

Shape Control and Associated Magnetic Properties of Spinel Cobalt Ferrite Nanocrystals

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Abstract: By combining nonhydrolytic reaction with seed-mediated growth, high-quality and monodisperse spinel cobalt ferrite, CoFe_2O_4 , nanocrystals can be synthesized with a highly controllable shape of nearly spherical or almost perfectly cubic. The shape of the nanocrystals can also be reversibly interchanged between spherical and cubic morphology through controlling nanocrystal growth rate. Furthermore, the magnetic studies show that the blocking temperature, saturation, and remanent magnetization of nanocrystals are solely determined by the size regardless the spherical or cubic shape. However, the shape of the nanocrystals is a dominating factor for the coercivity of nanocrystals due to the effect of surface anisotropy. Such magnetic nanocrystals with distinct shapes possess tremendous potentials in fundamental understanding of magnetism and in technological applications of magnetic nanocrystals for high-density information storage.

Introduction

The unique and novel size-dependent properties displayed by semiconductor nanocrystals have initiated the current worldwide intense research on nanomaterials.^{1,2} Recently, keen interests have been expanded into controlling the shape of nanomaterials and also into understanding the correlations between the material properties and its shape. The shape of nanomaterials can be as vital as the size in determining the uniqueness and novelty of material properties.^{3–5} Moreover, a large part of the societal impact by nanomaterials surely will be realized in a variety of devices consisting of nanomaterial components. Assembly of nano components is a key process in building devices, and the shape of nano building blocks and related properties will be crucial for the assembly and device designs. Shape-controlled synthesis of nanocrystals surely is an experimental challenge.⁶ Successes in shape control of nanocrystals have been reported in the syntheses of metals^{7,8} and semiconductors.⁹ Clearly, it is desirable to develop strategies for shape-controlled syntheses of complex metal oxides possessing rich properties, especially the magnetic characteristics.

Monodisperse metal oxide nanocrystals have been synthesized by several nonhydrolytic methods using precursors of

organometallic and coordination compounds.^{10–13} The shape of these nanocrystals typically is spherical. In addition, it has been demonstrated that the seed-mediated growth is an effective route for size-controlled synthesis of magnetite¹³ and gold nanocrystals.¹⁴

Magnetic properties of a material usually are very sensitive to its shape due to the dominating role of anisotropy in magnetism. Here we report that by using a seed-mediated growth approach, monodisperse spinel cobalt ferrite, CoFe_2O_4 , nanocrystals can grow into a nearly spherical shape or an almost perfect cube in a highly controllable manner. The shape of the nanocrystals can also be reversibly interchanged between spherical and cubic shape by controlling nanocrystal growth rate. Furthermore, the magnetic studies show that the blocking temperature, saturation, and remanent magnetization of nanocrystals are solely determined by the size regardless of the spherical or cubic shape. However, the shape of the nanocrystals is a dominating factor for the coercivity of nanocrystals. Such magnetic nanocrystals with distinct shapes possess tremendous potentials in technological applications of magnetic nanocrystals for high-density information storage and also in fundamental understanding of magnetism. The cubic nanocrystals should greatly facilitate the theoretical modeling for understanding magnetic properties since their topology offers well-defined crystallographic surfaces and easily recognizable magnetization axes.

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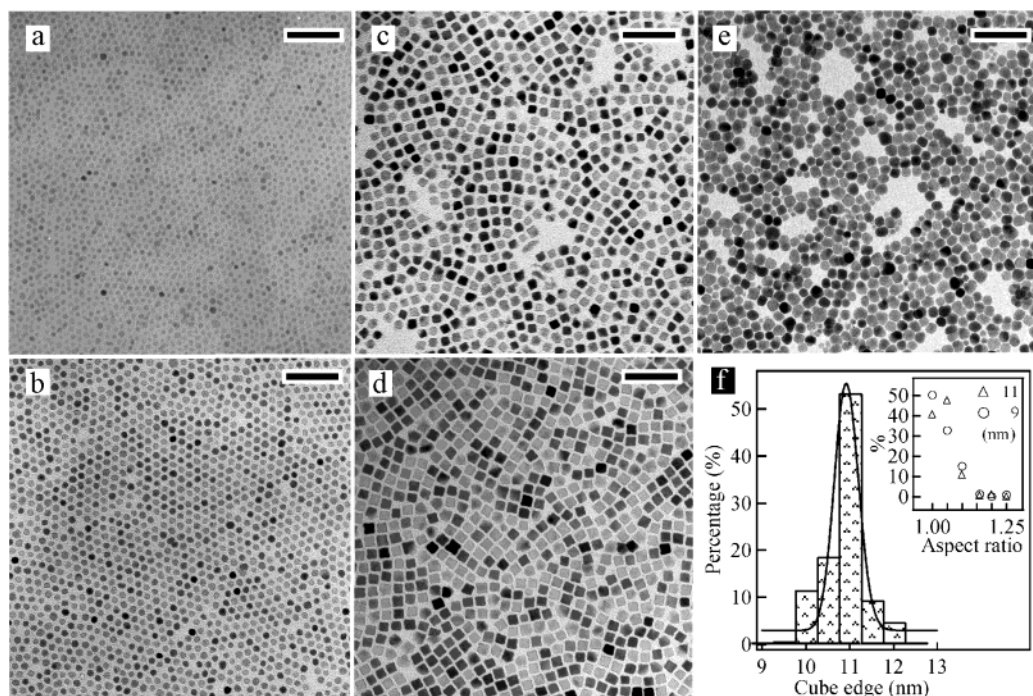


Figure 1. TEM micrographs with the scale bar as 50 nm. The size in panel (a) and (b) is 5.2 ± 1.1 and 7.9 ± 0.5 nm spherical CoFe₂O₄ nanocrystals, respectively. Panels (c) and (d) show 9.1 ± 0.5 and 10.9 ± 0.6 nm cubic CoFe₂O₄ nanocrystals, respectively. Panel (e) is 11.8 ± 1.3 nm spherical CoFe₂O₄ nanocrystals. Panel (f), as a representative histogram, shows the size distribution of cubic nanocrystals in panel (d) after measuring over 400 nanocrystals. The inset in panel (f) displays the aspect ratios of cubic nanocrystals in panels (c) and (d).

Experimental Section

Synthesis of Magnetic Nanoparticles. Monodisperse CoFe₂O₄ nanocrystals are synthesized by using a combination of a nonhydrolytic process and seed-mediated growth. The general strategy is using coordination compounds of iron(III) and cobalt(II) acetylacetonate, Fe(acac)₃ and Co(acac)₂, as precursors in a nonhydrolytic process to synthesize CoFe₂O₄ spherical nanocrystals with a mean diameter of 5 nm. Such 5 nm nanocrystals then serve as seeds to grow larger spherical or cubic nanocrystals in the seed-mediated growth process.

In a typical synthesis, a mixture of 2 mmol of Co(acac)₂, 40 mL of phenyl ether, 20 mmol of 1,2-hexadecanediol, 10 mL of oleic acid, and 10 mL of oleylamine was heated to 140 °C followed by a droplet addition of 4 mmol Fe(acac)₃ in 20 mL of a phenyl ether solution. The temperature of the nonhydrolytic reaction was then increased quickly to 260 °C, and the mixture was kept at reflux for 30 min before being cooled down to room temperature. After addition of ethanol and centrifuging, spherical CoFe₂O₄ nanocrystals with a diameter of 5 nm were obtained.

Such 5 nm nanocrystals were used as seeds to grow 8 or 9 nm spherical nanocrystals in the solution of Co(acac)₂ and Fe(acac)₃ precursors. For instance, to produce 8 nm spherical nanocrystals, 100 mg of seeds was used in a particle growth solution consisting of 1 mmol of Co(acac)₂, 2 mmol of Fe(acac)₃, 10 mmol of 1-octadecanol, 5 mL of oleic acid, and 5 mL of oleylamine. Then, the solution temperature was raised to 260 °C at a rate of 10–15 °C/min and kept at reflux at 260 °C for 30 min. The nanocrystals precipitated out after ethanol was added. The nanoparticulate samples were suspended in hexane for transmission electron microscopy (TEM) studies.

Magnetic Measurement. The magnetic properties of the nanocrystals have been studied at various temperatures by using a Quantum Design MPMS-5S SQUID magnetometer with a magnetic field strength up to 5 T.

Transmission Electron Microscopy. TEM studies have been performed using a JEOL 100C at 100 kV. The nanocrystals were dispersed on holey carbon grids for TEM observation. High-resolution TEM studies were conducted by using a JEOL 4000EX at 400 kV.

Results and Discussion

From the nonhydrolytic process as the first step of the synthesis, spherical CoFe₂O₄ nanocrystals with a diameter of 5 nm were obtained. Figure 1a shows a TEM micrograph of monodisperse nanocrystals with a diameter of 5.2 ± 1.1 nm. X-ray and electron diffraction studies confirmed such nanocrystals and all other subsequently obtained nanocrystals possessing a spinel structure. Chemical analysis using the inductively coupled plasma atomic emission spectroscopy (ICP-AES) method showed Co and Fe having a 1/2 molar ratio in all these nanocrystals.

The 5 nm nanocrystals served as the seeds for the seed-mediated growth as the second step of the synthesis for the nanocrystals with a diameter of 8 or 9 nm. The size of the nanocrystals was controlled through the ratio between the quantity of nanocrystalline seeds and the amount of precursors in the solution for seed-mediated growth. The growth procedures described in the Experimental Section have generated a sample consisting of 8 nm spherical nanocrystals together with a tiny fraction of nanocrystals having a ~5 nm diameter. Monodisperse 8 nm nanocrystals (Figure 1b) were obtained after a small amount of acetone was added into the hexane suspension of as-grown nanoparticulate sample.

Monodisperse nanocrystals with a 9 nm diameter can be obtained using the same procedures but with increased concentration of precursors in the particle growth solution. Although nanocrystals with a larger diameter can also be prepared with 5 nm seeds, the quality of nanocrystals in term of size distribution usually deteriorated. Therefore, monodisperse nanocrystals with larger diameters were typically produced by incrementally increasing the size of nanoparticulate seeds. For instance, 8 nm nanocrystals were used in seed-mediated growth to synthesize monodisperse nanocrystals with a diameter of 10 or 12 nm.

It is very intriguing that the shape of CoFe_2O_4 nanocrystals can be tuned to cubic during the seed-mediated growth process. Growth reaction parameters such as heating rate, temperature, reaction time, ratio of seed to precursors, and ratio of oleic acid to oleylamine have been systematically studied for the control of size and shape of nanocrystals. The results indicated that heating rate and growth temperature control the shape of CoFe_2O_4 nanocrystals. Using the same 5 nm spherical seeds and the same growth solution as for the preparation of 8 or 9 nm spherical nanocrystals, cubic CoFe_2O_4 nanocrystals were produced with an edge length of 8 or 9 nm when the temperature was raised only to 210 °C at a rate of 2–3°/min. The product was mainly monodisperse nanocubes (Figure 1c). A very tiny fraction of the product consisted of ~5 nm spherical nanocrystals, which can be easily separated from the cubes through addition of acetone into the hexane suspension. By using 8 nm spherical seeds, nanocubes with an edge length of 10 or 11 nm have been produced (Figure 1d).

Due to the decisive effect of heating rate and growth temperature on shape control, Figure 1e shows almost spherical monodisperse CoFe_2O_4 nanocrystals with a 12 nm diameter, which were prepared by using nanocube seeds with an 8 nm edge length. Such a reversible shape formation clearly demonstrated that the shape of CoFe_2O_4 nanocrystals can be precisely controlled through the temperature and heating rate. The quality of spherical and cubic nanocrystals is very high. Figure 1f displays a histogram from TEM studies showing a narrow size distribution of nanocubes with an almost uniform shape. The inset shows more than 80% of the nanocubes having an aspect ratio between 1 and 1.05. Both spherical and cubic CoFe_2O_4 nanocrystals are single crystals as high-resolution TEM (HRTEM) studies have shown (Figure 2). Figures 2b and 2c show an interesting short range order in the nanocube assembly.

The nanocrystal growth rate is the key in shape control. The precursor molecules had a decomposition temperature around 190 °C. As a surfactant, oleic acid stabilized the nanocrystals. Oleylamine was used to provide a basic condition essential for the formation of spinel oxides. The long chain alcohol also was essential in nucleation and growth processes since it probably made ferrous cations available, which peculiarly always facilitated the formation of CoFe_2O_4 nanocrystals.^{15–17} A slow heating rate kept a low concentration of available metal cations from the decomposition of precursors, which combined with the low growth temperature gave a slow rate in crystal growth. The growth of cubic CoFe_2O_4 nanocrystals was terminated at {100} planes (Figure 2d), which were predicted to have the lowest surface energy.^{18,19} When a much faster heating rate was employed, a high concentration of metal cations was present. A faster growth rate at a higher temperature with plenty of metal cations available resulted in the crystal growth much less

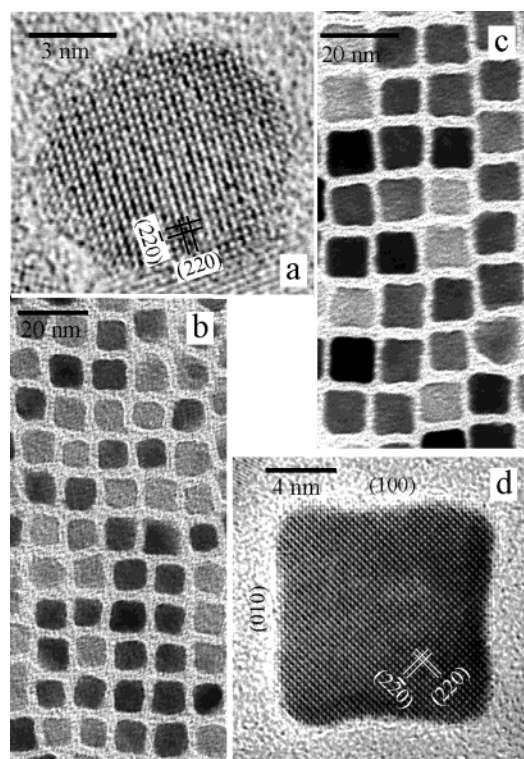


Figure 2. HRTEM micrographs. Panel (a) is a ~8 nm spherical CoFe_2O_4 nanocrystal. Panels (b) and (c) display the short-range order in ~9 and ~11 nm nanocube assemblies. Panel (d) shows a ~12 nm cubic CoFe_2O_4 nanocrystal. The spacing of atomic lattice plane (220) in panels (a) and (d) is 2.994 Å, and the zone-axis is [001].

selective in directions and hence produced spherical CoFe_2O_4 nanocrystals.

The magnetic properties of CoFe_2O_4 nanocrystals with different shapes can provide great insights to the fundamentals in nanomagnetism. Figure 3a shows the zero-field-cooling (ZFC) magnetization curves of spherical and cubic nanocrystals. Clearly, the blocking temperature T_B increases with increasing volume of nanocrystals and falls into the same line for both shapes of nanocrystals (Figure 3b). The field dependences of magnetization for spherical and cubic nanocrystals are presented in Figure 4. Although the saturation magnetization (M_S) and remanent magnetization (M_R) show volume dependences in both shapes, the spherical or cubic shape of nanocrystals does not make a difference (Figure 5a). As the volume increases, the coercivity (H_C) displays almost the same trend for spherical and cubic nanocrystals. However, the coercivity of nanocubes is drastically lower than the spheres having the same volume (Figure 5b).

The correlation between blocking temperature and the volume of nanocrystals is well consistent with the Stoner–Wohlfarth theory,^{20,21} which expresses that the magnetocrystalline anisotropy (E_A) of a nanocrystal is proportional to its volume (V) as

$$E_A = KV \sin^2 \theta \quad (1)$$

where K is an anisotropy constant and θ is the angle between the easy axis and magnetization direction. Magnetic anisotropy (E_A) serves as an energy barrier for blocking the superpara-

(15) The synthesis of CoFe_2O_4 nanocrystals using normal micelle method requires starting reagent of a ferrous salt as ref 16 describes in details. Ferrous cations are oxidized by oxygen during the synthesis process and give out ferric cations in the final product of CoFe_2O_4 nanocrystals, which has been confirmed by the display of a single sextet in Mössbauer spectrum as shown in ref 17.

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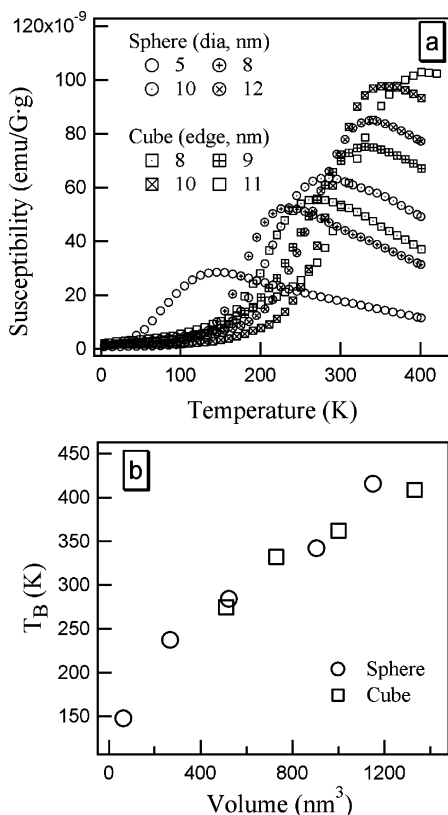


Figure 3. The temperature dependence of zero-field-cooling (ZFC) magnetization of spherical and cubic CoFe₂O₄ nanocrystals under 100 G applied field, panel (a). Panel (b) shows the volume dependence of blocking temperatures of spherical and cubic nanocrystals.

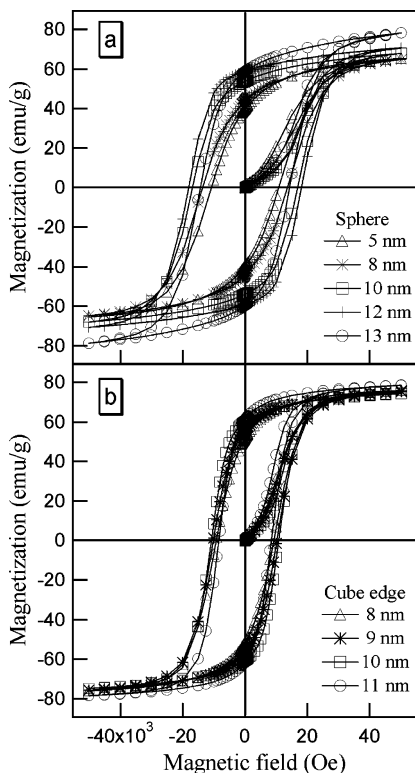


Figure 4. Magnetic hysteresis of spherical, panel (a), and cubic, panel (b), CoFe₂O₄ nanocrystals at 5 K.

magnetic relaxation of nanocrystals, and blocking temperature represents the temperature required to overcome this energy

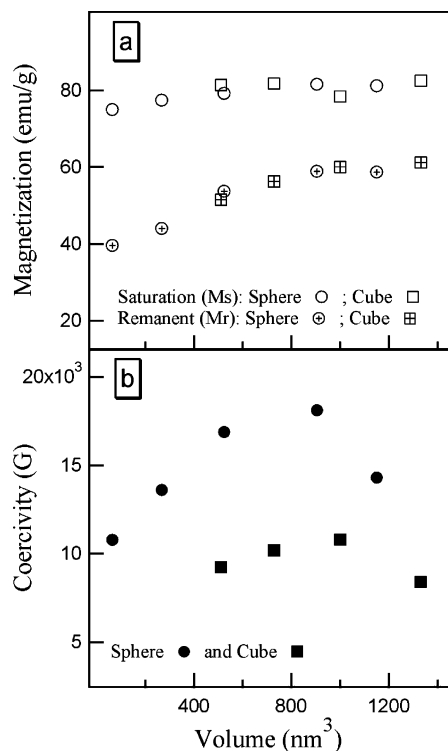


Figure 5. Panel (a) shows the saturation and remanent magnetization as a function of the volume of spherical and cubic nanocrystals. Panel (b) displays the volume-dependent coercivity of spherical and cubic nanocrystals.

barrier by thermal activation. Thus, blocking temperature increases as the volume of nanocrystals increases (Figure 3b).

The increase in coercivity initially with increasing volume has been considered due to the increase in magnetic anisotropy since an applied field at a given temperature should be able to overcome the energy barrier and change the orientation of magnetization. The eventual decrease in coercivity is usually attributed to a switch of magnetization process from coherent to curling. The coercivity of nanoparticles from Stoner–Wohlfarth theory is determined by anisotropy constant and saturation magnetization:

$$H_C = 2K/(\mu_0 M_S) \quad (2)$$

where μ_0 is a universal constant of permeability in free space. Judging from the blocking temperature and saturation magnetization studies, K and M_S essentially should be the same in equal volume spherical and cubic nanocrystals. Certainly, the dramatic difference in coercivity between the equal volume spherical and cubic nanocrystals strongly implies that this model alone cannot fully address the fundamental issues in magnetic hysteresis of nanocrystals.

Cubic morphology with an aspect ratio of almost 1 is magnetically quasi-isotropic, and hence, magnetic shape anisotropy should not have any influence in cubic nanocrystals. Coercivity has to be considered together with the surface pinning of magnetic moments and the resulting surface anisotropy.²² The surface magnetic disorder and pinning originate from missing coordinating oxygen atoms around surface metal cations. When the coordination of surface metal cations has a closer similarity to the coordination symmetry of the metal

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cations in the core of a nanocrystal, the surface anisotropy should be lower.²³ Compared to the curved topology of spherical nanocrystals, the flat surfaces of cubic nanocrystals enable the surface metal cations to possess a more symmetric coordination and fewer missing coordinating oxygen atoms. Therefore, the surface anisotropy should be much smaller in cubic nanocrystals than the one in spheres. Consequently, cubic nanocrystals show a much lower coercivity than the spherical nanocrystals having the same volume. Clearly, the surface anisotropy shows a dominance in determining the coercivity over the core anisotropy, which are proportional to the volume (Figure 5b).

The saturation and remnant magnetization have shown an increase with the increasing volume (Figure 5a). Such increases have usually been attributed to a decreasing proportion of the pinned surface magnetic moments in overall magnetization as the nanocrystals grow in size. The nanocrystals with different shapes have demonstrated the distinctly different coercivities that imply different surface pinning. However, the saturation and remanent magnetization display indifference toward the spherical or cubic shape of the nanocrystals. This inconsistency surely calls for systematic studies to specifically address the fundamental issues on such important properties as saturation and remanent magnetization. Furthermore, it would be important to know why surface anisotropy does not seem to affect the blocking temperature and what the fundamental difference is between thermally and magnetically overcoming the anisotropy energy barriers.

Conclusions

The nonhydrolytic synthesis has been developed to produce high-quality and monodisperse CoFe_2O_4 nanocrystals. The shape

of the nanocrystals is remarkably controllable through adjusting the crystal growth rate. This synthesis method is possibly applicable to the synthesis of different spinel ferrite and other metal oxide nanoparticles though the precursors may need to be chemically modified. A comparison of the magnetic properties possessed by spherical and cubic nanocrystals offers rich insights on the fundamentals of nanomagnetism. Addressing the interesting and important fundamental issues raised by these size and shape-dependent studies surely promises further advancement in the understanding and application of magnetism in the nanometer regime. Furthermore, the assembly of these cubic nanocrystals may result in a breakthrough toward using nanocrystals as one particle one bit magnetic media to achieve ultrahigh-density data storage. Instead of numerous possible crystallographic orientations for each nanocrystal and therefore completely disordered magnetization in a 2-D assembly of spheres, a cube would only have six possible crystallographic orientations in an assembly. If the magnetic anisotropy of the cubic material is cubic, all such six directions are magnetically identical, and hence the magnetically ordered assembly is greatly simplified.

Acknowledgment. We are grateful to Drs. Z. L. Wang, X. Y. Kong, and Y. Ding and Mr. P. X. Gao for their assistance in HRTEM studies. All TEM work was carried out at the Electron Microscopy Center at the Georgia Institute of Technology. This work was supported in part by NSF (DMR-9875892), Sandia National Laboratory, and the PECASE Program.

JA049931R

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