

Tailoring magnetic properties of core/shell nanoparticles

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Bimagnetic FePt/MFe₂O₄ (M=Fe, Co) core/shell nanoparticles are synthesized via high-temperature solution phase coating of 3.5 nm FePt core with MFe₂O₄ shell. The thickness of the shell is controlled from 0.5 to 3 nm. An assembly of the core/shell nanoparticles shows a smooth magnetization transition under an external field, indicating effective exchange coupling between the FePt core and the oxide shell. The coercivity of the FePt/Fe₃O₄ particles depends on the volume ratio of the hard and soft phases, consistent with previous theoretical predictions. These bimagnetic core/shell nanoparticles represent a class of nanostructured magnetic materials with their properties tunable by varying the chemical composition and thickness of the coating materials. © 2004 American Institute of Physics. [DOI: 10.1063/1.1776632]

Nanoscale magnetism has stimulated great interest due to its importance in mapping the scaling limits of magnetic information storage technology and understanding spin-dependent transport phenomena.^{1,2} Recent progress in the production of nearly monodisperse magnetic nanoparticles from metallic Fe, Co and Ni, to iron oxides, MFe₂O₄ and FePt and CoPt intermetallic compounds provides various systems suitable for nanomagnetic studies.^{3–6} An assembly of monodisperse magnetic nanoparticles with controlled interparticle spacing will allow detailed studies on magnetization, anisotropy, as well as magnetization reversal processes and interparticle interactions of the particles with different sizes and surface properties. An interesting magnetic nanoparticle system is that of core/shell structured nanoparticles in which the magnetic core is coated with a layer of a nonmagnetic, antiferromagnetic, or ferro/ferri-magnetic shell. A nonmagnetic coating is used routinely for magnetic core stabilization and surface functionalization for biomedical applications.⁷ An antiferromagnetic coating over a ferromagnetic core leads to exchange bias (a shift of the hysteresis loop along the field axis),⁸ and improvements in the thermal stability of the core.⁹ Compared with these two different types of core/shell systems, a bimagnetic core/shell one, where both core and shell are strongly magnetic (ferro- or ferri-magnetic) is less studied yet more interesting due to their potential in electromagnetic and permanent magnetic applications.^{10,11} In such a system, the intimate contact between the core and shell leads to effective exchange coupling and therefore cooperative magnetic switching, facilitating the fabrication of nanostructured magnetic materials with tunable properties.

Here we report magnetic properties of a bimagnetic core/shell nanoparticle system with ferromagnetic FePt core and thickness-tunable (0.5–3 nm), ferrimagnetic MFe₂O₄ (M=Fe, Co) shell. We observe a single-phase-like smooth variation of magnetization with field, indicating that the core

and the shell are effectively exchange coupled and magnetization of both core and shell reverses cooperatively. As a result, the magnetic properties, such as magnetization and coercivity, of these core/shell nanoparticles can be readily controlled by tuning the core/shell geometrical parameters and chemical compositions.

Monodisperse 3.5 nm FePt nanoparticles were synthesized by thermal decomposition of Fe(CO)₅ and polyol reduction of Pt(acac)₃ simultaneously as reported before.⁶ The iron oxide coating was achieved via mixing and heating the FePt nanoparticle seeds with Fe(acac)₃/polyol, or Co(acac)₂/Fe(acac)₃/polyol precursors as published elsewhere.¹² The structure of the nanoparticle assemblies was examined by transmission electron microscopy (TEM), electron diffraction, and x-ray diffraction (XRD). The magnetic properties were measured by a superconducting quantum interference device magnetometer.

Figures 1(a) and 1(b) show representative TEM images of the FePt/Fe₃O₄ and FePt/CoFe₂O₄ core/shell structured nanoparticles, respectively. The cores appear darker and shells lighter in the images due to the large difference in electron penetration efficiency on FePt and oxides. The FePt core has a diameter of 3.5 nm, the shell thicknesses are about 2 nm in both images. The shell thicknesses observed are quite uniform throughout the particles, with a standard deviation of about 10%. For FePt/Fe₃O₄ nanoparticles, the main phase of the shell composes Fe₃O₄ as it is obtained from the same chemistry used to make Fe₃O₄ particles previously,⁵ and its structure is confirmed by both XRD and high resolution TEM (HRTEM). Figure 2(a) is the HRTEM image of a single FePt/Fe₃O₄ particle. It reveals the crystalline shell with the distance between two lattice fringes matching with the lattice spacing of Fe₃O₄. The HRTEM also shows a partially coherent interface between the FePt core and the Fe₃O₄ shell, indicating possible epitaxial growth of the shell over core during the coating process. Figure 2(b) shows a typical electron diffraction pattern of FePt/Fe₃O₄ nanoparticles with 2 nm shell. Diffraction rings from both

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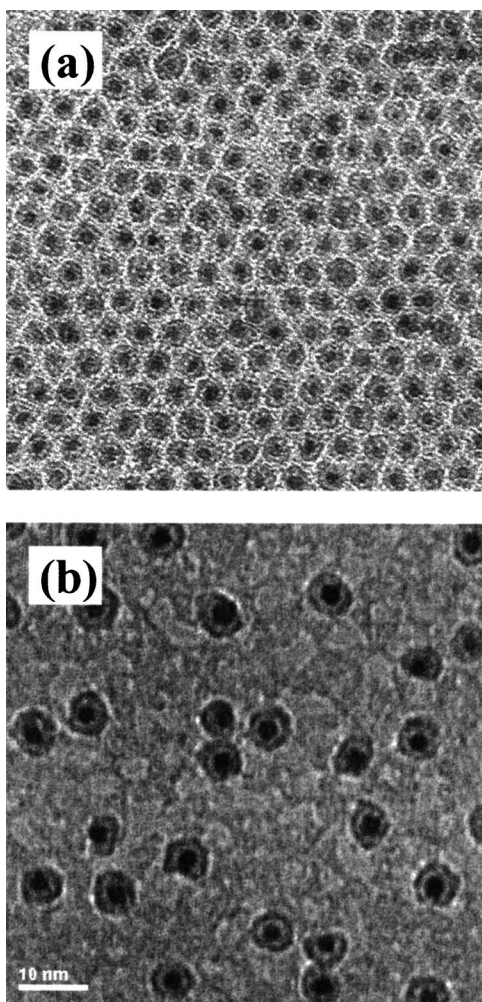


FIG. 1. TEM images of (a) FePt/Fe₃O₄ and (b) FePt/CoFe₂O₄ core/shell structured nanoparticle assembly with shell thickness of 2 nm.

disordered fcc FePt and spinel Fe₃O₄ phase can be clearly observed, as indexed in the figure.

Both FePt and Fe₃O₄ nanoparticles are ferromagnetic at 10 K. The coercivity for 3.5 nm FePt nanoparticles is 5.5 kOe, while that for 4 nm Fe₃O₄ is only 200 Oe. The large coercivity from disordered fcc FePt nanoparticles likely originates from a uniaxial surface anisotropy.^{13,14} The FePt/Fe₃O₄ core/shell nanoparticle is therefore a two-phase system consisting magnetically of a hard (FePt) and a soft (Fe₃O₄) phase. Figure 3(a) shows the 10 K hysteresis loop of the 3.5 nm FePt/1 nm Fe₃O₄ core/shell nanoparticle assembly. Despite consisting of both hard and soft phases, the hysteresis loop shows a single-phase-like behavior, with the magnetization changing with the applied field smoothly. The coercivity is determined to be 2.3 kOe, a value in between that of FePt and Fe₃O₄. This indicates that the intimate contact between the FePt core and Fe₃O₄ shell leads to an effective interphase exchange coupling, which results in cooperative magnetization switching of the two phases.

Earlier theoretical studies suggest that for hard and soft phases to reverse cooperatively in a hard-soft composite system, the critical dimension of the soft phase (*t_s*) should be less than twice the domain wall width (*δ_w*) of the hard phase.¹⁵ Using the measured 10 K *H_c* of the FePt nanoparticles as an approximation for the effective uniaxial anisotropy field, and *K_u* ~ *M_sH_K*, the effective anisotropy constant

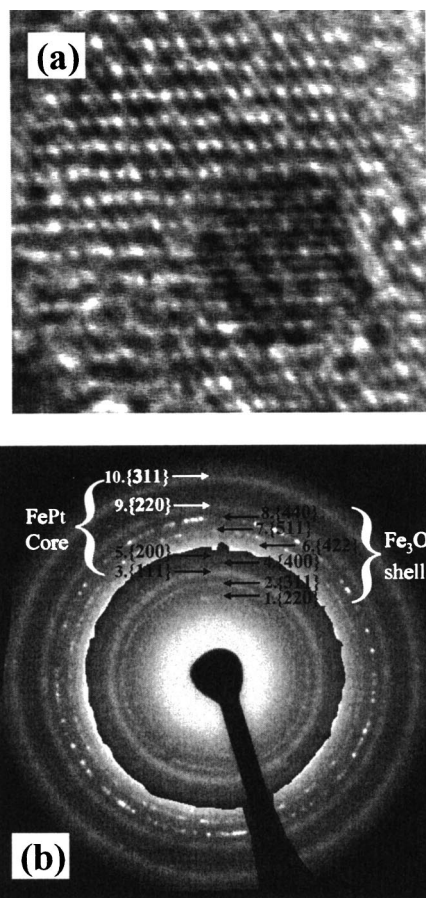


FIG. 2. (a) HRTEM image of a single FePt/Fe₃O₄ nanoparticle, and (b) electron diffraction pattern of an assembly of FePt/Fe₃O₄ nanoparticles.

K_u for the FePt nanoparticles is calculated to be on the order of 5×10^6 erg/cm³. Plugging this *K_u* value into $\delta_w \sim (A/K_u)^{1/2}$,¹⁶ where *A* is the exchange constant ($\sim 1 \times 10^{-6}$ erg/cm), we can estimate *δ_w* to be about 10 nm. The Fe₃O₄ shell in this study is less than 3 nm and well within

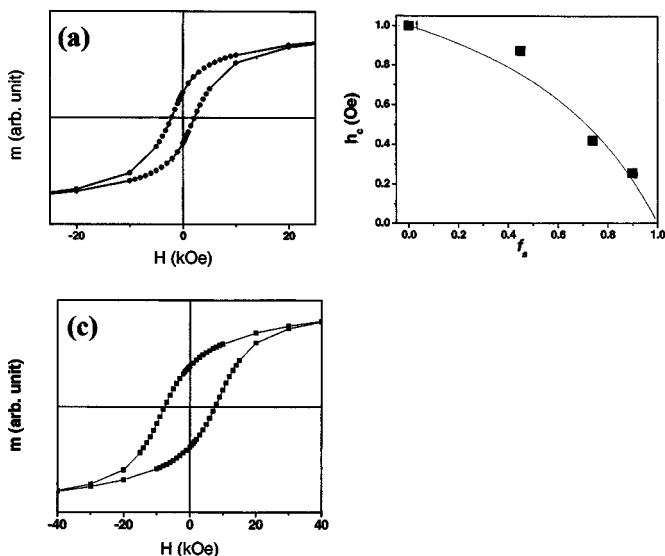


FIG. 3. (a) A typical magnetic hysteresis loop of an FePt/Fe₃O₄ nanoparticle assembly with shell thickness of 1 nm; (b) normalized coercivity *h_c* of FePt/Fe₃O₄ nanoparticles as a function of Fe₃O₄ volume fraction [the curve is calculated from Eq. (2), and dots are data points]; and (c) hysteresis loop of FePt/CoFe₂O₄ nanoparticles with CoFe₂O₄ shell thickness of 2 nm.

the limit $t_s \approx 2\delta_W$ of 20 nm. Hence, the switching of the hard and soft phase should indeed occur coherently, leading to a smooth magnetization transition.

The coercivity of the core/shell particles is observed to decrease with increasing shell thickness. According to Ref. 15, the coercivity of a hard-soft exchange-coupled system with collinear easy axis is

$$H_c = 2 \frac{K_H f_H + K_S f_S}{M_H f_H + M_S f_S}, \quad (1)$$

where K is the anisotropy constant, M the saturation magnetization, f the volume fraction, and the subscripts H and S denote the hard and soft phases, respectively. Equation (1) is only strictly valid for uniaxial anisotropy, with the easy axes of the hard and soft phases being collinear. Nevertheless, since K_H of 5×10^6 erg/cm³ is about 20 times larger than that of Fe₃O₄, we can ignore the term $K_S f_S$ in Eq. (1) for the thickness range we studied without introducing significant error. Based on this, Eq. (1) can be transformed into

$$h_c \approx \frac{1}{1 + \frac{M_S f_S}{M_H (1 - f_S)}}, \quad (2)$$

where h_c is the coercivity of the core/shell particles normalized by the coercivity H_{cH} of the hard phase ($h_c = H_c/H_{cH}$). If the above-presented analysis is correct, h_c should decrease monotonically with increasing volume fraction of the soft phase, following Eq. (2). Figure 3(b) plots h_c of the FePt/Fe₃O₄ nanoparticles as a function of f_s , in which the curve is calculated from Eq. (2) and dots are data points. We can see that they match each other reasonably well. This indicates that the coercivity of the FePt/Fe₃O₄ nanoparticles depends only on the volume ratio of core/shell, not on the actual size or thickness of the core and the shell, which is consistent with Ref. 15.

The situation of FePt/CoFe₂O₄ nanoparticles is different from that of FePt/Fe₃O₄. CoFe₂O₄ has much larger magnetocrystalline anisotropy than Fe₃O₄, and exhibits higher coercivity at low temperatures. Our study shows that at 10 K, the 8 nm CoFe₂O₄ nanoparticle assembly has an H_c of 12 kOe and the 18 nm one has H_c of 21 kOe. Compared to FePt/Fe₃O₄, the hard-soft phases in FePt/Fe₂CoO₄ core/

shell system are therefore reversed, with FePt being magnetically softer and CoFe₂O₄ harder. Figure 3(c) shows the 10 K hysteresis loop of FePt/Fe₂CoO₄ with 2 nm shell. It can be seen that the H_c increases from 5.5 kOe for FePt to 8 kOe, as expected for such an exchange-coupled system. Since the anisotropy of the hard and soft phase in this system is rather close, Eq. (2) cannot be used to describe such systems.¹⁷

In conclusion, a class of bimagnetic core/shell nanoparticles can be readily synthesized via solution phase chemistry. Magnetic properties of these core/shell nanoparticles can be tailored by controlling the core/shell dimensions, and by tuning the material parameters of both core and shell. Such systems may show interesting nanomagnetism emerging from the exchange-coupling between the core and the shell, and may yield finely tailored materials for various nanomagnetic applications.

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