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The influence of material properties on the assembly of ferrite nanoparticles into 3D structures

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HIGHLIGHTS

- Magnetically-directed assembly of ferrite nanoparticles into 3D structures.
- Strength of an applied field and particles size influence assemblies' morphology.
- Under an applied field of 0.5 T 20 nm-sized $CoFe_2O_4$ particles assemble into columns.
- The assembled columns displayed promising magnetic properties.
- The $CoFe_2O_4$ columns can be used for the preparation of 1–3 magneto-electric composites.

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ABSTRACT

The fabrication of patterned arrays consisting of magnetic nanoparticles is gaining more and more research activities due to the possibility of enhancing a material's properties for the use in various fields (i.e. magneto-electrics). Here we present the influence of the particle size, the magnetic interactions between the particles and the strength of the applied magnetic field on the magnetically-directed assembly of ferrite nanoparticles. The assemblies were prepared from cobalt ferrite and maghemite suspensions using the drop-deposition technique without or with applied magnetic fields of different strengths. The cobalt ferrite particles with diameter of 6, 8, 10, 12, 20 nm, and maghemite nanoparticles with a diameter of 14 nm were used. The particles' size influences their magnetic properties, the magnetic interactions between the particles and, consequently, the assemblies' morphology. At an applied magnetic field of 0.5 T the morphology of the assembled structures was gradually changing as the particles' size was increasing from flat films for the 6 nm-sized cobalt ferrite nanoparticles to ordered 3-dimensional structures with columnar shape for the 20 nm-sized cobalt ferrite and 14 nm-sized maghemite nanoparticles. The assembled 3-dimensional structures displayed promising magnetic properties and can be used as a basis for the preparation of magneto-electric composites.

1. Introduction

The focus of nanoscience and nanotechnology is increasingly shifting from the synthesis of individual components to their assembly into nanostructured materials and larger systems [1]. It is well known that nanoparticles often exhibit properties that differ from those of bulk samples of the same material. In the same way, nanoparticle assemblies can have properties that are different from those exhibited by individual nanoparticles or bulk samples. One of the reasons why the assembly of nanoparticles is being so intensively investigated [2–4] is the collective properties that an assembly of nanoparticles can display, i.e., improved optical (photonic crystals) [5] or magneto-electrical [6,7] properties for use in the fields of spintronics, magneto-electric or magneto-optic devices [6,8,9]. Furthermore, when assembling magnetic nanoparticles the exchange coupling between the surface atoms of the neighbouring particles can increase the energy product [10]. The use of external forces to control the assembly of particles from colloidal suspensions has enormous potential in the preparation of nanoparticle assemblies with different morphologies [2]. As an example, an assembly of magnetic nanoparticles under an applied magnetic field can be an easy and cost-effective way of preparing 3-dimensional structures, especially when compared with techniques like

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electron-beam lithography, focused-ion-beam irradiation etching and sputtering, X-ray interference lithography, UV lithography, laser-interference lithography, and other physical methods [3,8]. Therefore, a lot effort has been focused in this direction [3–5,11–15]. There are several reports on the formation of chains of ferrite nanoparticles when they are exposed to an external magnetic field. Wang et al. [14] reported on the formation of necklace-shaped chains of Ni-ferrite nanospheres with a width equal to one sphere and a length of a few microns, with the alignment parallel to the direction of the applied magnetic field. Similar to this, Sahoo [16] and co-workers observed the assembly of magnetite nanoparticles into elongated structures after being exposed to an applied magnetic field. The assembly of magnetite nanoparticles into higher structures was the topic of Ozdemir et al. [13]. They showed that the superparamagnetic magnetite nanoparticles assembled into columnar structures under an applied magnetic field when using a substrate template. Although the research on the assembly of magnetic nanoparticles is quite extensive, it is mainly limited to (super)paramagnetic nanoparticles. The aim of our work was to investigate the parameters that influence the magnetic-field-directed assembly of ferrite nanoparticles: ferrimagnetic cobalt ferrite and (for a comparison related to the magnetic interparticle interaction) also superparamagnetic maghemite. Cobalt ferrite is the only hard magnetic spinel ferrite and has the largest magnetostrictive coefficient among the oxide magnetic materials [17], as a result of which it is especially interesting as one of the constituent phases in magnetoelectric (ME) composites [9]. These ME composites can be, with respect to the distribution of the constituent phases (ferroelectric and ferro/ferrimagnetic), divided into three types. In the first one, also called the 0-3 composite, one of the phases is uniformly distributed in another one – the matrix phase. The second type is in the form of alternating layers (2-2 composites) of both materials, and the third type is the so-called, 1-3 composite, where the columns of one material (usually a ferromagnetic one) are embedded in a matrix of another material (usually ferroelectric) [6]. These 1-3-type composites were described as being the composites with the largest ME effect [18]. Therefore, an insight into the control of a magnetic nanoparticles assembly into 3-dimensional columnar structures can be an important step towards a simple and cost-effective way to prepare the first phase of 1–3 ME composites. This was also the focus of our work.

2. Materials and methods

Cobalt ferrite (CoF) nanoparticles with the composition $CoFe_2O_4$ were synthesized using the hydrothermal method [19]. Aqueous solutions of metal ions (0.1 mol/L Co^{2+}, 0.2 mol/L Fe^{3+}) were prepared from cobalt (II) sulphate heptahydrate ($CoSO_4{\cdot}7H_2O$, Alfa Aesar, 98%) and iron (III) sulphate hydrate ($Fe_2(SO_4)_3{\cdot}xH_2O$, Alfa Aesar, 99+%) salts. To the aqueous solution of Co^{2+} and Fe^{3+}, in a stoichiometric ratio, the sodium hydroxide (NaOH, Alfa Aesar, 98%) aqueous solution ($c = 5$ mol/L) was added at room temperature so that the mixture's pH was 13. The mixture was then put into a Teflon-lined, stainless-steel autoclave and kept at 120 °C for 5, 10, 30 and 120 min, and at 200 °C for 120 min. Maghemite, γ-Fe_2O_3, nanoparticles (MN) were precipitated from an aqueous solution of $FeSO_4$ (0.027 mol/L) and $Fe_2(SO_4)_3$ (0.0115 mol/L) with a concentrated ammonia solution (25%) in a two-step process [20]. In the first step, the pH value of the solution was raised to pH = 3 and maintained at a constant value for 30 min to precipitate the iron hydroxides. In the second step, the pH value was further increased to pH = 11.6. In this step the iron (II) hydroxide was oxidized by oxygen from the air, forming a spinel product.

The as-synthesized nanoparticles of both materials were stabilized with citric acid in water at a pH of 10.1. For the investigation of the influence of the particle size on the assembly, CoF suspensions with a concentration of 10 g/L were used. In order to investigate the influence of the suspension concentration, suspensions of CoF nanoparticles synthesized at 200 °C were prepared with different contents of solid phase – 10, 20 and 30 g/L (Table 1). Ten drops of suspension were deposited on an Al_2O_3 substrate positioned between two permanent magnets and dried under an applied magnetic field of 0.03, 0.5 T (Fig. 1) or without an applied magnetic field under ambient conditions. In order to inspect the influence of the magnetic interactions on the assembly of magnetic nanoparticles, a water-based maghemite suspension with a concentration of 10 g/L was used. All reagents were used as received, without any further purification.

The CoF nanoparticles were investigated with transmission electron microscopy (TEM, Jeol 2100) and with energy-dispersive X-ray spectroscopy (EDXS), while the particles' equivalent diameters were determined with the program Gatan (Digital Micrograph (TM) 1.70.16). The crystal structure of the as-synthesized CoF was analysed by X-ray powder diffraction (XRD; Siemens D5000 with the Cu-Kα radiation and EVA software (Bruker AXS)). The measuring step was 0.02°/s with 4 s of measuring time per step. The crystallite size was determined from the X-ray diffractograms with the Pawley method [21] using the crystallographic program Topas2R 2000 (Bruker AXS). The stability of the suspensions was evaluated from their zeta (ζ) potential, which was measured in the single-point mode with a ZetaProbe Analyzer. The room-temperature magnetic properties of the nanopowders, suspensions and deposits were measured with a vibrating-sample magnetometer (VSM, Lake Shore, 7404). The morphology of the deposits was investigated with a scanning electron microscope (SEM, Jeol 7600).

2.1. Theoretical model

There have been several models [22–27] developed to explain the experimental observations of the changes in magnetic fluids when they are exposed to (strong) magnetic fields. Satoh et al. in their work [23–25] state that nanoparticles in a magnetic fluid under an applied magnetic field first form clusters, which later aggregate into chain-like structures. They discussed the aggregation of chain-like structures into 2- or 3-dimensional thick structures by means of Monte Carlo simulations. Another model for the formation of chains is based on the assembly of individual magnetic nanoparticles under an applied magnetic field and was described by Rosensweig [27]. He anticipated the formation of chains and their lengths based on the magnetic interactions between the particles in a magnetic fluid. When an external magnetic field is applied, the particles' magnetic moments tend to align with the direction of the applied field. Each magnetic nanoparticle behaves

Table 1
CoF and MN suspensions and their properties.

Sample	Synthesis conditions	d (nm)	Suspension concentration (g/L)	ζ–potential (mV)
CoF1	120 °C, 5 min	6 (±2)	10	−63
CoF2	120 °C, 10 min	8 (±3)	10	−66
CoF3	120 °C, 30 min	10(±2)	10	−62
CoF4	120 °C, 120 min	12(±3)	10	−68
CoF5-1	200 °C, 120 min	20(±4)	10	−49
CoF5-2	200 °C, 120 min	20(±4)	20	−43
CoF5-3	200 °C, 120 min	20(±4)	30	−45
MN	co-precipitation	14(±3)	10	−40