solutions of each nanosystem were dropped on carbon coated grids and dried the solvent. Small angle X-ray scattering (SAXS) of samples in powder form were performed using a laboratory based point collimation small angle scattering instrument. The scattered intensities $I(q)$ were collected as a function of scattering vector transfer q $(= 4\pi \sin\theta/\lambda)$, where λ is the X-ray wavelength ($\lambda = 0.154$ nm) and 2θ being the scattering angle. The Raman spectra were recorded using a Renishaw In-Via Raman spectrometer (Renishaw, UK) at a resolution of 0.3 cm^{-1}. Ar^{+} laser of wavelength 514.5 nm was used for the measurements. The used laser power was 0.1 mW and passed through a 50 × objective for exciting the samples. All magnetic measurements were carried out using a Quantum design Dynacool PPMS (Physical Property Measurement System) with field range ±9 T and temperature range 1.9–400 K. FC and ZFC protocols were applied for *M–T* measurements. For FC measurement the sample was cooled from 300 K to 10 K in presence of a probe field from and magnetization was measured with warming sweep rate 2 K/min keeping the field constant. The same procedure was followed for ZFC measurement, the only difference is that here the cooling process was performed without applying any field. For TRM measurements, the sample was cooled similar to ZFC/FC and the magnetization was measured during warming in absence of magnetic field. The field dependence of remanent magnetization was measured using IRM (isothermal remanent magnetization) and DCD (direct current demagnetization) methods. For IRM, the sample was cooled to 10 K at zero field. Thereafter, a small field (starting with 50 Oe) was applied for 10 s, and then it was switched off and remanence was measured. The process was repeated with increasing magnitude of applied field up to 5 T. In contrast, for DCD, after cooling the sample at zero magnetic field to low temperature, 5 T field was applied for 10 s, and then a small field was applied in the opposite direction. After 10 s, it was switched off and remanence was measured. The process was repeated with increasing field up to −5 T. For FC memory study, samples were cooled in presence of 500 Oe magnetic field from 300 K to 10 K with some intermittent stopping intervals at temperatures 80 K, 60 K, 40 K and 20 K. Then magnetization was measured with continuous warming at the rate of 2 K/min. All magnetization values of *M–H* and *M–T* measurements were corrected with TGA data to neglect the effect of the non-magnetic contribution.

3. Results and discussion

3.1. Organizations and phase of iron oxide nanoparticles

Oleic acid capped iron oxide nanoparticles were synthesized by oxidation of ferrous salt in presence of oleic acid [20]. TEM (shown in Fig. 1a and d) shows the uniform distribution of the synthesized nanoparticles with average size 5 ± 2 nm. The average interparticle spacing is found to be ~6.3 nm. So-prepared nanoparticles were then functionalized with a microemulsion method using CTAB (Cetyltrimethylammonium bromide), which resulted in a network aggregation of the nanoparticles with interconnected chain morphology (shown in Fig. 1b and e) due to the fast solvent (chloroform) evaporation. This system of hydrophilic nanoparticles was further treated with the polyelectrolyte PAA (Polyacrylic acid) for clustering purpose (shown in Fig. 1c). These three steps methods are elaborated in the online Supplementary information (ES1). Wrapping nature of the polymer is thought to be responsible for the formation of separate clusters. TEM results reveal that in the cluster system (shown in Fig. 1f) a measurable interparticle spacing (~5.5 nm) among the nanoparticles has been achieved unlike the aggregate system (IO_{agg}@CTAB).

It should be emphasized that, since all the three systems have