Synthesis of high-coercivity cobalt ferrite particles using water-in-oil microemulsions

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Abstract

Magnetic nanoparticles of cobalt ferrite ($CoFe_2O_4$) have been synthesized using water-in-oil microemulsions consisting of water, cetyl trimethyl ammonium bromide (surfactant), n-butanol (cosurfactant), and n-octane (oil). Precursor hydroxides were precipitated in the aqueous cores of water-in-oil microemulsions and these were then separated and calcined to give the magnetic oxide. X-ray diffraction confirmed the formation of phase pure cobalt ferrite. These nanoparticles were less than 50 nm in size and had a high intrinsic coercivity (1440 Oe) and saturation magnetization (65 emu/g).

Keywords: Cobalt ferrite; Nanoparticles; Microemulsion; Magnetic particles; Coercivity; Remanence

1. Introduction

Nanometer-sized magnetic particles are the subject of intense research because of their potential applications in high-density magnetic recording and as constituents of magnetic fluids [1]. Since the 1940s, with the sudden growth in popularity of magnetic recording, γ-Fe_2O_3 in the form of small single-domain particles has dominated the magnetic storage materials technology [2]. γ-Fe_2O_3 particles currently used in recording media have typical coercivities of 300–400 Oe and saturation magnetization densities of about 350 emu/cm^3 of the coating. These properties, along with their great physical and chemical stability, make γ-Fe_2O_3 particles suitable for magnetic recording applications that do not require high recording densities [2,3].

However, pure iron oxides, due to their low coercivities, have a serious limitation for high-density recording applications [3]. The coercivities of iron oxides can be raised to well above 1000 Oe, while retaining their practical benefits (like good chemical and physical stability) by modifying them with cobalt. Cobalt-modified oxide particles are the predominant magnetic material used in video tapes today, but they are also used in audio tapes and in some tapes and disks for high-density digital recording. These uses make cobalt-modified oxides the most commercially significant particulate recording material today [2,3].

Cobalt modification was initially done by uniformly doping iron oxides with Co^{2+} ions to form cubic or acicular particles. These were basically cobalt ferrite ($CoFe_2O_4$) particles and had coercivi-

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ties greater than 1000 Oe [4]. This enhancement in coercivity takes place because the cobalt ions impart an increased magnetocrystalline anisotropy to the oxide structure (due to the coupling of the spins of the cobalt ions to the iron ions in the oxide structure). This results in particles with multiaxial anisotropy [3].

The magnetic characteristics of particles used for recording media depend crucially on their size and shape. These magnetic particles should be essentially single domain, i.e. all magnetic moments in the particle should be in one direction. For any magnetic material there exists a critical size, d_{SD}, below which it remains single domain. There also exists a characteristic size of the particle, d_{SP}, below which the material becomes superparamagnetic at the temperature of operation, i.e. no hysteresis, zero coercivity and zero remanence at the temperature of operation. Therefore, the size range over which a magnetic particle is useful in a storage medium is $d_{SP} < d < d_{SD}$ [5]. So, the material used for a high-quality recording medium should be ultrafine, chemically homogeneous, stable, with narrow particle size distribution and have a predetermined shape. These requirements demand a reliable and reproducible preparation technique.

The difficulty of obtaining uniform-sized nanoparticles of magnetic oxides stems from the fact that their preparations are mostly done in bulk aqueous media in which it is difficult to control nucleation and grain growth. Conventional techniques for the preparation of fine particles include bulk precipitation, sol–gel processing, spray-drying, freeze-drying, hot-spraying, evaporation–condensation, matrix isolation, laser-induced vapor phase reactions and aerosols [6–11]. Generally, in most types of fine particles prepared by these methods, it is usually not possible to control precisely the size and size distribution of the particles.

In order to try and overcome these difficulties, we have used constrained nanosize reactors such as the aqueous cores of water-in-oil microemulsions for the formation of microhomogeneous nanoparticles of magnetic oxides. In this paper, we report for the first time the synthesis of cobalt ferrite ($CoFe_2O_4$) nanoparticles by coprecipitating precursor hydroxides of Co^{2+} and Fe^{3+} (in the molar ratio 1:2) in water-in-oil microemulsions.

2. Microemulsions as nanoreactors

A microemulsion is generally defined as a thermodynamically stable, isotropic dispersion of two relatively immiscible liquids, consisting of microdomains of one or both liquids stabilized by an interfacial film of surface active molecules [12]. Microemulsions may be classified as water-in-oil (w/o) or oil-in-water (o/w) depending on the dispersed and continuous phases. In both cases, the dispersed phase consists of monodispersed droplets in the size range 10–100 nm [13].

Microemulsions have been shown to have a dynamic structure wherein the droplets of the dispersed phase are diffusing through the continuous phase and colliding with each other. These collisions are inelastic and have been termed 'sticky collisions', as the droplets coalesce and temporarily merge with each other but subsequently break to form separate droplets [14–18]. The average size and number of droplets remain the same as a function of time. This property of microemulsions is exploited for the synthesis of nanoparticles. For reactions in water-in-oil microemulsions involving reactant species totally confined within the dispersed water droplets, a necessary step prior to their chemical reaction is the exchange of reactants by the coalescence of two droplets. Conceptually, if one takes two identical water-in-oil microemulsions and dissolves reactants A and B, respectively, in the aqueous phases of these two microemulsions, upon mixing, due to collision and coalescence of the droplets, the reactants A and B come in contact and form AB precipitate. This precipitate is confined to the interior of the microemulsion droplets and the size and shape of the particle formed reflects the interior of the droplet. This is one of the principles utilized in the production of nanoparticles using microemulsions.

Synthesis of ultrafine particles using reactions in microemulsions was first reported by Boutonnet et al. [19], who obtained monodispersed metal particles (in the size range 3–5 nm) of Pt, Pd, Rh and Ir by reducing the corresponding salts in water pools of water-in-oil microemulsions with hydrazine or hydrogen gas (see also Ref. [20]). Microemulsions have also been used for the synthesis of magnetic nanoparticles of magnetite [21,22] and maghemite [23].

Recently, we have used microemulsions for the synthesis of high-coercivity barium ferrite for high-density perpendicular recording [24,25] and super-paramagnetic γ-Fe_2O_3 nanoparticles [26].

3. Experimental procedure

3.1. Materials

Ferric nitrate and cobalt nitrate ($> 99.99\%$ pure) were purchased from Aldrich. Ammonium hydroxide solution ($> 38\%$ NH_3); cetyl trimethyl ammonium bromide (CTAB) (technical grade); and n-butanol, methanol, and chloroform (all of HPLC grade) were purchased from Fisher Scientific. Octane ($> 97\%$ pure) was purchased from Phillips 66. All reagents were used without further purification. Water was deionized and distilled before use.

3.2. Methods

A microemulsion system with CTAB as the surfactant, n-butanol as the cosurfactant, n-octane as the oil phase and an aqueous solution as the water phase was chosen. This system has been shown to solubilize (dissolve into aqueous droplets) a large amount of aqueous phase in well-defined nanosize droplets [24].

Microemulsions were prepared by solubilizing different salt solutions into CTAB/n-butanol/n-octane solutions. Two microemulsions (I and II) with identical compositions (see Table 1) but different aqueous phases were taken. The aqueous phase in microemulsion I was a solution of 0.01 M cobalt (II) nitrate and 0.02 M ferric nitrate. The aqueous phase in microemulsion II was a solution of ammonium hydroxide, the precipitating agent, taken in a concentration 10% greater than that required stoichiometri-
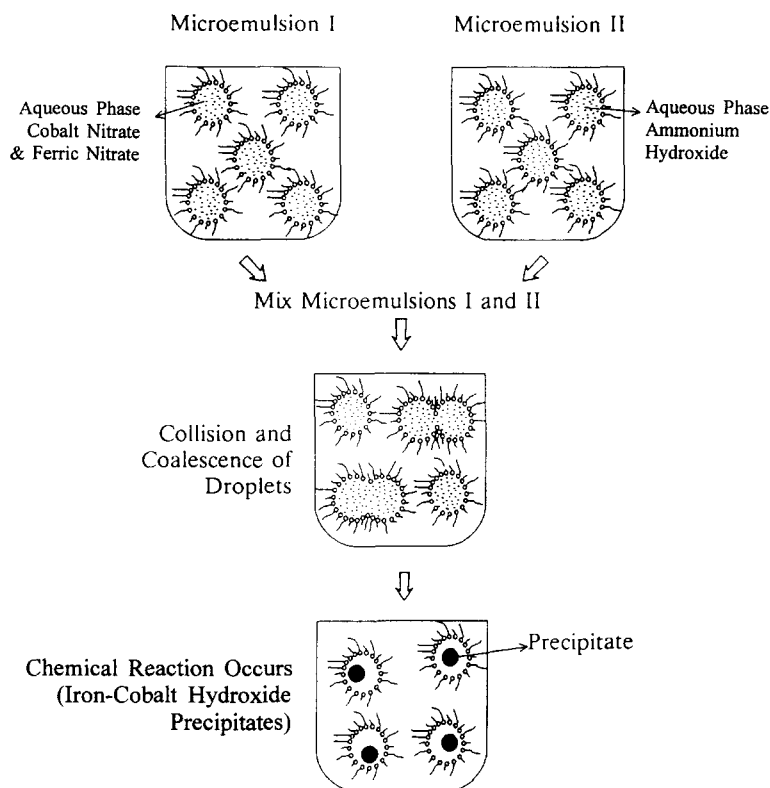

Fig. 1. Schematic representation of synthesis of cobalt ferrite precursors in water-in-oil microemulsions.

Table 1
Composition of the microemulsion system used for the synthesis reactions

	Microemulsion I	Microemulsion II	Weight fractions
Aqueous phase	0.01 M $Co(NO_3)_2$ + 0.02 M $Fe(NO_3)_3$	$(NH_4)OH$	0.34
Surfactant	CTAB	CTAB	0.12
Cosurfactant	n-butanol	n-butanol	0.10
Oil phase	n-octane	n-octane	0.44

cally for complete precipitation of the hydroxide. These two microemulsions were then mixed under constant stirring. Due to the frequent collisions of the aqueous cores of water-in-oil microemulsions [15,16], the reacting species in microemulsions I and II come into contact. This led to the precipitation of cobalt–iron hydroxide particles within the nanosize aqueous droplets of the microemulsion. Since the compositions of the two microemulsions (I and II) are identical, differing only in the nature of the aqueous phase, the microemulsion does not get destabilized upon mixing. The aqueous droplets act as constrained nanosize reactors for the precipitation reaction, as the surfactant monolayer provides a barrier restricting the growth of the hydroxide particles. This surfactant monolayer also hinders the coagulation of particles. A schematic representation of this process is shown in Fig. 1.

The cobalt–iron hydroxide precipitate synthesized in microemulsions was separated in a Sorvall RC-5B Superspeed centrifuge at 7000 rpm for 10 min. The precipitate was then washed with a 1:1 mixture of methanol and chloroform, followed by pure methanol to remove any oil and surfactant from the particles. The precipitate was then dried at 100°C. Sintering of particles is not expected at this temperature. The precursors were then calcined at 600°C for 5 h for complete conversion of the hydroxide into the magnetic ferrite ($CoFe_2O_4$).

Phase analysis of the calcined powder was done by powder X-ray diffraction on a Philips PW1700 powder diffractometer at room temperature using Cu $K\alpha$ radiation at 40 kV and 20 mA.

Transmission electron microscopy (TEM) was used to study the size and shape of the calcined particles. The calcined powder was ultrasonically dispersed in methanol prior to depositing it onto a carbon coated TEM grid. A JEOL 200CX transmission electron microscope was used for these studies.

Magnetization (M–H loop) measurements were done on an unoriented, random assembly of particles at room temperature on a vibrating sample magnetometer (LDJ 9600) with a maximum applied field of 5 kOe. The sample was prepared by hand pressing the calcined powder into a cylindrical pellet. No further heat treatments were done on the pellet.

4. Results and discussion

The X-ray diffractogram (see Fig. 2) of the calcined powder synthesized using microemulsions shows all the peaks for $CoFe_2O_4$ marked by their indices. No other peaks or impurities are detected. Therefore, X-ray diffraction confirmed the formation of phase pure cobalt ferrite ($CoFe_2O_4$).

TEM (Fig. 3) of the calcined particles showed agglomerates of particles less than 50 nm in size. Since these particles are smaller than the critical domain size (d_{SD}) for cobalt ferrite [2], all particles should be single domain in size. However, some particles may be smaller than the superparamagnetic limit (d_{SP}) at room temperature, but the high value of coercivity obtained for this material indicates that the number of such particles should be very few. These particles are not needle-shaped as expected for cobalt ferrite particles [2]. This is so because precursors synthesized (precipitated) in these microemulsions are typically spherical in shape, reflecting the shape of the microemulsion droplets in which they were formed, and in the size range of 5–20 nm [24–26]. It is evident that growth of particles has taken place during calcination to obtain cobalt ferrite, but this growth does not result in a change of shape from spherical to needle-shaped. This also shows that calcination time and temperature are important in controlling the size and growth of particles synthesized using microemulsions.
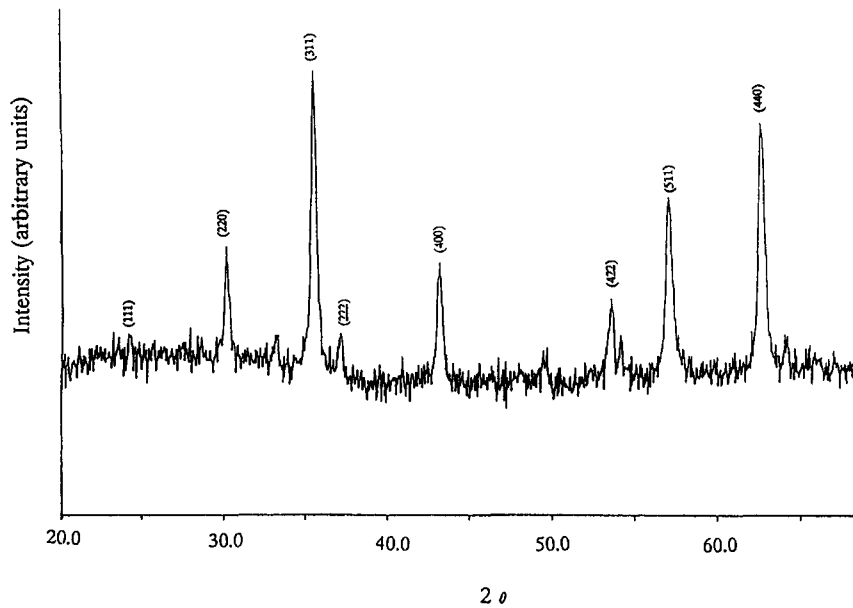
Fig. 2. X-ray diffractogram of cobalt ferrite particles synthesized using microemulsions.

Magnetic measurements were done at room temperature on a VSM with a peak field of 5 kOe (see Fig. 4 for the M–H loop). This yielded a saturation magnetization (M_s) of 65 emu/g, a remanent magnetization (M_r) of 29 emu/g and a high coercivity of 1440 Oe. This high coercivity value indicates that the particles formed are indeed single domain with no nonmagnetic impurities. The enhancement in coercivity due to the addition of cobalt arises from the increase in magnetocrystalline anisotropy imparted by cobalt to the oxide. However, for this reason,

cobalt-modified iron oxides also have stronger dependencies of the coercivity on temperature and stress than do pure iron oxides. To avoid these shortcomings, alternative methods have recently been used to enhance the coercivity of iron oxides. This was achieved by surface coating the iron oxide particles with cobalt, and it resulted in improved stability with respect to temperature and stress [3]. We are currently pursuing the synthesis of cobalt surface-modified iron oxide nanoparticles using microemulsions.
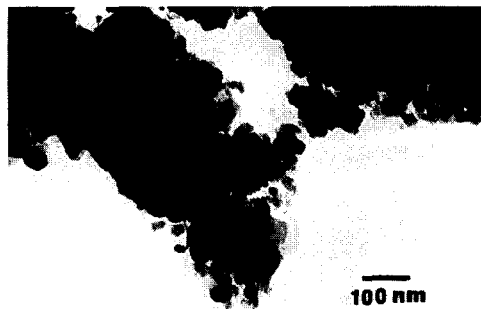

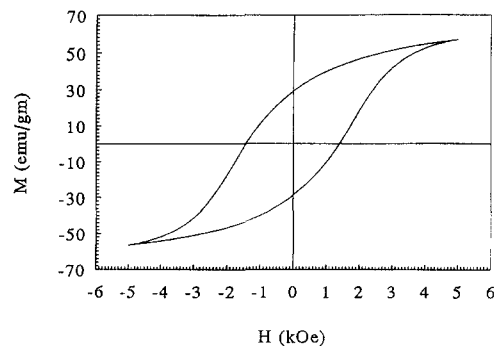Fig. 3. Transmission electron micrograph of cobalt ferrite particles synthesized using microemulsions.

Fig. 4. Magnetization loop for cobalt ferrite particles synthesized using microemulsions.

5. Conclusions

In this paper, we have presented a new technique for the synthesis of nanoparticles of cobalt-modified iron oxide ($CoFe_2O_4$) with high intrinsic coercivity. In this technique, the aqueous cores of water/CTAB/n-butanol/octane microemulsions have been used for the precipitation of precursor hydroxides of Co^{2+} and Fe^{3+}. These hydroxides were then calcined to obtain the oxide. The formation of $CoFe_2O_4$ was confirmed by X-ray diffraction. TEM was used for particle size and shape analysis, while the magnetic properties were measured using a VSM at room temperature.

Acknowledgements

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