Surface functionalized magnetic nanoparticles as switchable building blocks for soft nanotechnology

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ABSTRACT

α-Fe₂O₃ (hematite) particles can be synthesized by forced hydrolysis of iron salts. Playing with physical and chemical means allows the control of size and shape of the obtained ferromagnetic particles. Here we will summarize our recent work on the synthesis of hematite cubes and spindle type particles, which can be obtained with large aspect ratios such as 7. These particles can then be coated with a silica layer, allowing the creation of a specific surface functionality for their incorporation in polymer matrices or simply for their stabilization in a given solvent. We demonstrate that a moderate magnetic field (2-12 mT) is sufficient to orient our particles, and how we can use them as nanoprobes to investigate local rheological properties of complex fluids.

Keywords: α-Fe₂O₃, spindle particles, cubic particles, active micro rheology, nanocomposite.

1 INTRODUCTION

Hematite particles have gained interest in the last years as interesting magnetic nanoparticle model systems. This is due to the existing possibilities to tailor their shape and size by playing with various physical and chemical means such as the precursor concentration [1] and type [2], the variation of the reaction time [3, 4], the pH [5], the temperature, or the ionic strength [5, 6]. More recently, we demonstrated that the intermediate crystalline structure (akaganeite) formed during the synthesis of hematite can also be used as a starting point to control the monocrystallinity of the subsequently obtained particles [7].

Depending on the solvent or the medium in which the particles have to be dispersed, the particle-particle and particle-medium interactions play an important role in any attempt to avoid aggregation. This is particularly important when using hematite particles as magnetic building blocks for nanocomposites or as tracer particles in more complex environments. Here we demonstrate how one can coat hematite particles with a silica layer as a convenient basis for further surface modifications through an additional silane coupling agent [8]. The method used follows the general scheme proposed by Graf et. al. [9]. It consists in adsorbing a non-ionic amphiphilic polymer polyvinylpyrrolidone (PVP) on the surface of our colloidal particles. A modified Stöber approach [10] then leads to a homogeneous coating with a silica layer of controlled thickness. Subsequent additional synthesis steps then allow us to prepare magnetic core-shell particles with a specific surface functionalization that can then be used in various applications.

Here we concentrate in particular on microrheological applications of these particles. Microrheology uses the fact that the motion of colloidal tracer particles in a complex medium reflects the underlying rheological properties of the suspending matrix. Most studies published so far have primarily concentrated on passive microrheology, where particle tracking or diffusing wave spectroscopy combined with the application of a generalized Stokes-Einstein relation has been used to measure the viscoelastic properties of complex fluids [11, 12]. Very few groups have extended the microrheology approach to active measurements where tracer particles are moved via optical tweezers or other external fields through a complex fluid [13]. While such experiments are much more demanding experimentally and theoretically, they also offer in principle an extension of microrheology to the non-linear regime that is not accessible for classical microrheology based on thermal fluctuations only.

Here, we focus on two aspects of our hematite-based nanoparticle research. We first describe the synthesis of functionalized hematite particles with controlled shape and size. We then describe the lay-out of a simple set-up based on [14] that allows us to control the orientation of the hematite nanoparticles in a medium. This then allows us for example to create interesting nanocomposite systems with magnetic properties via in-situ polymerization. However, in this presentation we will primarily focus on a demonstration of the feasibility of active microrheology experiments where we use the magnetic nanoparticles as a nanorheometer.

2 EXPERIMENTAL SECTION

2.1 Materials and methods

Spindle shaped hematite particles were synthesized using iron (III) perchlorate (Alfa Aesar) or iron III chloride (Sigma-Aldrich), urea (Fluka) and NaH₂PO₄, 2H₂O (Fluka). For the coating of spindle hematite with silica, Tetraethyloxysilicate (TEOS), Tetramethyldimethylammonium-hydroxide (TMAH, 25% in methanol), and ethanol were purchased by VWR, Polyvinylpyrrolidone (PVP 90K,
Sigma-Aldrich) is dissolved in ethanol before being added to the particle to be coated. All chemicals were used without further purification. MilliQ water (Resistivity-18.2 MΩ·cm) was used to for the synthesis.

Carbon TEM grids (300 Mesh) were prepared 4 hours before the measurement; we typically dry one droplet of colloidal solution (~1%) at ambient temperature on the grid and store it in a dust free box.

### 2.2 Synthesis of hematite particles with controlled size, aspect ratio and surface functionality.

Here, we present as an example, the synthesis of spindle type hematite with an aspect ratio of 7 and its silica coating for surface functionalization.

Spindle hematite cores used for the coating were synthesized using forced hydrolysis of iron perchlorate precursor in the presence of urea and phosphate salt based on Ocana’s method [2]. In a typical reaction 115.5g of iron perchlorate are dissolved with 1.62g phosphate salt and 15g of urea in 2.5L of MilliQ water into a tightly closed glass bottle. The solution is kept for 24 hours in an oven at 98°C. After cooling, the so-obtained solution is centrifuged and repeatedly washed with water.

The thus-obtained spindle type hematite particles are then coated with silica based on Graf’s method [9]. In a typical reaction, 4 g of PVP are dissolved in 60 mL of MilliQ water using mechanical stirring and ultrasonication. 222 mg spindle hematite particles are then added to this polymer solution. The solution is stirred for 24 hrs at ambient temperature. The dispersion is repeatedly centrifuged to wash the particles from the non adsorbed polymer. Hematites with adsorbed PVP are then finally dispersed into 210g of ethanol in which 27 g H2O and 150 mg of 25% tetramethylammoniumhydroxide (TMAH) in methanol are added. A mixture of 9 ml TEOS and 6 ml of ethanol are injected into the stirred particle suspension. This coating step can be repeated and permits a perfect control of the thickness of the silica shell combined with a decreasing aspect ratio of the initial spindle form which becomes ellipsoidal.

### 2.3 Cross polarizer set-up

A temperature controlled sample holder is located between two pairs of Helmholz coils as shown in the cartoon on figure 1. Two sinusoidal currents with phase shift of 90° drive the coils and create a magnetic field with constant amplitude that rotates in the plane perpendicular to the optical axis with a variable rotation frequency. The subsequent orientation of the magnetic particles is probed with a laser beam in cross polarization geometry. This design allows us to determine the phase lag $\alpha$ of the particles when compared to the driving magnetic field as function of the frequency.

![Figure 1: Helmholz coil set-up that allows to create a rotating external magnetic field and probe the induced orientation of the magnetic nanoparticles using a combination of crossed polarizers and a photodiode.](image)

### 3 RESULTS AND DISCUSSION

#### 3.1 Functionalized core-shell hematite particles: Overview and characterization

The combination of hematite-based nanoparticles with a subsequent silica coating provides us with a series of building blocks that offer the possibility to create functionalized magnetic nanoparticles with a wide range of different architectures and properties. Figure 2 presents a schematic overview of the degree of complexity that is accessible with this system. Depending upon the choice of the synthesis parameters, we can tailor the particle size, the degree of anisotropy as well as create core-shell particles with an internal structure provided by several layers and subsequent surface functionalization. This is also demonstrated by electron microscope images of hematite particles illustrating the range of sizes, aspect ratios and functionalities which can be obtained from the different synthesis pathways of hematite.

![Figure 2: TEM and SEM images of hematite particles (a) with an aspect ratio of 7, coated with 25nm (b), 55nm (c) and 95nm (d) of silica.](image)
The enormous variability in size offered by the system is shown with the example of isotropic magnetic hematite particles. As illustrated by the different electron micrographs, we can create single crystal cubes [7], round shaped or pseudocubical magnetic particles with sizes ranging from 80nm to 600nm. These different systems can be obtained through a variation of the iron III chloride concentration from 0.01M to 0.06M in water. Three different mechanisms of formation were reported in the past [7, 15].

We are not restricted to cubic or globular shape, but can create rod-like shapes with a varying degree of particle anisotropy with axial ratios between 1 and 7. This can be achieved through a variation of the concentration of NaH2PO4 used. The largest aspect ratio obtained is 7, which is the synthesis example described in the experimental section.

Finally, surface functionality can then be obtained using a core-shell structure where surfactants, adsorbed polymers or a layer of silica are attached to the hematite particles. The size of the silica layer can conveniently be controlled and allows for a further surface modification through more than 2000 silane coupling agents [16]. In figure 2, we illustrate this with two examples of silica-coated spindle type hematite and hematite-silica-polystyrene core-shell particles, respectively.

The size, shape and internal structure of the colloidal particles can be characterized in detail and on a large range of different length scales using a combination of electron microscopy (SEM and TEM) and small-angle x-ray scattering (SAXS). Figure 3 shows the characteristic pattern evolution observed as we increase the size of the silica layer on the hematite spindle cores.

3.2 Hematite-(silica) nanomagnets and their applications

The small permanent magnetic moment of the hematite particles provides us with a number of different opportunities where we can use an external magnetic field to either induce an orientation of the particles and thus create a nanostructured material with anisotropic magnetic, mechanical or optical properties, or use the particles as a "nanorheometer" to locally probe the viscoelastic properties of a complex fluid. The feasibility of the latter application is demonstrated in Figure 4. Here we use the Helmholz coil set-up described in Figure 1 in order to orient and turn the particles at different rotation frequencies f and magnetic field strength B and measure their orientation. Figure 4 then shows the phase lag expressed by the phase angle $\alpha$ between the driving field and the orientation of uncoated hematite particles as a function of B and f, where B varies between 2mT and 6mT. Figure 4 demonstrates that for the simple fluid chosen the phase lag $\sin \alpha$ is inversely proportional to the strength of the applied field and increases linearly with a rescaled frequency $f/B$. A full analysis of the particle dynamics in the external driving field then shows that we can relate the relationship between phase lag and magnetic torque generated to the frequency-dependent viscoelastic properties of the suspending medium.

![Figure 3: Small Angle X-Ray Scattering (SAXS) data and EM pictures obtained from (a) bare hematite cores; and core-shell structures coated with (b) 25nm, (c) 55nm and (d) 95nm of silica.](image)

![Figure 4: Phase lag between external magnetic field and induced particle orientation as a function of the magnetic field rotation frequency scaled by the applied magnetic field strength.](image)

4 CONCLUSIONS

Hematite nanoparticles represent a very interesting model system that provides us with full control of the final size, shape and internal structure through a series of synthesis, coating and functionalization steps. The final coating step with a functional layer based on silica and silane coupling agents then allows us to disperse the particles in virtually any medium which can be either a simple liquid or a polymer solution or melt. Due to their...
magnetic properties with a weak permanent magnetic moment we can orient the particles using an external field but avoid aggregation or chaining usually observed in ferrofluids based on magnetic particles with stronger moments. This provides us with a wealth of interesting applications where we either explore their magnetic properties to create anisotropic materials with tunable properties or use them to investigate the viscoelastic properties of the suspending medium.

REFERENCES
[16] Silane agent can be purchased on www.abcr.de