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The synthesis of spinel–ferrite nanoparticles using precipitation in microemulsions for ferrofluid applications

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Abstract

Magnetic maghemite nanoparticles with a narrow size distribution were prepared in water–CTAB–hexanol–butanol microemulsions. The particle size was controlled with the composition of the microemulsion (water-to-CTAB ratio) and the temperature during synthesis. The saturation magnetization of the nanoparticles depended mainly on their size, ranging from 22 emu/g for a particle size of 3.4 nm to 64 emu/g for a size of 15.3 nm.

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1. Introduction

For the preparation of magnetic fluids, superparamagnetic nanoparticles with a particle size of the order of 10 nm and with a narrow size distribution are needed [1].

The most exploited magnetic materials for the preparation of magnetic fluids are two magnetic iron oxides: magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3) [1]. Both oxides have basically a spinel structure and differ mainly in their content of Fe^{2+}. By co-precipitation of the Fe^{2+} and Fe^{3+} ions in the ratio of 1:2 in an inert environment, magnetite ($Fe^{2+}Fe_2^{3+}O_4$) is formed, which transforms with oxidation into maghemite ($Fe_2^{3+}O_3$) [2].

The synthesis of nanoparticles with co-precipitation is problematic because of a lack of control over the particle size and morphology. A possible solution to the problems of controlling the particle size and morphology during the synthesis of nanoparticles is to use a microemulsion method, which involves co-precipitation in water-in-oil microemulsions [3]. In this method, co-precipitation occurs in tiny droplets of water embedded with a surfactant, so-called reverse micelles, which are distributed in an oil phase. Water pools of reverse micelles act as microreactors for the synthesis of the particles, in which the particle size of the product is controlled by the size of these pools. The size of the reverse micelles is thermodynamically determined, in particular by the water-to-surfactant molar ratio and temperature [3]. Different preparation routes for the microemulsion-mediated synthesis of magnetite/maghemite nanoparticles have been reported [4–7]. In this study, nano-sized, superparamagnetic maghemite

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particles were prepared using synthesis in the water pools of reverse micelles in a microemulsion system consisting of hexanol as the oil phase, *n*-hexadecil trimethylammonium bromide (CTAB) as the surfactant, butanol as the co-surfactant and an aqueous solution of reactants as the water phase.

2. Experimental

To select a proper compositional range that would form a microemulsion in the water–CTAB–*n*-hexanol–-butanol system, the region of microemulsion stability was determined by the titration method [8] coupled with conductivity measurements. For the preparation of maghemite nanoparticles with a different particle size, three different microemulsion compositions were chosen. All microemulsions contained 15 wt% of hexanol and they all had the same ratio of surfactant (CTAB) to co-surfactant (butanol), equal to 60/40. However, they differed in the concentration of the aqueous solution. The contents of the aqueous solution in the microemulsions were 15 wt% (sample E15), 30 wt% (E30), and 45 wt% (E45). The microemulsion E45 had the composition very close to the aqueous-phase-rich border of the microemulsion stability region.

For the synthesis of the nanoparticles, two microemulsions of the same composition were heated to various temperatures (50, 70, 90 °C). Microemulsion A contained aqueous solutions of $FeSO_4$ (0.135 mol/l) and $Fe_2(SO_4)_3$ (0.113 mol/l), whereas Microemulsion B contained an aqueous solution of the precipitation agent tetramethyl ammonium hydroxide ($(CH_3)_4NOH$—TMAH) (0.5 mol/l). The nanoparticles were precipitated by admixing Microemulsion A into Microemulsion B in air. The quantity of the microemulsions was controlled in order to obtain a final pH value after precipitation of ~11.5. After the aging time of 1 h, allowed for the oxidation of the product in air, the microemulsion with product nanoparticles was mixed with a water/ethanol mixture and centrifuged. Finally, the product was washed with absolute ethanol and dried at 70 °C.

The synthesized nanoparticles were characterized by X-ray diffractometry (XRD) (Bruker AXS, D4 Endeavor) and transmission electron microscopy (TEM) (Jeol JEM 2000 FX). For the determination of Fe^{2+} content, the nanoparticles were dissolved in hot HCl under an inert atmosphere. The solution was then titrated with $K_2Cr_2O_7$ (an indicator was 0.2% aqueous solution of $C_{12}H_{10}NNaO_3S$). The magnetization of the nanoparticles was measured using a suscepto-magnetometer (Model DSM-8, Manics-67120). The temperature dependence of magnetization under zero-field cooling (ZFC) and field cooling (FC) at 10 Oe was measured from 4 to 250 K (Quantum Design SQUID).

3. Results and discussion

Fig. 1 shows the X-ray diffractograms of the synthesized nanoparticles. The diffractograms show only broad reflections, which can be ascribed to the cubic spinel cell. The two iron oxides, magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3), have basically the spinel structure. Thus, it is difficult to differentiate between these two oxides on the basis of XRD. However, the two magnetic iron oxides differ in terms of Fe^{2+} content. The chemical analyses of the synthesized nanoparticles

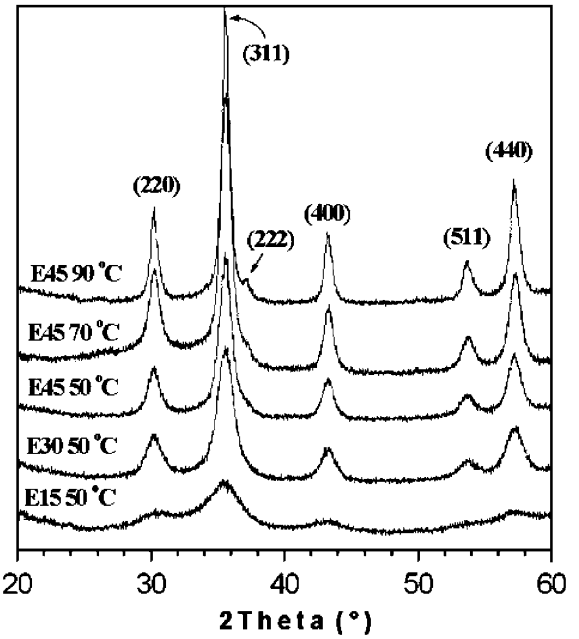

Fig. 1. XRD of synthesized samples.

Table 1
Size of nanoparticles (d_{XRD}—estimated from XRD, d_{TEM}—measured from TEM images) and saturation magnetization (σ_s) as a function of the temperature of synthesis (T) and the microemulsion composition expressed as a water-to-CTAB molar ratio (w)

Sample	w (/)	T (°C)	d^{*}_{XRD} (nm)	d^{**}_{TEM} (nm)	σ_s (emu/g)
		50	3.4	4.5 ± 1.1	22.3
E15	7.2	70	5.9	/	44.7
		90	9.0	/	53.6
		50	6.6	/	49.5
E30	18.4	70	10.4	/	51.2
		90	14.9	/	55.3
		50	9.0	8.1±1.9	60.0
E45	60.8	70	11.0	/	61.1
		90	15.3	13.0±3.2	64.1