Magnetic Response of Hydrothermally Prepared Self-Assembled Co_3O_4 Nano-platelets

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In the present communication, we report a strong ferrimagnetic behavior of self-assembled Co_3O_4 nano-platelets, which most likely originates from the intrinsic spin structure of the unique Co_3O_4 structure. The microsphere-like structures are composed of nano-platelets that are entangled together to form the organized network. These anomalous ferrimagnetic properties can be rationalized by supposing that one of the Co^{3+} and one of the Co^{2+} ions are switched between the octahedral and tetrahedral sites. The powder sample was also characterized by x-ray diffraction and superconducting quantum interface device magnetometry.

Key words: Hydrothermal synthesis, Co_3O_4 platelets, magnetic materials, x-ray techniques

INTRODUCTION

Magnetism of nanostructured materials is of increasing interest because of their specific structures and nanosized distribution which lead to interesting properties such as superparamagnetism and magnetic anisotropy energy per particle, which is potentially responsible for holding the magnetic moment along certain directions.[1–5] Morphologies, dimensions, and material parameters usually govern the magnetic properties of nanostructured materials. For example, as the material size decreases, the domain structure changes from a multidomain to a single-domain structure due to a competition between magnetostatic energy and domain-wall energy; the coercive force increases monotonically with a decrease in the diameter of spherical particle. However, a transition between the single-domain state and vortex state, below a

critical dimension, has been observed in many magnetic nanostructures.[6,7]

Metal oxide nanostructured materials have been widely studied owing to their scientific significance as well as potential applications. Co_3O_4 belongs to the transition metal oxides group, has a stable phase, and has a normal spinel crystal structure based on a cubic close packed array of oxide ions, in which Co(II) ions occupy the tetrahedral $8a$ sites whereas Co(III) ions reside in the octahedral $16d$ sites.[8] Antiferromagnetic p-type semiconductor characteristics,[9] unique magnetic properties, excellent optical response, brilliant field emission features and attractive electrochemical properties have made nanometric-scale Co_3O_4 suitable for catalysis technology,[10] magnetic storage,[11] sensors,[12] and lithium-ion batteries.[13–15] Antiferromagnetism behavior of the bulk Co_3O_4 compound with a Néel temperature of about 40 K is well-documented phenomenon.[16] However, based on the reduced coordination of the surface spins and alternation in the magnetic order, superparamagnetic behavior or a weak ferromagnetism of the nanometric-sized

particles of the antiferromagnetic materials has been predicted. In this context, key studies on the magnetization and magnetic relaxation behavior of the various dimensions of Co_3O_4 nanostructures at different magnetization temperatures are concisely described.[3] For example, Makhlouf et al. observed a narrow cusp in 20 nm thin Co_3O_4 nanoparticles at 25 K in zero field-cooling (ZFC) magnetization and irreversibility in the field-cooling mode (FC), whilst both FC and ZFC modes bifurcate at lower temperatures (8 K), whereas a higher (60 K) magnetization temperature measurement (M–T) obeys Curie–Weiss law with a negative (θ) value at about 85 K.[17] In another study, Ana et al. reported weak ferrimagnetisms at low temperature (8 K) of 16 nm Co_3O_4 nanoparticles and associated this phenomenon with uncompensated surface spins of the Co_3O_4 nanoparticles and moreover documented that the M–T followed a Curies–Weiss law without irreversibility at high magnetic field.[18] Similarly, Ichinagi et al. also reported identical magnetic behavior of extremely small Co_3O_4 nanoparticles (3.1–9.2 nm).[19]

Nanoscale magnetic materials in distinct morphologies (i.e. wires,[20,21] rods,[22] cubes,[23] hollow spheres,[24–26] cobalt nanoparticle rings/disks[27]) have been fabricated by employing diverse thermal-assisted and solvent chemistry synthesis techniques such as thermal decomposition, chemical spray pyrolysis, co-precipitation, sol–gel, micro-emulsions, hydrothermal, solvothermal and aqueous solution methods. However, simplicity, low cost and multiplicative morphologies of the products have made the hydrothermal method attractive compared to other processes.

Here, we depict a simple hydrothermal synthesis route and magnetic characterization of self-assembled Co_3O_4 nano-platelets and distinctive magnetic behavior associated with this unique morphology of Co_3O_4 crystals is presented.

EXPERIMENTATION

The experiments in this study were carried out using analytically extra pure chemicals from Aldrich without further purification. In a typical procedure for the preparation of self-assembled Co_3O_4 nano-platelets into spheres, a beaker with 40 mL absolute ethanol containing 0.1 M of $Co(NO_3)_2 6H_2O$ was prepared. Then, 0.05 M of cetyltrimethylammonium bromide (CTAB) was introduced into the beaker and the mixture was stirred for 30 min. The mixture was transferred into a 60-mL Teflon-lined autoclave reactor. The autoclave was maintained at 150°C for 50 h and cooled to room temperature naturally. The resulting product was repeatedly washed with double-distilled water and absolute ethanol by centrifugation at 3000 rpm. The resulting precipitate was dried at 80°C overnight in the vacuum oven. The microstructural properties of the prepared samples were characterized by field emission scanning electron microscopy (FESEM;

HITACHI S-4700), x-ray diffraction (Rigaku x-ray diffractometer, Japan). The magnetic properties were studied by using superconducting quantum interface device (SQUID) magnetometry.

RESULTS AND DISCUSSION

Figure 1a represents the overall morphology of the sample; it indicates a large amount of microsphere-like structures composed of nano-platelets that are entangled together to form organized network. The self-assembled Co_3O_4 nano-platelets are shown in the inset of Fig. 1a with thicknesses of about 50–60 nm. This architecture of Co_3O_4 was obtained when ethanol was used as a solvent in the presence of CTAB. It can be seen from Fig. 1b that the average diameter of each sphere-like assembly is about 5 μm. Figure 1c and d shows the morphology of the formed crystals when the ethanol solvent was replaced with water, indicating that the resulting structure could be controlled by the nature of the solvent. The possible growth mechanism for the cobalt crystals can be elucidated by a precipitation–dissolution–renucleation–growth–aggregation mechanism.[28] Step 1: when the $Co(NO_3)_2$· $6H_2O$ (0.1 M) and cetyltrimethylammonium bromide (CTAB, 0.05 M) reaction mixture in water reaches supersaturation, the primary precipitates are rapidly formed; step 2: the process is followed by dissolution of unstable precipitates which then offer renucleation and growth of crystallites.[29–31]

Figure 2 shows the x-ray diffraction (XRD) patterns of the as-prepared product of Co_3O_4 and commercialized bulk Co_3O_4 powder. All the reflections on the XRD pattern could be indexed to a pure phase of Co_3O_4 with the space group of $Fd3m$ and a lattice constant of $a = 0.8084$ nm.* The well-resolved diffraction peaks (at 31.1, 36.6, 44.6, 59.1, and 65.0) suggest a good crystallinity of the Co_3O_4 nanostructures obtained. The XRD peak at about 33° possibly initiates from $Co(OH)_2$. No other peaks were observed in the spectrum. Powder x-ray diffraction (XRD) peaks of Co_3O_4 nano-platelets were slightly shifted to lower angle. This result might be attributed to structural change of Co_3O_4 nano-platelets.

The grown structure has an inverse spinal structure and ferromagnetic spinel correlation. Figure 3a shows magnetization curves at several temperatures. Below, a transition temperature of $T < 20$ K, magnetization of Co_3O_4 nano-platelets shows hysteric curve with coercive field of $H_c \sim 100$ Oe and magnetic moment is saturated at high magnetic field of $H > 20$ kOe, where the saturation magnetic moment M_{sat} is close to 1 μ_B/f.u. The temperature-dependent magnetization, divided by applied magnetic field, $M(T)/H \equiv \chi$, is plotted in Fig. 3b. At $H = 0.5$ kOe, the Co_3O_4 nano-platelets
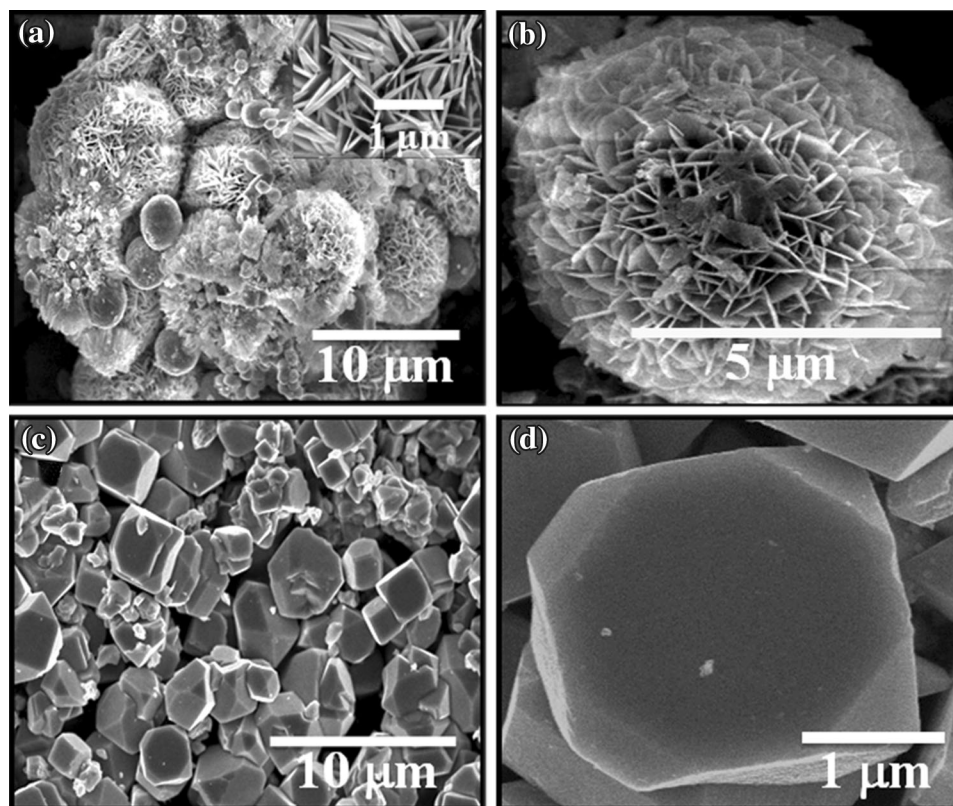
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*JCPDS Card No. 43-1003.

Fig. 1. SEM images of (a) assembled Co_3O_4 nano-platelets with an inset image of high magnification, of (b) a single Co_3O_4 microsphere assembly, of (c, d) the Co_3O_4 crystals with low and high magnification, respectively.
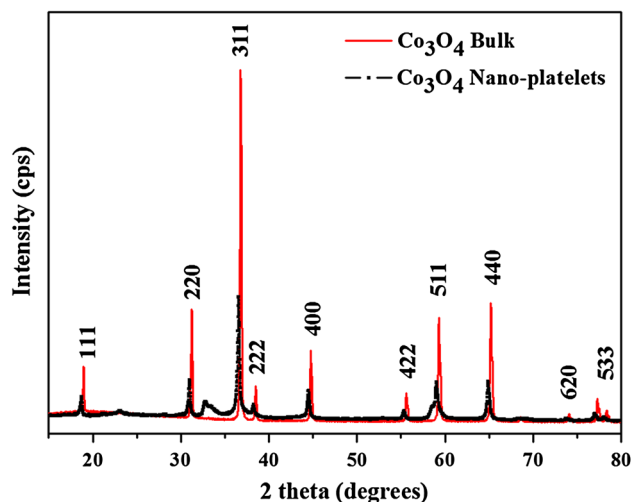

Fig. 2. The XRD analysis of bulk Co_3O_4 and self-assembled Co_3O_4 nano-platelets.

show a magnetic transition with transition temperature of $T_c \approx 20$ K and reveal a magnetic irreversibility of field-cooled (FC) and zero-field-cooled (ZFC) magnetization below the transition temperature. Such phenomena disappear in a high magnetic field ($H > 10$ kOe). From the Curie–Weiss fit of $\chi(T)$ at high temperatures, as shown in the inset of Fig. 3b, the Weiss temperature was found to be

$\theta = -65.8$ K, which is consistent with an antiferromagnetic interaction between the magnetic moments of Co ions. The estimated effective magnetic moment μ_{eff} was ca. 6.8 μ_B, which is somewhat larger than a theoretical value of bulk Co_3O_4. This magnetization behavior implies that the magnetic ground state of the self-assembled Co_3O_4 nano-platelets is ferrimagnetic state. Theoretically, bulk Co_3O_4 represents a formula unit of AB_2O_4 and exhibits a normal spinel crystal structure with occupation of tetrahedral A sites by Co^{2+} and octahedral B sites by Co^{3+}. Due to its crystalline field, the Co^{2+} ions at tetrahedral sites have magnetic moments with three free spins ($S = 3/2$). On the other hand, Co^{3+} ions in octahedral sites have no magnetic moment ($S = 0$).[3,4]

Bulk Co_3O_4 shows an antiferromagnetic transition with the Neel temperature of $T_N \approx 40$ K, in which each Co^{2+} ion in the A-site is neighbored by four Co^{2+} ions of opposite spins.[5] The magnetic properties of Co_3O_4 nano-platelets were quite different from the bulk Co_3O_4. Negative Weiss temperature implies antiferromagnetic interaction between magnetic moment of Co ions, but low temperature magnetization shows hysteresis loop. These anomalous magnetic properties can be rationalized by supposing that one of the Co^{3+} and the Co^{2+} ions would switch the octahedral and tetrahedral sites. If the Co^{3+} ion is located in the

Fig. 3. (a) Hysteresis loop at 5 K, 30 K and 300 K for the self-assembled Co_3O_4 nano-platelets, and (b) temperature dependence of the ZFC and FC magnetization curves. Inset shows inverse magnetic susceptibility and Curie–Weiss fit of magnetic susceptibility at high temperatures.

CONCLUSION

In summary, we represent a simple hydrothermal synthesis route for the preparation of interesting self-assembled architecture of Co_3O_4 nano-platelets. The magnetic properties demonstrated a strong ferrimagnetic behavior, which originates from intrinsic spin structure of Co_3O_4 nano-platelets. These anomalous ferrimagnetic properties can be rationalized by supposing that one Co^{3+} and one Co^{2+} ions are switched between the octahedral and tetrahedral sites. The estimated effective magnetic moment μ_{eff} was ca. 6.8 μ_B, which is somewhat larger than a theoretical value of bulk Co_3O_4. Ultimately, the resulting products may find a wide range of applications.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

tetrahedral sites, it has magnetic moment with four free spins (S = 2) but the magnetic moments of the Co^{2+} ion does not change even it is located in an octahedral site (S = 3/2). The antiferromagnetic interaction between the switched Co^{3+} and Co^{2+} ions can make excessive spontaneous magnetic moment of 1 μ_B/f.u., which is consistent with the experimental result.

Consequently, Co_3O_4 nano-platelets have inverse spinel structure and ferrimagnetic spin correlation. In previous reports, the nano-sized Co_3O_4 shows complex magnetic properties that might come from an uncompensated surface spin effect.[17,32–34] But in the present report, it is noticeable that the ferrimagnetic property of the self-assembled Co_3O_4 nano-platelets originates from its intrinsic spin structure and the complex magnetic properties of nano-sized Co_3O_4 might be explained from partial switching of $Co^{3+/2+}$ ions. This result may indicate a structural difference between the self-assembled Co_3O_4 nano-platelets and the common crystalline Co_3O_4 phase.

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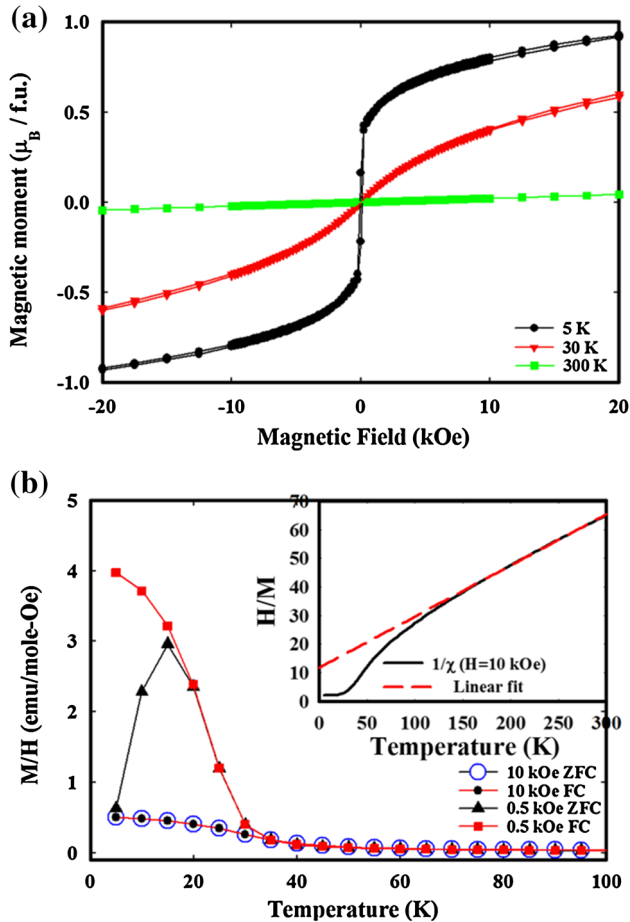19. Y. Ichinagi and S. Yamada, *Polyhedron* 24, 2813 (2005).

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