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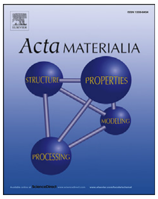

Full length article

How shape and internal structure affect the magnetic properties of anisometric magnetite nanoparticles

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A three-step aqueous approach to obtain large (>50 nm) magnetite single-core particles has been developed. The steps are a) synthesis of antiferromagnetic nanoparticles, b) particle coating and c) subsequent reduction of the core material to magnetite. By variation of precursor material and process conditions, the synthesis yielded rhombohedra, discs or needles below 200 nm. A combination of X-ray diffraction, ^{57}Fe Mössbauer spectroscopy and infrared spectroscopy confirmed magnetite to be the dominant final core material. From transmission electron microscopy, we identified porous structures after the reduction. Magnetic characterization of the different magnetic nanopaticles revealed strikingly different magnetic behaviour depending on their shape, internal structure and reduction process. We conclude that each of these parameters have to be considered in further characterization of large magnetite nanoparticles.

1. Introduction

In the last years, iron oxide magnetic nanoparticles (MNPs) have been widely used for biomedical applications. Examples of these applications include new ways of cancer treatment such as magnetic drug targeting [1] and magnetic hyperthermia [2], or the use of MNPs as contrast agents or tracers in Magnetic Resonance Imaging [3] and Magnetic Particle Imaging [4]. Each application requires MNPs with customized structural and magnetic properties, which are strongly dependent upon both particle size and shape [5]. As an example, ultra-small superparamagnetic MNPs with magnetic core sizes below 10 nm were suitable for the exploration of tumour permeability [6]. However, the uptake of MNPs by macrophages was most effective for MNPs with a core size of 10–30 nm, while for magnetic hyperthermia, maximum heating rate is obtained at the transition from multidomain to single domain magnetic behaviour occurring in a relatively broad size range at about 30 nm with a change of magnetic energy into thermal energy (Néel or Brown) [7]. Moreover, if collective magnetic behaviour of the cores exists, originated from interactions within a nanoparticle, heating rates can go up to one order of magnitude higher than for single-domain nanoparticles [8,9].

Nanoparticle shape can also have significant impact on the magnetic behaviour of MNPs in applications. Firstly, the magnetic shape anisotropy of the MNPs can assume much larger values than the magnetocrystalline anisotropy and thus can strongly affect the orientation of magnetic moments inside the particles. In addition, dipolar interactions between MNPs also depend on the particle shape and will influence the structural agglomerate formation leading to, for example, chain-like arrangements biomimicking magnetotactic bacteria [10] or hollow spheres consisting of oriented aggregates of nanocrystals [11,12].

One of the current challenges in nanoparticle research is the production of particles [13] comprising a large magnetite core that is well-controlled in size and shape, with a large magnetic moment and long term colloidal stability. Over the past decades, direct syntheses of magnetite NPs with different sizes and morphologies have been reported, including nano- spheres [13], cubes [14,15], wires [16], rods [17], octahedral [18], plates [19] and prisms [20].

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Synthesis of each of these shapes was performed out in organic media, so that, in general, nanocrystal shape control was achieved by selective adhesion of surfactant to a particular crystal facet and this subsequent slow growth along this direction. Without surfactants, nanoparticles can aggregate into dense or hollow micrometre spheres [11,12]. Synthesis in organic media is limited by the small particle batches that require further steps to be transferred to water, which results in low yields.

In the present paper, we describe an alternative aqueous-based approach to produce single-core magnetite MNPs with different morphologies and core sizes above 25 nm, which could be scalable for large production. Magnetic iron oxide nanorods were already produced by a similar method and showed interesting magnetic properties and tuneable surface functionality [21]. We propose a three-step process (Fig. 1) from which uniform rhombohedra, discs and elongated MNPs can easily be obtained. First, an aqueous synthesis route is followed to obtain uniform antiferromagnetic precursors such as goethite or hematite, whose size and shape can be tuned by changing the synthesis conditions including temperature, pressure, and nature and concentration of the salts used [22]. Then, the antiferromagnetic precursor particles are coated by a silica layer that prevents their aggregation [23,24]. Finally, the silica coated antiferromagnetic particles are reduced to magnetite. This is either performed on particles in powder form (dry-reduction), by exposing them to a hydrogen atmosphere at a certain partial pressure [25], or in liquid form, using oleic acid and an organic solvent (wet-reduction). In each process, the hydrogen and oleic acid act as the reducing agents [26,27]. Transformation of these antiferromagnetic phases into magnetite particles requires the full control of key parameters including temperature, atmosphere and pressure to produce pure single phases and avoid core sintering.

The products are physicochemically characterized by electron microscopy, X-ray diffraction, ^{57}Fe Mössbauer spectroscopy and infrared spectroscopy. Their magnetic behaviour is analysed by field and temperature dependent magnetization measurements. This characterization allows for comparing the products of dry reduction and wet reduction.

2. Experimental

2.1. Synthesis of the precursors

The preparation of uniform and nanometer precursor particles requires slight modifications of reported synthetic routes for hematite [26] and goethite [28] to obtain particle sizes below 200 nm and keep the uniformity.

(i) **Hematite:** The synthesis of hematite (α-Fe_2O_3) nano-sized rhombohedra and discs was carried out in a glass bottle dissolving $FeCl_3 \cdot 6H_2O$ in 50 mL of pure ethanol and 10 mL or 1 mL of water for rhombohedra or discs respectively under vigorous magnetic stirring. Then sodium acetate was added while magnetically stirring and the solution was homogenized by sonication for 10 min. The final solution had a concentration of $FeCl_3$ of 0.082 and 0.096 M for rhombohedra and discs, respectively. The concentration of sodium acetate was 0.49 and 0.58 M for rhombohedra and discs, respectively. The mixtures were sealed in a teflon-lined autoclave (125 mL) and maintained at 180 °C for 12 h for solvothermal crystallization. After natural cooling to ambient temperature, the resulting red solid product was washed with distilled water, filtered and finally dried overnight in an oven at 50 °C.

(ii) **Goethite:** The synthesis of goethite (α-FeOOH) nano-sized needles was performed by precipitation of a Fe(II) sulfate 0.15 M aqueous solution by the addition of a 0.225 M solution of sodium carbonate. The resulting dispersion was then oxidized at constant temperature. The concentration ratio of the reagents $[CO_3^{-}]/[Fe(II)]$ is 1.5. These processes were carried out according to the following procedure. Oxygen was first removed from the distilled water by N_2 bubbling to prevent Fe(II) oxidation during the dissolution of $FeSO_4$. The Fe(II) and sodium carbonate solutions 125 mL, each) were prepared with the desired concentrations. The sodium carbonate solution was then introduced into a thermostatic water bath at 44 °C under moderate stirring and the Fe(II) solution was added applying a constant air flow with a rate of 2 $Lmin^{-1}$ through the resulting suspension. Particles of goethite are then formed by aerial oxidation. After 180 min of reaction, the resulting precipitate was cooled, centrifuged and washed several times with distilled water. Finally, the powdered solid was collected by filtration and dried overnight at 50 °C.

2.2. Coating and reduction to magnetite

Silica coating and subsequent reduction of the precursor particles were carried out by optimizing procedures described elsewhere [25–27]. Silica coating ensures both, steric and electrostatic protection and it acts as dispersing agent of many electrostatic colloids. These advantages render silica an ideal, low-cost material to tailor surface properties. Additionally, this coating should endow the cores with several beneficial properties, such as the biocompatibility and the possibility of subsequent functionalization by connecting the silanol groups on the surface with other organic molecular agents [29].

For the silica coating, 100 mg of the precursor particles in powder form were dispersed in a 2-propanol/H_2O 2:1 v/v solution of 300 mL, NH_4OH 28% v/v and tetraethyl orthosilicate (TEOS) were added during sonication and the reaction was allowed to continue for 15 min. The final volume was 320.2 mL and the final concentration of the reagents was: $[NH_4OH] = 4.5 \times 10^{-4}$ M,

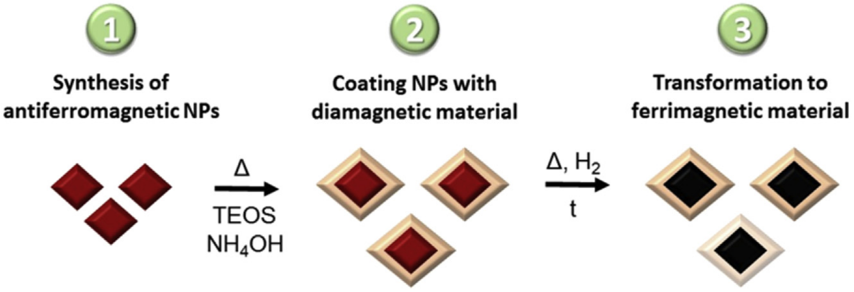

Fig. 1. General scheme for the synthesis of single-core MNPs.