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Pure dipolar-interacted $CoFe_2O_4$ nanoparticles and their magnetic properties

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ABSTRACT

The mono-dispersed and uniform $CoFe_2O_4$ nanoparticles were synthesized by the thermal decomposition of $Fe(acac)_3$ and $Co(acac)_2$. Then the $CoFe_2O_4$ nanoparticles were diluted in amorphous SiO_2 matrix with different $CoFe_2O_4$ nanoparticles' concentrations. All samples show the positive or negative exchange bias behavior, indicating the presence of canted spin layer at the $CoFe_2O_4$ nanoparticles' surface. The large effective anisotropy constant (3.38×10^6 erg/cm^3) was observed, which can be attributed to the induced surface anisotropy by the canted surface spins. The reduced magnetization (M_r/M_s) was dominated by the interparticle dipolar interaction while the coercivity (H_c) was determined by the synergistic effects of the surface anisotropy, interparticle dipolar interaction and interface effect. By suitably diluting $CoFe_2O_4$ in the SiO_2 matrix, the high H_c (3056 Oe) and the M_r/M_s (0.63) can be obtained, which is larger than most of those reported before. The present work is meaningful for revealing the underlying mechanism in nano-scaled magnetic system and improving the magnetic performance.

1. Introduction

The magnetic nanoparticles (NPs) usually serve as ideal model systems to study the exchange bias [1], exchange spring [2–4], interparticle dipolar interaction (IPDI) [5–7] and the finite-size effect [8] apart from their applications in many fields [9–11]. The exchange bias and the exchange spring effects were earlier studied and some widely-accepted results were obtained. However, the study on the IPDI has fallen behind relatively, and some conflicting results were reported. For examples: the IPDI was suggested to enhance the coercivity (H_c) which was attributed to additional anisotropy by the IPDI [7] while the opposite conclusions were reported by others [5] concluded that the strong IPDI suppresses both the H_c and the remanence to saturation magnetization ratio (M_r/M_s), and the effects of IPDI can be negligible as the interparticle distance exceeds to three times of the particle size (diameter).

Besides the magnetic parameters (H_c and M_r/M_s) as mentioned above, the magnetic ordering states were also sensitively affected by the IPDI. For examples: (1) the IPDI may result in the antiferromagnetic ground state for the two-dimensional (2D) magnetic NPs [7]; (2) in extremely diluted samples, superparamagnetism was observed [12]; (3) in concentrated systems, in which the magnetic NPs are close to each other, the strong IPDI results in a super-spin glass (SSG) or a super-spin-glass-like (SSG-like) arrangement [13].

So far the effects of the IPDI have still been focused on and some controversial issues deserve further clarification. In order to predominantly investigate the effects of the IPDI on the magnetic properties, firstly it is important to synthesize the good quality magnetic NPs with uniform size and high dispersity in order to exclude the size effects and the exchange-coupling interaction, leading to pure dipolar interactions. In previous studies on the magnetism of the NPs system, such a point has not been paid enough attention to. Specifically, according to the Stoner–Wohlfarth model [14], for noninteracting single domain particles with the randomly oriented easy axis, M_r/M_s is given by 0.5 for uniaxial anisotropy, and 0.832 ($K_1 > 0$) or 0.87 ($K_1 < 0$) for cubic anisotropy [15]. Experimentally the M_r/M_s ratio of $CoFe_2O_4$ NPs, synthesized by many methods, was smaller than the theoretical value [4,16–18], which were attributed to the effects of particle size and crystallinity; by observing their scanning/transmission electron microscopic results, one can notice that their $CoFe_2O_4$ NPs seriously agglomerate. In such the system of agglomerated $CoFe_2O_4$ NPs, many factors, such as the broad size distribution,

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effective anisotripy and exchange-coupling interaction, synergetically affects the magnetic properties; of course there inevitably exists the IPDI because it is a universal phenomenon in the nano-scaled system, and the IPDI should be taken into account for the magnetic properties. However, the agglomerated $CoFe_2O_4$ NPs are not beneficial to reveal whether and how the IPDI affect the magnetic properties because they are not a pure dipolar interaction system.

In this work, the $CoFe_2O_4$ NPs were first synthesized by thermal decomposition of $Fe(acac)_3$ and $Co(acac)_2$ in the mixture solution of oleic acid, oleylamine and benzyl ether at 290 °C, which exhibit the good dispersity and uniform size of 10.5 ± 2 nm. Then the $CoFe_2O_4$ NPs were dispersed in the amorphous SiO_2 matrix in order to obtain the pure dipolar interaction system with different dipolar interaction strength. Our results show that the M_r/M_s ratio strongly depends on the strength of IPDI. Furthermore, the high coercivity H_c (3056 Oe) and M_r/M_s (0.63) were obtained for the suitable concentration of $CoFe_2O_4$ NPs.

2. Experimental procedures

The synthesis of composite $CoFe_2O_4$–SiO_2 was carried out by two steps: $CoFe_2O_4$ NPs were first synthesized and then they were dispersed in the SiO_2 matrix. All raw materials include absolute ethanol, $Co(acac)_2$ (97%), $Fe(acac)_3$ (98%), benzyl ether (BE, 97%), oleic acid (OA, 90%), oleylamine (OAM, 80–90%), tetraethyl orthosilicate (TEOS) and ammonia solution.

2.1. Synthesis of $CoFe_2O_4$ NPs

$Fe(acac)_3$ (9.586 g), $Co(acac)_2$ (3.526 g), OA (80 ml), OAM (80 ml) and BE (400 ml) were mixed into a 1000 ml three-necked round-bottom flask with magnetically stirring under a flow of nitrogen (99.999%). Then the mixture was heated to 120 °C and kept for 0.5 h to remove the air and moisture, and subsequently heated to 200 °C under reflux and kept for 2 h. Next the mixture was heated to 290 °C and kept for 1 h. After the mixture was cooled naturally to room temperature, absolute ethanol (about 500 ml) was added to produce the precipitate. The precipitate was separated via centrifugation (3000 rpm, 10 min) and washed with absolute ethanol several times to obtain $CoFe_2O_4$ NPs.

2.2. Synthesis of $CoFe_2O_4$–SiO_2 nanocomposite

$CoFe_2O_4$ NPs were equally divided into five parts and each part was added to the solution of ethanol (20 ml), distilled water (10 ml), ammonia solution (0.5 ml) and different amount of TEOS with sonicating for 3 h. Then ethanol was added to form precipitate. The precipitate was subsequently separated by centrifugation, washed with ethanol and water to remove unreacted molecules. The precipitate was dried at 80 °C and annealed at 500 °C in muffle furnace for 2 h to obtain the final $CoFe_2O_4$–SiO_2 nanocomposite. Samples having different amount TEOS of 0, 0.5, 1.0, 1.5, 2.0, and 2.5 ml are hereafter referred to as B0, B1, B2, B3 and B4, respectively.

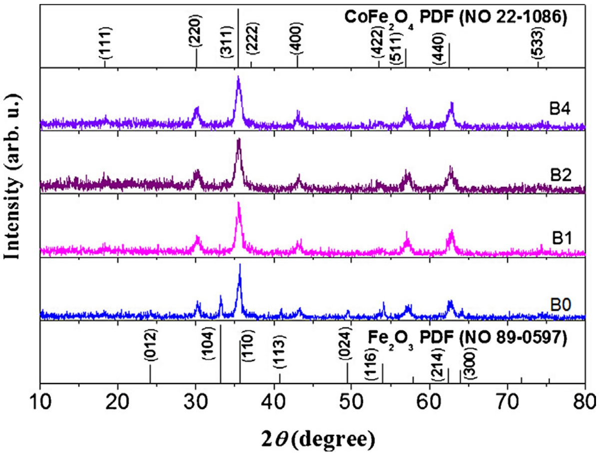

Fig. 1. XRD patterns of samples B_0, B_1, B_2 and B_4 and standard X-ray diffraction PDF cards of $CoFe_2O_4$ (No. 22-1086) and Fe_2O_3 (No. 89-0597).

The crystal structure of the products was characterized by X-ray diffraction using an X-ray diffractometer (XRD; DX-2000 SSC) with Cu Kα irradiation ($\lambda = 1.5406$ Å) in the scanning range 20–80° with a step of 0.02°. Fourier transformed infrared (FT-IR) spectra were recorded in the 400–2500 cm^{-1} range (Nicolet IR-76 200) at a spectral resolution of 2 cm^{-1} by preparing KBr pellets (0.1 wt% sample). (High resolution) transmission electron microscopy ((HR) TEM, JEOL JEM-2100) was used to observe lattice fringes, and to obtain selected area electron diffraction (SAED) patterns of samples which were dispersed in octane. Magnetic measurements were carried out using a Quantum Design superconducting quantum interference device (SQUID) PPMS system (PPMS EC-II).

3. Results and discussion

3.1. Crystal structures and morphology analysis of all samples

Firstly, the crystal structures of the obtained samples are analyzed. Fig. 1 representatively shows XRD patterns for samples B0, B1, B2 and B4 and the standard X-ray diffraction PDF cards of $CoFe_2O_4$ (No. 22-1086) and Fe_2O_3 (No. 890-597). For the sample B0, the main diffraction peaks can be indexed to the cubic spinel $CoFe_2O_4$ ferrite. Several weak peaks result from the α-Fe_2O_3 phase, as observed in references [19,20] which is nonmagnetic and has no contribution to the magnetic properties when it exists in a magnetic material as the secondary phase. The cell lattice parameter a of $CoFe_2O_4$ can be obtained from $\sin^2\theta = \lambda^2/4a^2 (H^2 + K^2 + L^2)$, where a is the lattice parameter, θ the diffraction angle, λ the wavelength of the Cu $K\alpha$ irradiation, and (HKL) the crystal plane index. The obtained lattice parameter a is equal to 0.8503 nm, so the X-ray density $d_x = 8\,M/Na^3$ can be calculated to be 5.08 g/cm^3, where M and N are the molecular weight and Avogadro's number [21,22]. While $CoFe_2O_4$ was capsulated by SiO_2, the reflection of α-Fe_2O_3 impure phase disappeared maybe because the capsulated SiO_2 prohibits the formation of α-Fe_2O_3. Additionally the XRD patterns of all capsulated samples show the similar characteristic besides the slightly different diffraction intensities, and do not show any reflections related to SiO_2 indicating that SiO_2 is amorphous, which is consistent with the SAED result below.

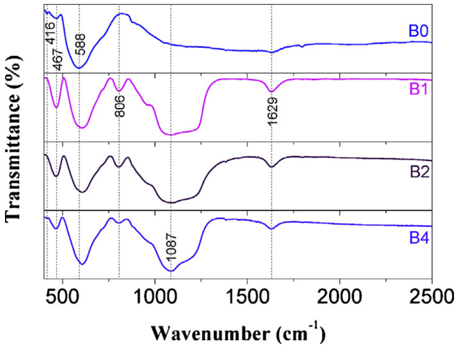

Fig. 2. FT-IR spectra of the samples B0, B1, B2 and B4.