

Iron Oxide-Based Multi-Compartment Colloids with Complex Structures

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Abstract

This dissertation deals with the synthesis and characterization of iron oxide-based multi-compartment colloids combining the chemical and physical properties of inorganic nanoparticles with different polymers. All colloids are synthesized in solution by template-free bottom-up approaches.

In the first part an insight into the intrigued world of hematite nanoparticles is given. During the synthesis in aqueous solution the morphology can be adjusted to range from spherical to spindle-type shapes. Analyses concerning chemical composition of different species as well as selected physical properties are performed. In the further chapters, these nanoparticles are used as templates for the formation of more complex structures.

Next, the coating of spherical and ellipsoidal hematite colloids with silica using different coating methods is presented. The chapter opens with detailed investigations of standard silica coating procedures focusing especially on the role of adhesion promoters during the silica deposition in organic media. Subsequently, a silica coating process is presented where highly functional, water-soluble hyperbranched polyalkoxysiloxanes are used. In a surfactant-free water-based coating procedure, the resulting hematite core silica shell nanoparticles are decorated with reactive groups on the surface.

Asymmetric multi-compartment lemon- and dumbbell-shaped colloids are the main topic of the following part. Some of the monomers used for the asymmetric polymer coating, are hydrophobic in nature, but also water-soluble, functional monomers, e.g. *N*-vinylcaprolactam, are used making the polymer shell more hydrophilic, reactive and responsive. Furthermore, structures described are used to deposit silica selectively on the free edges of the ellipsoids to obtain dumbbells.

Finally, different methods of encapsulation of magnetic nanoparticles into PVCL microgels are discussed. One approach describes the grafting of polymer from the spherical hematite nanoparticle surface resulting in core-shell nanocomposites. Loading of sub-10 nm FePt colloids by a solvent exchange method into microgels is the other subject here. For both hybrid material responsiveness to external stimuli is observed.

Zusammenfassung

In dieser Dissertation wird die Synthese und Charakterisierung eisenoxid-basierter Multi-Kompartiment-Kolloide beschrieben, welche die chemischen und physikalischen Eigenschaften anorganischer Nanopartikel mit verschiedenen Polymeren kombinieren. In diesem Fall wurden alle Kolloide nach templat-freien Bottom-up-Ansätzen aus Lösung synthetisiert.

Im ersten Teil wird ein Einblick in die faszinierende Welt der Hämatit-Nanopartikel gewährt. Ihre Morphologie kann während der Synthese aus wässriger Lösung von runden bis spindelförmigen Formen variiert werden. Analysen, bezüglich chemischer Zusammensetzung der verschiedenen Partikelspezies sowie ausgewählter physikalischer Eigenschaften, werden durchgeführt. In den weiteren Kapiteln werden diese Nanopartikel als Template zum Aufbau komplexerer Strukturen verwendet.

Als nächstes wird die Beschichtung sphärischer und ellipsoider Hämatit-Kolloide mit Silika unter Verwendung verschiedener Methoden vorgestellt. Dieses Kapitel beginnt mit detaillierten Untersuchungen der Standardmethode zur Silika-Beschichtung. Dabei wird ein besonderer Fokus auf die Rolle des Haftvermittlers während der Silika-Abscheidung in organischer Lösung gelegt. Anschließend wird ein Silika-Beschichtungsverfahren präsentiert, in welchem ein hoch funktionales, wasserlösliches, hochverzweigtes Polyalkoxysiloxan verwendet wird. In einem tensid-freien, wasserbasierten Prozess werden die erhaltenen Kern-Schale-Nanopartikel in demselben Schritt mit reaktiven Gruppen an der Partikeloberfläche dekoriert.

Asymmetrische Multi-Kompartiment-Kolloide, welche zitronen- oder hantelförmig sind, sind das Hauptthema im folgenden Teil. Einige der Monomere, welche für die asymmetrische Polymerbeschichtung verwendet werden, sind von ihrer Natur aus sehr hydrophob. Jedoch werden auch wasserlösliche, funktionelle Monomere, z.B. *N*-Vinylcaprolactam, verwendet, welche die Polymerschale hydrophiler, reaktiv und responsiv machen. Weiter werden diese Strukturen verwendet, um durch selektive Abscheidung von Silika auf den unbeschichteten Ecken der Ellipsoide, hantelförmige Kolloide zu erhalten. Schlussendlich werden verschiedene Methoden zur Verkapselung

magnetischer Nanopartikel in PVCL-Mikrogele diskutiert. In einem Ansatz wird das Wachsen des Polymers von der Oberfläche des sphärischen Hämatit-Nanopartikels beschrieben, welches zu Kern-Schale-Nanokompositen führt. Die Beladung von Mikrogelen mit unter 10 nm großen FePt-Kolloiden durch ein Lösungsmittelaustauschverfahren ist das andere Thema hier. Für beide Hybridmaterialien wird eine Responsivität auf externe Stimuli beobachtet.

Abbreviations and Symbols

AMPA	2,2'-Azobis(2-methylpropionamidine)dihydrochloride
a.u.	arbitrary unit
BIS	<i>N, N'</i> - methylenebisacrylamide
DLS	dynamic light scattering
DVB	divinylbenzene
EM	electrophoretic mobility
FePt	iron platinum
FTIR	fourier transform infrared
GMA	glycidyl methacrylate
H	magnetic field
HDA	16-heptadecenoic acid
H ₂ O	water
KPS	potassium persulfate
<i>l</i> _{TEM}	silica shell thickness determined with TEM
<i>L</i> _{TEM}	length of longitudinal axis measured with TEM
M	magnetization
NP	nanoparticles
η	dynamic viscosity of liquid (continuous phase)
$\Delta\rho$	different densities (continuous and dispersed phase)
PEG	polyethylene glycol
PEOS	hyperbranched poly(ethoxysiloxane)
PEOS-PEG	polyethylene glycol functionalized PEOS
PEOS-PEG-V	PEG and vinyl functionalized PEOS
PS	poly(styrene)
PSGD	poly(styrene-co-glycidyl methacrylate-co-divinylbenzene)
PSVD	poly(styrene-co- <i>N</i> -vinylcaprolactam-co-divinylbenzene)
PVCL	poly(<i>N</i> -vinylcaprolactam)
PVP	poly(vinylpyrrolidone)
PVP-10	PVP (<i>M</i> _w = 10 kg/mol)

PVP-40	PVP ($M_w = 40$ kg/mol)
PVP-55	PVP ($M_w = 55$ kg/mol)
q	scattering vector
$r_{\frac{polymer}{hematite}}$	polymer to hematite ratio
R_H	hydrodynamic radius
RITC	rhodamine B isothiocyanate
rpm	rounds per minute
R_{TEM}	particle radius determined with TEM
σ	swelling ratio
t	shell thickness
T	absolute temperature
TEM	transmission electron microscopy
TEOS	tetraethyl orthosilicate
TGA	thermal gravimetric analysis
THF	tetrahydrofuran
T_{TEM}	length of transversal axis measured with TEM
USAXS	ultra-small angle X-ray scattering
UV-Vis	ultraviolet-visible
VCL	<i>N</i> -vinylcaprolactam
VPT	volume phase transition
VPTT	volume phase transition temperature
v_{sed}	sedimentation velocity for dilute samples
wt	weight
wt loss	weight loss
wt-%	weight percent
xg	centrifugal acceleration
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ξ	zeta potential

1 Introduction

Multi-compartment colloids with complex structures have attracted the interest of researchers in the last decades. In general they are defined as “colloidal structures which are composed of multiple phase-separated domains in the core”^[1]. The combination of several materials, including organic and inorganic components, results in an incredible quantity of nanocomposites and the diversity of their complex geometries is even many greater.^[2, 3]

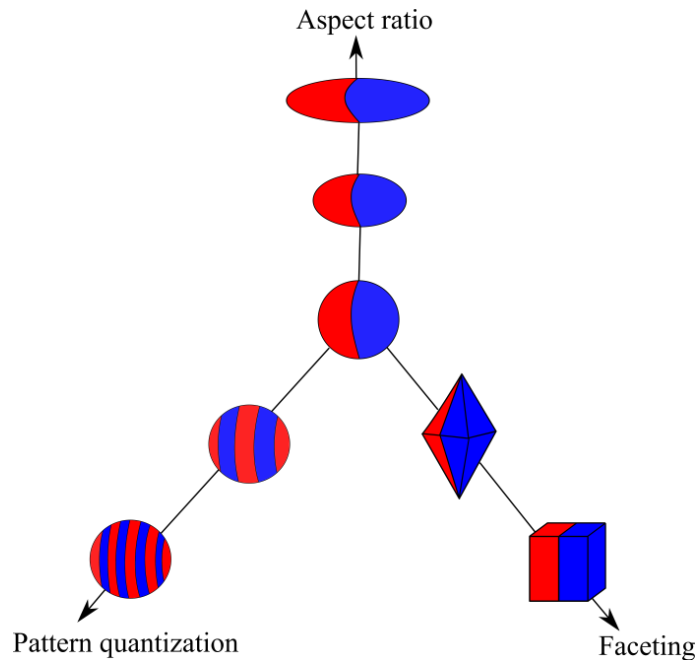


Figure 1.1. Combining a ‘minimal’ set of dimensions of particle anisotropy can generate many new building blocks. (Redrawn from reference ^[3])

Multi-compartment colloids combine the properties of all components used leading to completely new properties and application possibilities. The engineering of nanomaterials with multiple functionalities and enhancement of properties of one component is a challenging task. But even more difficult is the selective arrangement of materials into single hybrid particles on the nanoscale to obtain structures with a complex, asymmetric morphology.^[4] In many studies, methods have been developed to synthesize nanocomposites. The targeted synthesis of very uniform multi-compartment

particles direct from solution remains challenging. Also problems such as scaling-up processes need to be solved.

This work focuses on synthesis and characterization of multi-compartment colloids combining the chemical and physical properties of inorganic magnetic nanoparticles with different inorganic materials or polymers. All colloids are synthesized from solution by template-free bottom-up approach. For characterization I am using different analytical methods to determine composition and structure of the complex hybrid nanoparticles. This first chapter gives a short introduction into the vast field of multi-compartment colloids and furthermore an overview of all the following chapters.

The second chapter provides an insight into the intrigued world of hematite nanoparticles. The nanoparticles described here are synthesized from aqueous solution by hydrolysis of aqueous ferric chloride solutions. *Ozaki et al.*^[5] developed a procedure to obtain monodisperse hematite nanoparticles with a narrow size distribution as well as tunable size and morphology. Morphology can be adjusted to range from spherical to spindle-type shapes. Analyses concerning chemical composition of different species as well as selected interesting physical properties are characterized carefully.

In the third chapter, the coating of spherical and ellipsoidal hematite colloids with silica using different silica precursors is presented. The chapter opens with detailed investigations of standard silica coating procedures focusing especially on the role of adhesion promoters during the silica deposition in organic media. Subsequently, a silica coating process is presented where I use a highly functional, water-soluble hyperbranched polyalkoxysiloxane. Here I developed a surfactant-free water-based coating procedure. The resulting hematite core silica shell nanoparticles are decorated with reactive groups on the surface. In a model reaction I will show that those functional groups can be addressed and used for post-modification of the particles surface.

Asymmetric multi-compartment colloids are the main topic of the fourth chapter. Here I describe the asymmetric coating of different copolymers on ellipsoidal hematite nanoparticles resulting in lemon-shaped and core-shell colloids. Some of the monomers used, such as styrene and divinylbenzene, are hydrophobic in nature, but also water-soluble functional monomers like glycidyl methacrylate (GMA) and *N*-vinylcaprolactam (VCL) are used making the polymer shell more hydrophilic, reactive and responsive. Additionally to a higher hydrophilicity, the structures containing PVCL

as a copolymer show a temperature dependent swelling behavior of the polymer shell. Furthermore, structures described are used to deposit silica selectively on the free edges of the ellipsoids to obtain dumbbells.

The fifth chapter deals with the encapsulation of magnetic nanoparticles into PVCL microgels. Different type of microgel hybrids are synthesized based on different synthetic strategies. One approach describes the grafting of polymer from the spherical hematite nanoparticle surface resulting in inorganic core PVCL shell nanocomposites. Here PVCL shells with variable shell thicknesses were synthesized. The hybrid nanocomposites obtained show classical volume phase transition behavior as already known for microgel nanoparticles. Loading of sub-10 nm FePt colloids into microgels is the other subject of the chapter. By a solvent exchange method, small nanoparticles could be distributed inside microgels. Analyses of hybrid microgel characteristics, e.g. loading degree or distribution of the filler inside the microgels, are presented. Additionally, I also describe the responsiveness of hybrid microgel to external stimuli for example temperature or a magnetic field.

The sixth chapter gives general conclusions to sum up the complete thesis.

Some of the results shown in this dissertation have already been published in part in peer reviewed international journals.

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2 Hematite Nanoparticles– From Spindles to Spheres

2.1 Introduction

Hematite is known to be the most stable polymorph of iron(III) oxide under ambient conditions. In recent years, hematite has attracted particular interest of researchers as a cheap, environmentally friendly and thermodynamically stable iron oxide.^[1] It crystallizes in a rhombohedral crystal structure and has unusual magnetic properties; below ~260 K it behaves as an ideal antiferromagnet, above as a weak ferromagnet or a canted antiferromagnet.^[2, 3] Hematite (α -Fe₂O₃) shows further interesting properties, such as high resistivity to corrosion and a small band gap (2.1 eV).^[4, 5] The small band gap makes α -Fe₂O₃ nanoparticles attractive for research in the field of solar cells. Hematite nanostructured particles combine typical properties of bulk material, e.g. magnetic properties, and enhanced reactivity of the nanoparticles due to the large surface to volume ratio. The hematite particles described here are synthesized by hydrolysis of aqueous ferric chloride solutions. To obtain ellipsoidal hematite particles, phosphate needs to be added.^[6] In this chapter I show how differences in the synthetic route lead to a variety of different morphologies and sizes tunable by the reaction conditions.

In the following chapters hematite nanoparticles will be used as templates for the formation of hybrid multi-compartment systems. Mainly hematite will be used to graft inorganic and organic polymers onto the surface. The resulting nanocomposites feature a multiplicity of shape anisotropy and combined properties, for example responsiveness to temperature as well as magnetic fields or interesting swelling behaviors.

2.2 Size and Morphology Investigations on Hematite Nanoparticles in Dried State and Dispersion

In a concentration series, five different hematite particles species are synthesized showing strong variations of aspect ratios, ranging from sphere-shaped to spindle-type nanoparticles (Figure 2.1). Sizes and morphologies for all samples have been determined with various analytic techniques. The synthetic method following *Ozaki et al.*^[6] offers a possibility to tune size and morphology of particles from spherical to ellipsoidal shape very accurately by adding different phosphate concentrations. Spherical hematite particles can be obtained in the absence of phosphate ions.

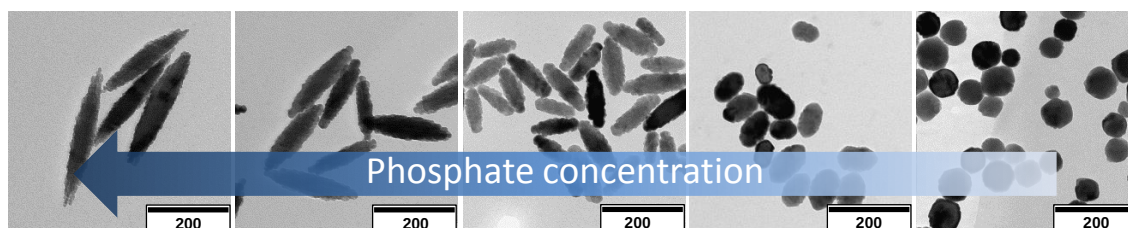


Figure 2.1. TEM images displaying size and morphology of hematite nanoparticles.

2.2.1 TEM Investigation of Dried Hematite Samples

TEM investigations were performed for a series of samples, where size and aspect ratio were varied. Figure 2.2a displays the proposed mechanism of *Ocana et al.*^[7] for the formation of ellipsoidal hematite nanoparticles from FeCl_3 solution in the presence of phosphate ions. In a first step nucleation starts, followed by an adsorption of phosphate ions on the surface planes of the nuclei. The phosphate ions adsorb parallel to the c axis of the hematite nuclei. In a further step, the anisotropic primary particles grow and start to aggregate. The aggregation occurs along the c axes of the particles accompanied by desorption of the phosphate ions. This ordering might be caused by magnetic interactions of the primary particles. It is suggested that Fe-O-Fe bonds are formed at the interfaces of the primary particles resulting in a monocrystalline structure. Finally, ripening of the primary particles induces further growth until the final size of the spindle-type hematite particles is reached.^[1, 7]

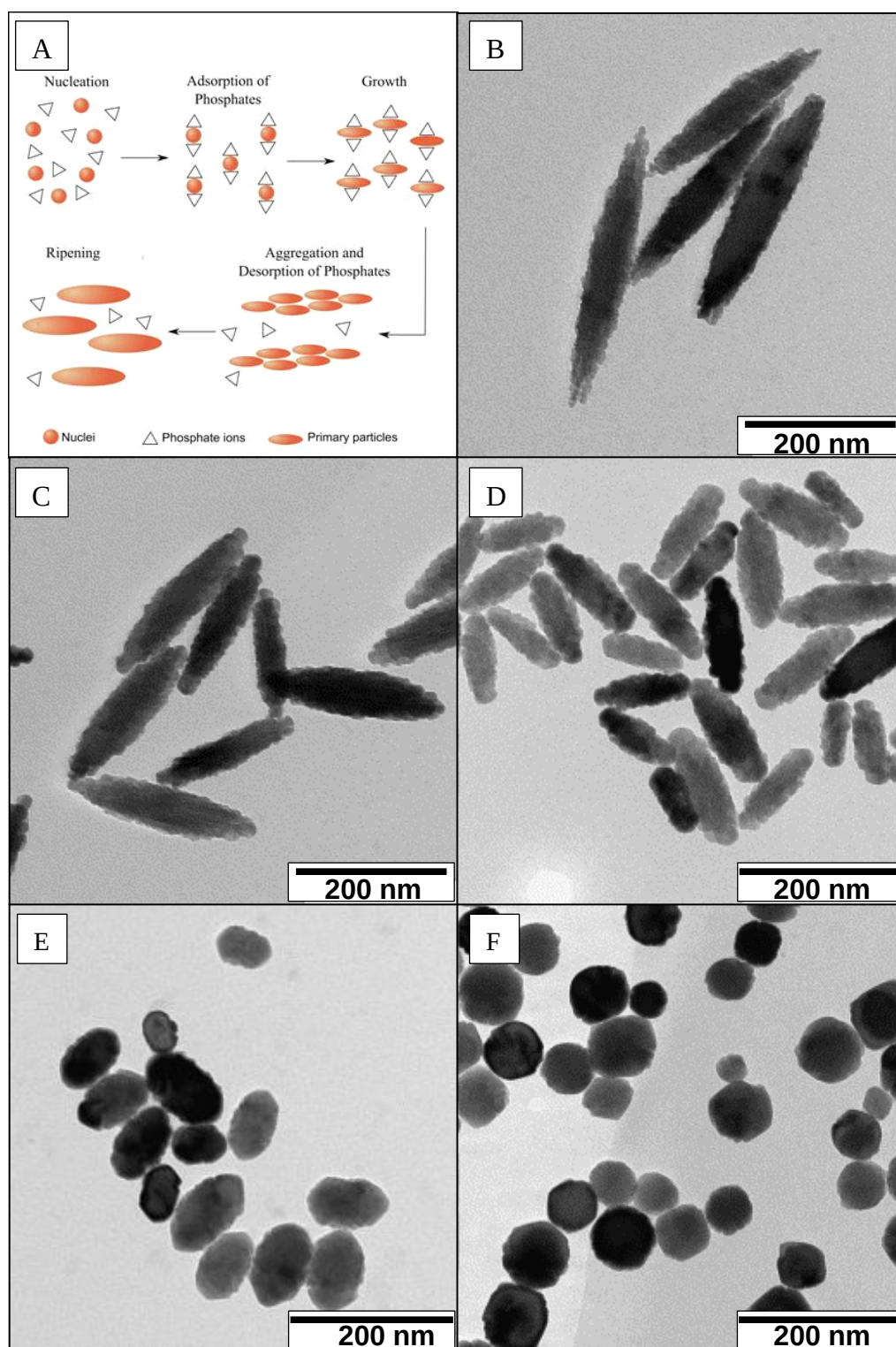


Figure 2.2. a) Schematic illustration of the formation mechanism for ellipsoidal hematite nanoparticles from FeCl_3 solution in the presence of phosphate ions by directional aggregation of small hematite ellipsoids. The figure refers to the process in the direction of c axis (Redrawn from reference ^[7]); b-f) TEM images for hematite nanoparticles with different morphologies: b) $\alpha\text{-Fe}_2\text{O}_3\text{-el-1}$; c) $\alpha\text{-Fe}_2\text{O}_3\text{-el-2}$; d) $\alpha\text{-Fe}_2\text{O}_3\text{-el-3}$; e) $\alpha\text{-Fe}_2\text{O}_3\text{-el-4}$ and f) $\alpha\text{-Fe}_2\text{O}_3\text{-sp}$.

In Figure 2.2b-f, TEM micrographs are displayed showing particles with different sizes and morphologies. Strongly elongated spindle-type nanoparticles (Figure 2.2b) were synthesized as well as spherical particles (Figure 2.2f).

The sizes of the two axes measured from TEM images are summarized in Table 2.1 values displayed were measured and averaged for minimum 100 particles. The aspect ratio was calculated by the Equation 2.1:

$$\text{Aspect ratio} = \frac{L_{\text{TEM}}}{T_{\text{TEM}}} \quad (2.1)$$

L_{TEM} [nm] Longitudinal axis

T_{TEM} [nm] Transversal axis

For a series of five samples, the aspect ratio varied within a range between 1.0 (spherical particles) and 6.2 (spindle-type particles). For ellipsoidal particles, sizes of longitudinal axes varied between 333 and 105 nm. Transversal axes differ between 54 and 67 nm for ellipsoidal particles. Spherical particles show a diameter of 73 nm.

Table 2.1. Aspect ratios, longitudinal axis (L_{TEM}) and transversal axis (T_{TEM}) of ellipsoidal and spherical hematite nanoparticles determined by TEM as shown in Figure 2.2.

Sample	Aspect ratio	L_{TEM}	T_{TEM}
		[nm]	[nm]
$\alpha\text{-Fe}_2\text{O}_3\text{-el-1}$	6.2	333 ± 41	54 ± 5
$\alpha\text{-Fe}_2\text{O}_3\text{-el-2}$	3.7	216 ± 36	59 ± 9
$\alpha\text{-Fe}_2\text{O}_3\text{-el-3}$	2.6	135 ± 30	51 ± 7
$\alpha\text{-Fe}_2\text{O}_3\text{-el-4}$	1.6	105 ± 17	67 ± 9
$\alpha\text{-Fe}_2\text{O}_3\text{-sp}$	1.0	73 ± 13	73 ± 13

2.2.2 Size Investigations in Dispersion using USAXS and DLS

Light scattering methods offer the possibility to measure particle dimensions in dispersion excluding any effects resulting from drying phenomena.

DLS experiments were performed for highly diluted aqueous dispersion of spherical hematite nanoparticles resulting in a determination of a hydrodynamic radius of 50 nm (Figure 2.3).

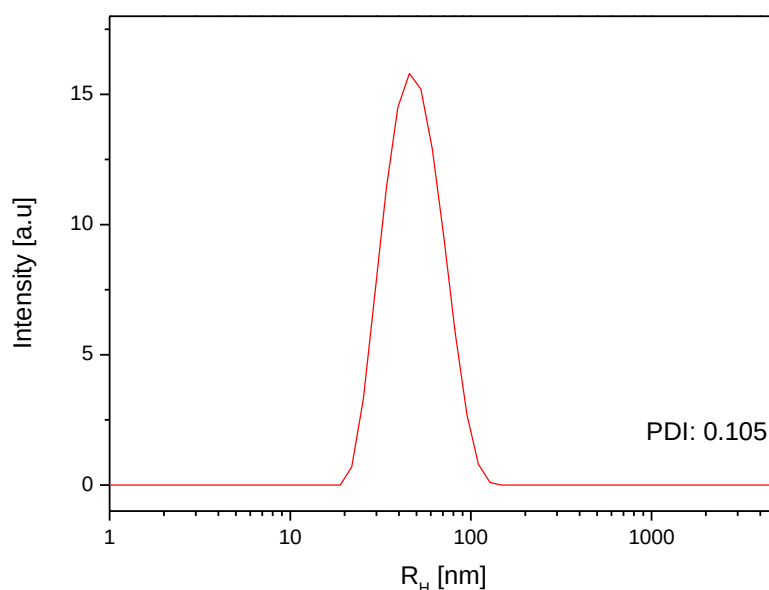


Figure 2.3. DLS curve for spherical hematite nanoparticles (α -Fe₂O₃-sp).

The particles were found to be well dispersed without any surfactants or stabilizers and no tendency to agglomeration was measured. This observation has been confirmed by the polydispersity index (PDI), which was found to be relatively narrow with a value of 0.105.

The ellipsoidal particles used are rotational ellipsoids having two semi-axis. They are called semi-axis *a* (longitudinal axis) and *b* (transversal axis). For determination of the length of these two axes USAXS experiments were performed in highly diluted dispersions exemplary shown for sample α -Fe₂O₃-el-3.

Figure 2.4 shows the scattering curve of the ellipsoidal hematite particles. For a quantification of the scattering data, a form factor for ellipsoids based on free size distribution functions was fitted to the scattering curve. The fit matches the scattering data quite well.

The calculated size distribution functions of the semi-axes are presented in Figure 2.5. Here 70 nm could be found for the longitudinal semi-axis a and 30 nm for the transversal semi-axis b . The sizes determined for the semi-axes show a very good consistency with the TEM results.

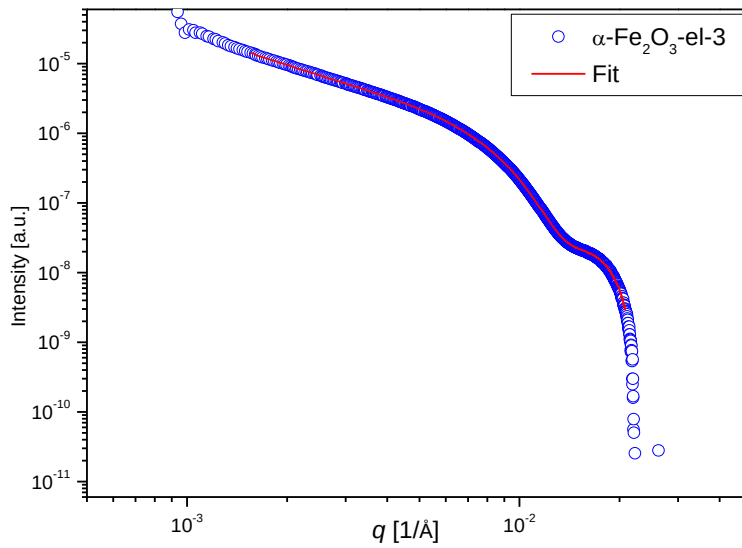


Figure 2.4. USAXS results for ellipsoidal hematite nanoparticles ($\alpha\text{-Fe}_2\text{O}_3\text{-el-3}$), a) scattering curve (blue) and fit (red).

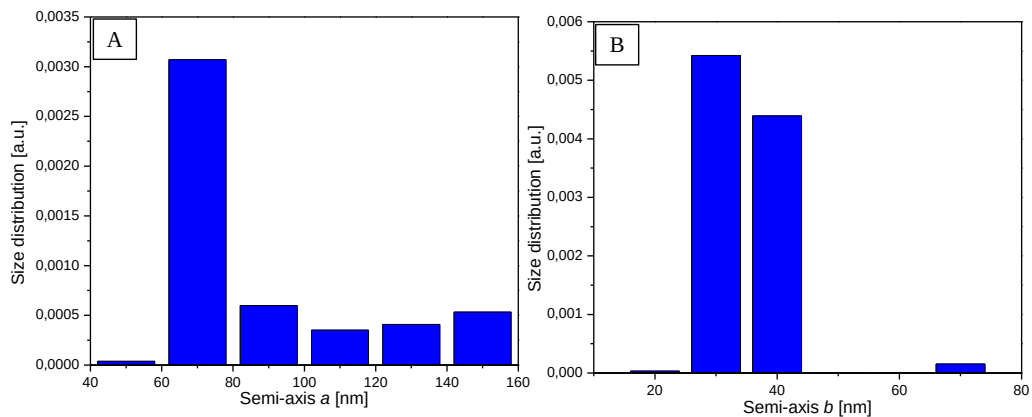


Figure 2.5. Histogram of semi-axis a and b determined from USAX measurements for ellipsoidal hematite nanoparticles ($\alpha\text{-Fe}_2\text{O}_3\text{-el-3}$).

2.2.3 Colloidal Stability of Different Hematite Particles Species

The colloidal stability of hematite nanoparticle dispersions was determined by an analytical centrifuge. The sedimentation behavior was investigated by a centrifuge equipped with an integrated optoelectronic sensor system allowing spatial and temporal measurements respective changes of light transmission during centrifugation process. The transmission was determined over the complete sample length simultaneously. The sedimentation process was followed by transmission profiles recording the shift of phase boundary between supernatant and sediment for several timings. From this data sedimentation curves and velocities can be derived.

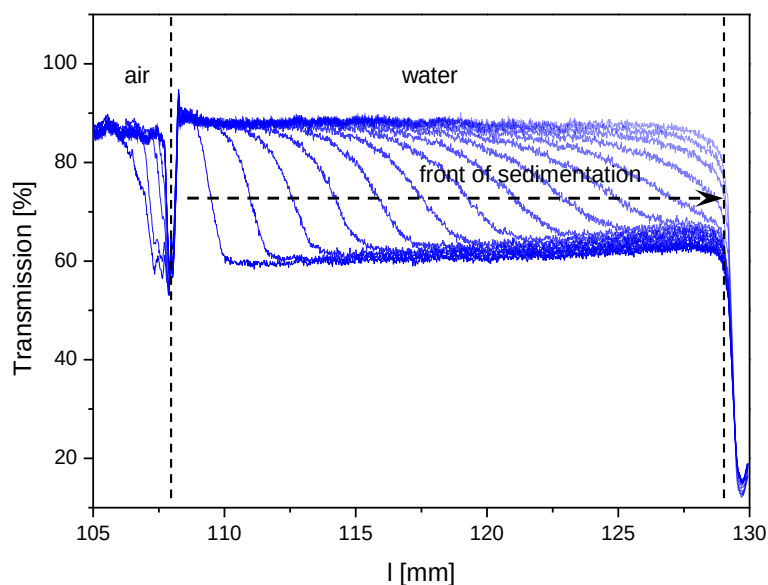


Figure 2.6. Transmission profiles of sedimentation for ellipsoidal hematite nanoparticles with an aspect ratio of 6.2 (α -Fe₂O₃-el-1) (centrifugation speed: 1,000 rpm, 20 °C).

Figure 2.6 displays a transmission profile of sedimentation for a sample of ellipsoidal hematite nanoparticles showing continuous decrease in sediment height due to compression of the sediment parallel to cuvettes bottom. In this case the transmission profiles were recorded every 15 s; every 10th measurement is shown here. Recorded transmission profiles can be transformed into transmission curves depending on time. The movement of the particles towards the bottom of the cell can be followed by

increasing transmission. In Figure 2.7 sedimentation curves with respect to time for hematite nanoparticles species exhibiting various aspect ratios are shown.

The slope of the linear regions for the curves is equal to the sedimentation velocity of colloids. According to Stokes' Law (Equation 2.1) the sedimentation velocity for diluted samples is proportional to the square of the radius of the particles and their difference in density to the continuous phase:

$$v_{sed} = \frac{\Delta\rho \cdot r^2 \cdot x\vec{g}}{18\eta} \quad (2.1)$$

v_{sed}	[m/s]	sedimentation velocity according to Stokes for diluted samples
$\Delta\rho$	[kg/m ³]	density difference (continuous and dispersed phase)
r	[m]	particle radius
$x\vec{g}$	[m/s ²]	centrifugal acceleration
η	[Pa · s]	dynamic viscosity of liquid (continuous phase)

When the curve reaches the plateau, all particles are completely settled. For hematite particles with an aspect ratio between 6.2 and 2.6, a sedimentation speed of 9.00-9.86 $\mu\text{m} \cdot \text{s}^{-1}$ was measured.

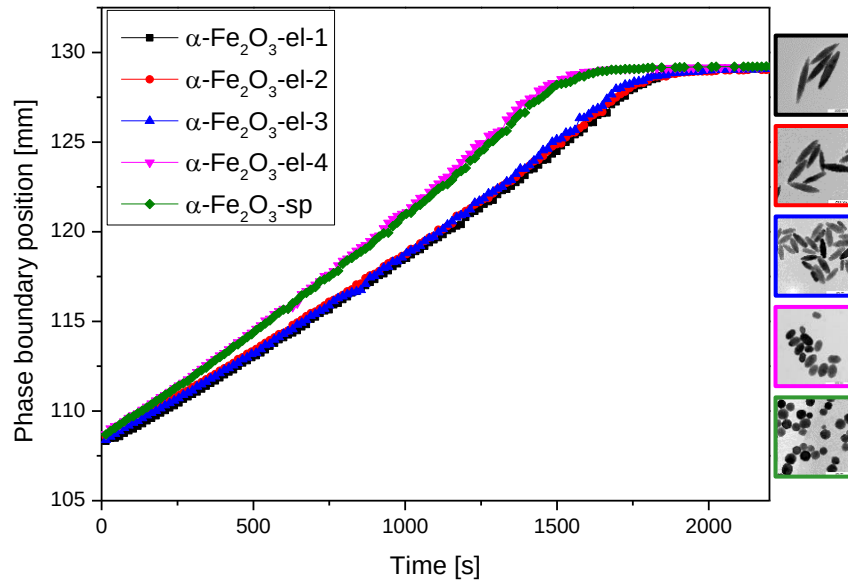


Figure 2.7. Sedimentation curves for hematite nanoparticles with various aspect ratios (centrifugation speed: 1,000 rpm, 20 °C).

Hematite particles with an aspect ratio below 1.6 showed a sedimentation velocity of 11.28-11.46 $\mu\text{m} \cdot \text{s}^{-1}$. This is only a slight increase in sedimentation velocity, but following Stokes' Law which states that sedimentation velocity is proportional to the radius of the particle, one could expect a higher sedimentation velocity for larger particles, here ellipsoids.

Table 2.2. Hematite nanoparticle properties like sedimentation velocity (v_{sed}) and aspect ratio.

Sample	v_{sed} [$\mu\text{m} \cdot \text{s}^{-1}$]	Aspect ratio
$\alpha\text{-Fe}_2\text{O}_3\text{-el-1}$	9.00 ± 0.47	6.2
$\alpha\text{-Fe}_2\text{O}_3\text{-el-2}$	9.72 ± 0.17	3.7
$\alpha\text{-Fe}_2\text{O}_3\text{-el-3}$	9.86 ± 0.33	2.6
$\alpha\text{-Fe}_2\text{O}_3\text{-el-4}$	11.46 ± 0.29	1.6
$\alpha\text{-Fe}_2\text{O}_3\text{-sp}$	11.28 ± 0.23	1.0

Furthermore, the differences of the sedimentation velocities for different particle morphologies are very small. A clear influence of the particle shape is not observed. All sedimentation velocities are summarized in Table 2.2.

2.2.4 Investigation of Chemical Composition and Surface Properties

For further characterization of the synthesized particles, investigations concerning their chemical composition and surface properties were performed.

To characterize the crystal structure of hematite nanoparticles with different sizes and shapes XRD was used. Recorded X-ray diffraction data are displayed in Figure 2.8. The data indicate that just hematite is present in all three samples. Characteristic signals can be found in all three spectra.^[8] Only slight differences are visible in the X-ray diffraction spectra for different morphologies indicating a monocrystalline growth for all species. The crystal structure was found to be rhombohedral in all cases.

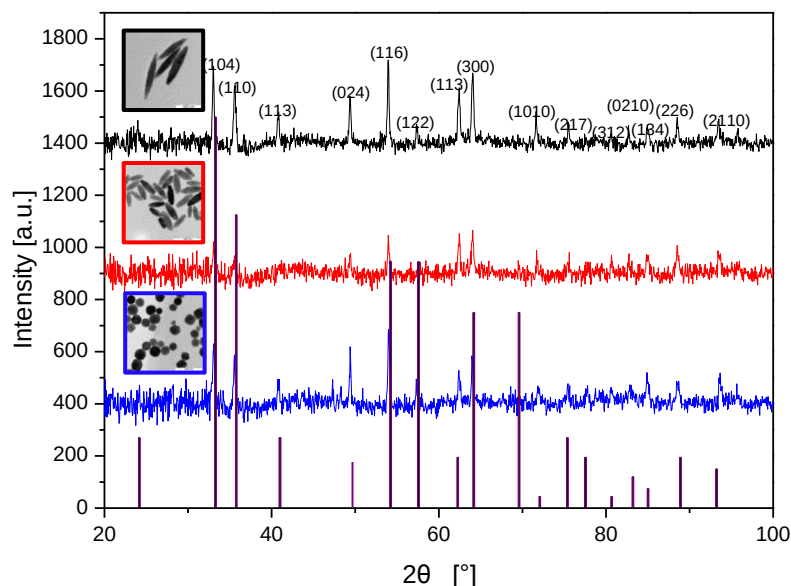


Figure 2.8. X-ray diffraction pattern for $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles with three different morphologies: $\alpha\text{-Fe}_2\text{O}_3\text{-el-1}$ (black); $\alpha\text{-Fe}_2\text{O}_3\text{-el-3}$ (red); $\alpha\text{-Fe}_2\text{O}_3\text{-sp}$ (blue); reference values^[8] (purple).

Additionally, the surface charge of different hematite species was determined by zeta potential measurements in a pH range of 3 to 10. Figure 2.9 displays pH dependent zeta potential curves for three samples with different aspect ratios. A very similar trend was observed in all samples, all of which show a strong positive zeta potential in the acidic pH region, namely between +20 mV to +40 mV at pH 3. A decrease of positive charges on the surface was observed with increasing pH. The point of zero charge, also called isoelectric point (IEP), was found to be around pH 7 for all samples. Above pH 7 the zeta potential drops dramatically. For pH 10 characteristic values for zeta potential were determined between -30 mV to -40 mV. This behavior is suggested to be caused by protonation and deprotonation of hydroxy groups located on the surface.

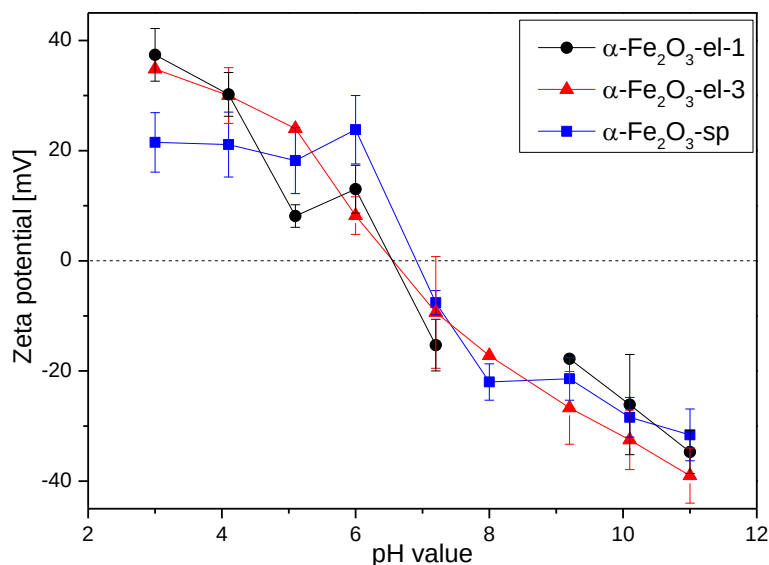
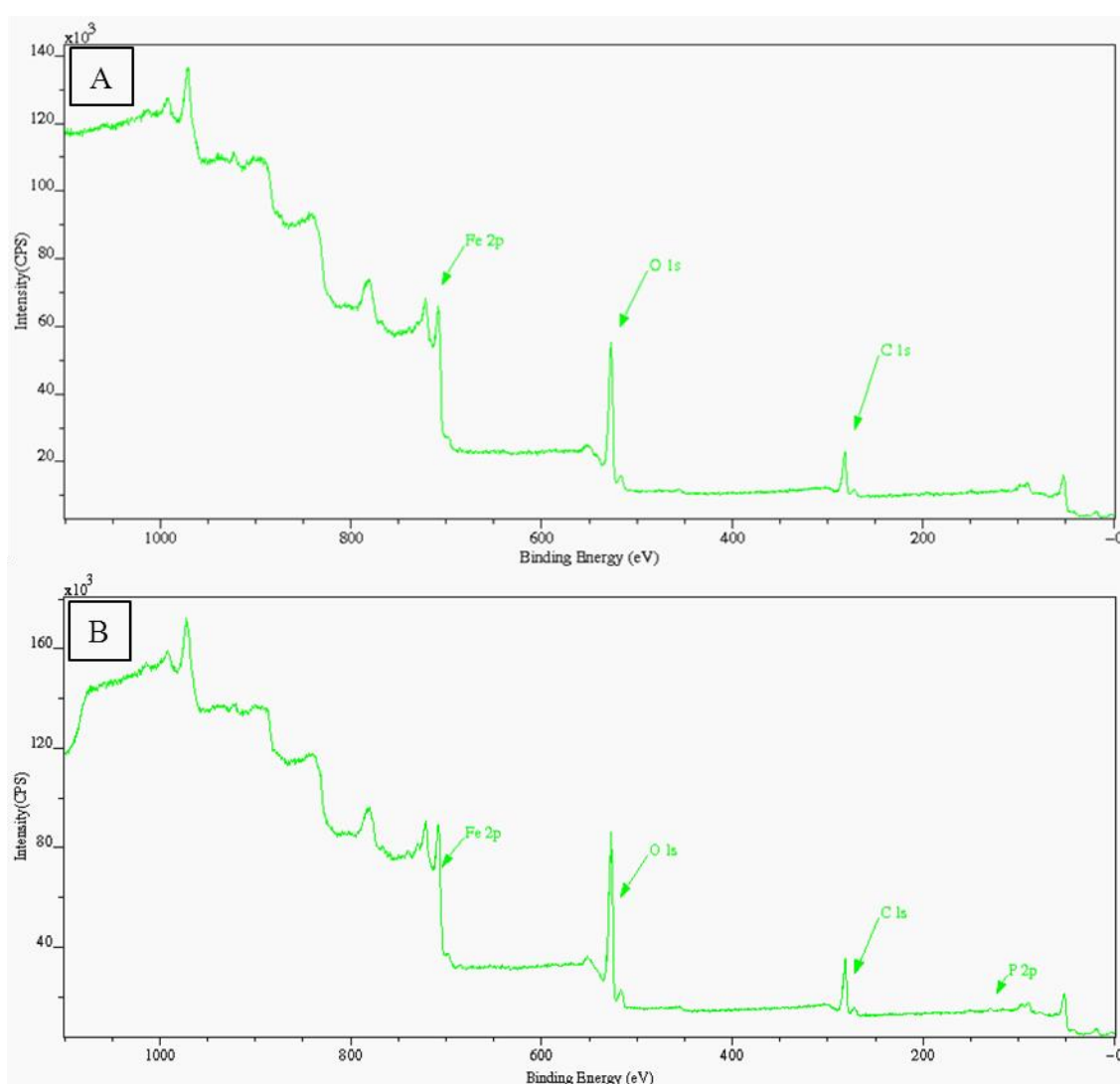


Figure 2.9. pH dependent zeta potential curves for hematite nanoparticles with aspect ratios between 1 (spheres) and 6.2 (very elongated ellipsoids): $\alpha\text{-Fe}_2\text{O}_3\text{-el-1}$ (black); $\alpha\text{-Fe}_2\text{O}_3\text{-el-3}$ (red); $\alpha\text{-Fe}_2\text{O}_3\text{-sp}$ (blue).

X-ray photoelectron spectroscopy (XPS) was performed for spherical ($\alpha\text{-Fe}_2\text{O}_3\text{-sp}$) and for ellipsoidal ($\alpha\text{-Fe}_2\text{O}_3\text{-el-1}$) hematite particles to analyze the surface properties of both species in more detail. XPS can detect the quantity of those elements that are present within the top 10 nm of the sample surface. Here the question was addressed, whether both samples are chemically identical on the surface or whether there are some phosphate ions left on the surface for sample $\alpha\text{-Fe}_2\text{O}_3\text{-el-1}$ after purification. A comparison of both spectra shows that for sample $\alpha\text{-Fe}_2\text{O}_3\text{-el-1}$ (Figure 2.10) a very small amount of phosphorus was found. But this amount was found to be only 0.99 % of the atomic concentration. As expected, iron and oxygen were also detected for both samples (Figure 2.3). Additionally, a carbon signal appears in the spectra. This signal might be due to adsorption of atmospheric chemical compounds containing carbon. The amount of iron and oxygen was found to be almost similar for both species and only a small amount of phosphate is still bound to the nanoparticles surface.

Table 2.3. Element content (Atomic conc) measured with XPS for ellipsoidal and spherical hematite nanoparticles.

Elements	α -Fe ₂ O ₃ -sp Atomic conc [%]	α -Fe ₂ O ₃ -el-1 Atomic conc [%]
Fe	14.52	17.99
O	44.65	45.21
C	39.84	36.80
P	0.99	-

**Figure 2.10.** XPS spectra of spherical (A, α -Fe₂O₃-sp) and ellipsoidal hematite nanoparticles (B, α -Fe₂O₃-el-1).

2.3 Summary

Hematite particles with different sizes and morphologies were synthesized and characterized in detail in this chapter. TEM analysis show ellipsoidal particles with longitudinal axes between 333 and 105 nm and transversal axes between 54 and 67 nm. The average diameter of spherical particles was found to be around 73 nm.

Scattering experiments confirmed the values for the investigated samples. So, DLS experiments resulted in a hydrodynamic radius of around 50 nm for spherical particles. For ellipsoidal nanoparticles USAXS measurements were performed exemplary for one sample. The longitudinal semi-axis a was found to be 70 nm and the transversal semi-axis b 30 nm.

Furthermore, the colloidal stability was investigated using an analytical centrifuge. The sedimentation velocity was found to be almost similar for all samples. A slight increase of sedimentation speed was detected for more spherical shaped particles compared to extremely elongated nanoparticles.

XRD proved that all samples consist of hematite, which is crystalized in the rhombohedral crystal structure. All samples showed characteristic peaks and a good crystallinity.

Zeta potential behavior was, as expected, found to be positive in the acidic pH and negative in the basic medium. Isoelectric point (IEP) was determined at around pH 7. All hematite nanoparticles exhibited hydroxyl groups on the surface, which could be protonated and deprotonated in different pH.

In general it can be concluded that there are very minor differences in the chemical properties. All the differing effects can be attributed mainly to differences in size and shape. Small differences in chemical composition or chemical differences on the surface of the particles, e.g. small phosphate amounts on ellipsoidal particles, do not seem to significantly influence the properties. All experiments lead to the conclusion that the major differences consist in differences of particle size and shape.

2.4 Experimental

2.4.1 Synthesis of Spherical and Ellipsoidal Hematite Nanoparticles

To synthesize dispersions of uniform hematite nanoparticles, a precipitation method following the approach of Matijevic and co-workers was used.^[5] In a general procedure, 1,000 mL of a 0.02 M FeCl_3 solution containing NaH_2PO_4 in a concentration ranging between 0 M and $4.5 \cdot 10^{-4}$ M was heated to boiling point under reflux conditions. If NaH_2PO_4 was added, ellipsoidal particles ($\alpha\text{-Fe}_2\text{O}_3\text{-el}$) were obtained, otherwise spherical ($\alpha\text{-Fe}_2\text{O}_3\text{-sp}$) particles were synthesized. The solution was kept at boiling point for the next 48 h. Afterwards, the dispersion was cooled down to room temperature and the solvent removed partially by vacuum evaporation. The particles were collected from the concentrated dispersion with an Eppendorf® Centrifuge 5810 by centrifuging at about 10,000 rpm for 10 min. The precipitates obtained by this method were repeatedly centrifuged and washed with distilled water to remove excess ions from the dispersion.

2.4.2 Sample Preparation and Measurement Conditions

The device designations of instruments used for the measurements can be found in the Appendix I.

For the preparation of the TEM samples a drop of the particle dispersion was trickled on a piece of Formvar and carbon coated copper grid. Before being placed into the TEM specimen holder, the copper grid was air-dried under ambient conditions.

ImageJ and WinTEM™ software was employed to process the TEM digital images to analyze the particle size and morphology. At least 100 particles were measured.

For DLS and zeta potential measurements one drop of the dispersion is diluted with 5 mL of distilled water. For measurements 1 mL of the diluted dispersion was used.

USAXS measurements were performed for diluted samples. Therefore, one drop of the dispersion was diluted with 5 mL of distilled water. Afterwards, the dispersion was filled in a capillary with a diameter of 1.5 mm.

The sedimentation velocities of nanoparticles were measured with an analytical centrifuge. The measurements were performed with a centrifugal speed of 1,000 rpm. Throughout the measurement, 255 transmission profiles are recorded within intervals of 10 seconds. All measurements are performed at 25 °C. The concentrations of the samples measured are 3.2 mg per mL.

XRD and XPS were performed for powders of dried nanoparticles.

2.5 References

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3 Silica Coating on Hematite Nanoparticles¹

3.1 Introduction

Silica coating on nanoparticles is frequently used to obtain multi-functional surfaces.^[2-4] For many metal or metal oxides chemical modifications are limited but coating with silica offers a reliable way to bridge this gap.^[5,6] Silica shows affinity to metals as well as many metal oxides^[7-10]; silica surfaces can be decorated by functional alkoxysilanes with a variety of functionalities like amines^[11], thiol^[12] or vinyl^[13] groups. The above mentioned functionalities make inert nanoparticles accessible to chemical processes performed on the particle surface.

Studies dealing with functionalization of hematite nanoparticles with reactive silica surfaces almost unanimously describe multi-step approaches. The first step is the coating with silica^[14-16] followed by a further immobilization of alkoxysilanes carrying reactive groups. Functional groups can be used to bind e.g. enzymes,^[17] polymers^[18, 19] or drugs^[20] to the surface. Applications of composite colloids consisting of inorganic and organic compounds are of significant interest in the fields of pigments, catalysts or contrast agents. Besides its accessibility to manifold chemical reactions, silica is crucial to enhance the dispersibility and stability of nanoparticles in different media along with increasing biocompatibility.

Two silica coating methods are presented in this chapter showing different techniques to create hematite core silica shell structures with tunable shell properties. The first method described focuses on the role of adhesion promoters in a well-known coating process using TEOS as silica precursor. The second part deals with a water-based surfactant-free procedure using water-soluble functional polyalkoxysiloxanes. Both coating processes are performed for hematite nanoparticles with different sizes and

¹ Results shown in this chapter are partially published in reference [1].

morphologies; coating processes are performed for spherical and ellipsoidal hematite nanoparticles.

3.2 Silica Coating on Hematite Nanoparticles with TEOS – Influence of Adhesion Promoter on Silica Shell Formation

In this work I investigated the influence of the molecular weight of the commonly used adhesion promoter poly(vinylpyrrolidone) (PVP) on the silica coating process with tetraethyl orthosilicate (TEOS) as precursor.^[7, 21] This method is well-known in literature and used frequently to coat different metal oxide nanoparticles with a uniform silica shell. It has already been described how an adhesion promoter enables one to create a shell on particles with less affinity to silica due to its amphiphilic structure.^[7] In this paragraph I will describe the results of experiments using PVP with three different molecular weights to coat hematite particles with a silica shell. The spherical and ellipsoidal hematite particles are pre-functionalized with PVP having varying chain lengths. The coating with silica is performed in three to five coating cycles including the coating and several purification steps.

3.2.1 Determination of Silica Shell Thickness on Hematite Nanoparticles using Scattering Methods

The silica shell thickness in solution was investigated using scattering methods. The following paragraph describes the results obtained for spherical and ellipsoidal core-shell particles. For spherical particles, DLS was used. USAXS was used to investigate properties of ellipsoidal particles.

DLS measurements for spherical hematite core silica shell nanoparticles are presented in Figure 3.1. With an increasing number of coating cycles, a linear increase of hydrodynamic radii was determined for all samples. The average increase per coating step is 20 to 25 nm. PVP-40 showed slightly higher radii as determined for PVP-10 and PVP-55. So it could be concluded that there is no trend observable indicating that the

molecular weight of adhesion promoters has a significant influence on the shell formation in the chosen molecular weight range of the polymers.

Reference measurements were performed for α -Fe₂O₃ nanoparticles and PVP pre-functionalized α -Fe₂O₃ nanoparticles in water. For hematite nanoparticles, a hydrodynamic radius of about 45 ± 1 nm was found. Radii for PVP pre-functionalized hematite particles showed nearly the same sizes for all samples not depending on the molecular weight of PVP. But the increase in size was significantly higher compared to bare nanoparticles. The PVP chains adsorb to the surface changing the diffusion coefficient of the particles considerably. A large decrease in size was measured after first SiO₂ coating performed on the particle surface.

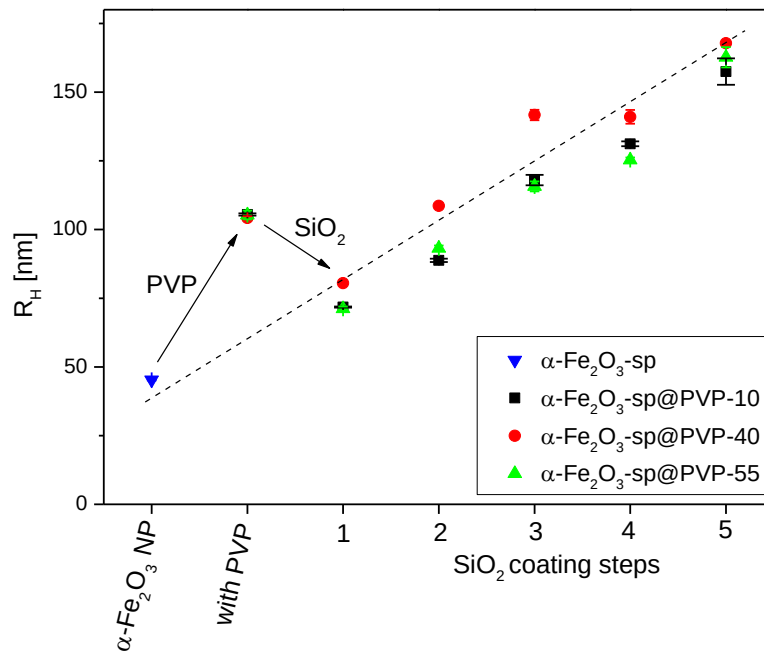


Figure 3.1. Hydrodynamic radii of α -Fe₂O₃-sp (blue), PVP covered α -Fe₂O₃-sp and α -Fe₂O₃-sp@SiO₂ using PVP-10 (black), α -Fe₂O₃-sp@SiO₂ using PVP-40 (red), α -Fe₂O₃-sp@SiO₂ using PVP-55 (green) for several coating steps (PVP concentration: 65 mg/ mL). All measurements were performed for 20°C.

Possible reasons for that observation might be that the polymer chains get buried below the silica layer or that PVP migrates from the surface during the coating process. However, the first hypothesis is considered to be more favorable. *Scanna et al.* showed that the silica layer became more porous if a PVP layer was added to the surface in

between of each coating cycle.^[21] It should be noted that the results presented are preliminary results. Described phenomena will have to be investigated in more detail.

USAXS measurements were performed on a series of three different ellipsoids with core-shell structure. For each ellipsoidal particle, samples with three different shell thicknesses were synthesized. In general USAXS experiments can show the two main semi-axes of the rotational ellipsoids as well as values for the shell thicknesses. To analyze the scattering curves properly, a model was developed showing a rotational ellipsoid with core-shell geometry (Figure 3.2). The longitudinal semi-axis is called a , the transversal semi-axis is called b and shell thickness is called t .

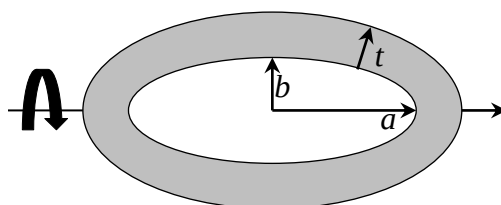


Figure 3.2. Model for calculations; rotational ellipsoid with core-shell geometry.

Table 3.1. USAXS and TEM data for shell thickness t and transversal semi-axis b .

Sample	Shell thickness t		Semi-axis b	
	[nm]		[nm]	
	t_{TEM}	t_{SAXS}	TEM	SAXS
$\alpha\text{-Fe}_2\text{O}_3\text{-el-1@PVP10@SiO}_2\text{-1}$	2	8	18	20
$\alpha\text{-Fe}_2\text{O}_3\text{-el-1@PVP10@SiO}_2\text{-2}$	6	8-15	18	24
$\alpha\text{-Fe}_2\text{O}_3\text{-el-1@PVP10@SiO}_2\text{-3}$	10	8-15	18	24
$\alpha\text{-Fe}_2\text{O}_3\text{-el-2@PVP10@SiO}_2\text{-1}$	3	9	24	26
$\alpha\text{-Fe}_2\text{O}_3\text{-el-2@PVP10@SiO}_2\text{-2}$	7	11	24	23
$\alpha\text{-Fe}_2\text{O}_3\text{-el-2@PVP10@SiO}_2\text{-3}$	11	20	24	16
$\alpha\text{-Fe}_2\text{O}_3\text{-el-3@PVP10@SiO}_2\text{-1}$	2	-	32	36
$\alpha\text{-Fe}_2\text{O}_3\text{-el-3@PVP10@SiO}_2\text{-2}$	7	12	32	32
$\alpha\text{-Fe}_2\text{O}_3\text{-el-3@PVP10@SiO}_2\text{-3}$	10	18	32	34

The scattering curves (Figure 3.3a) were fitted (Figure 3.3b). From the fitted data semi-axis b and shell thickness t could be determined. Table 3.1 displays a comparison with data analyzed from TEM images.

As already shown in the Table 3.1, the values were found to be well in consistency of both methods. Semi-axis a could not be determined properly with USAX because the determined value is proportional to $1/q$, meaning the analysis of this axis has to be done in a region for small q values. Within this region, interparticular interactions overlay the needed information about the longitudinal semi-axis a resulting in values which are not comparable with measured TEM data, consequently only values for axis b and shell thickness t are shown here. Therefore, for further analysis the longitudinal semi-axis a was set to a fixed value measured by TEM to calculate b and t . Figure 3.3c shows histograms for all three shell thicknesses t of the samples. An increase is clearly visible. For Figure 3.3d-f histograms for semi-axis b are displayed which are expected to be more or less identical since the same ellipsoidal core was used. The deviations of the results show that there is some need for optimization regarding the calculation methods. Improvement of this method is performed in cooperation with the group of Prof. Klemradt, II. Physical Institut B, RWTH Aachen. Detailed information can be found in the master thesis of Alexander Nent.^[22]

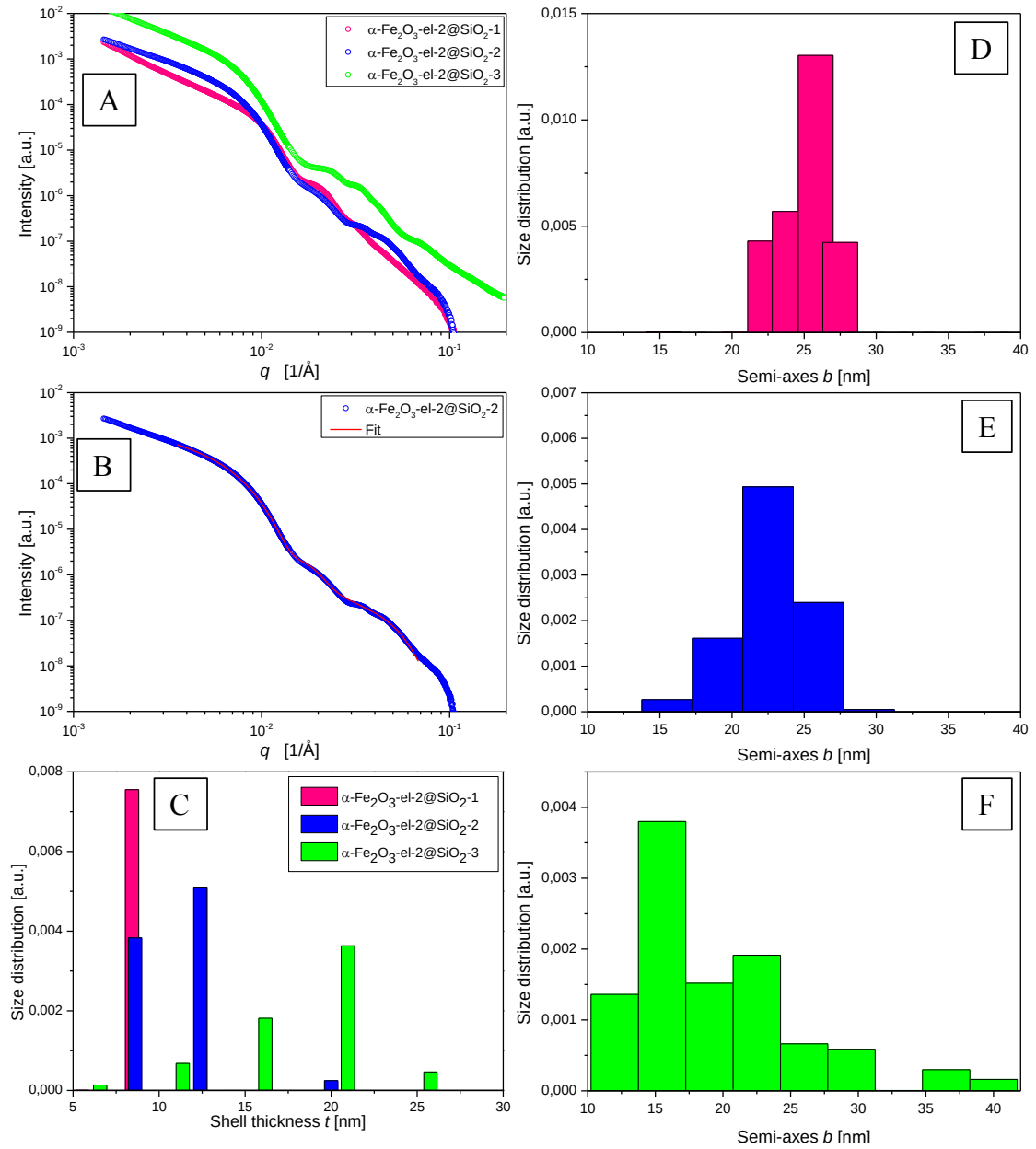


Figure 3.3. a) Scattering curves, b) scattering curve with fit, c) histograms of shell thicknesses t , d-f) semi-axis b for three samples with same core, but three different shell thicknesses: $\alpha\text{-Fe}_2\text{O}_3\text{-el-2@SiO}_2\text{-1}$ (pink); $\alpha\text{-Fe}_2\text{O}_3\text{-el-2@SiO}_2\text{-2}$ (blue); $\alpha\text{-Fe}_2\text{O}_3\text{-el-2@SiO}_2\text{-3}$ (green).

3.2.2 Investigation of Core-Shell Structure using TEM

Due to the high difference in density, hematite and silica can be easily distinguished with TEM. So, the core-shell structure is readily visible; TEM is the method of choice to analyze shell thickness and surface morphology of silica shell.

Figure 3.4 shows that spherical as well as ellipsoidal hematite particles could be uniformly coated with silica uniformly. For the first coating cycle, the silica shell was not clearly detectable. The shell was more defined from the second coating step onwards. Stabilization of hematite particles worked properly for all three PVP polymers. Nearly no particles with multiple cores could be observed leading to the conclusion that the range of molecular weight was appropriate for experiments performed here.

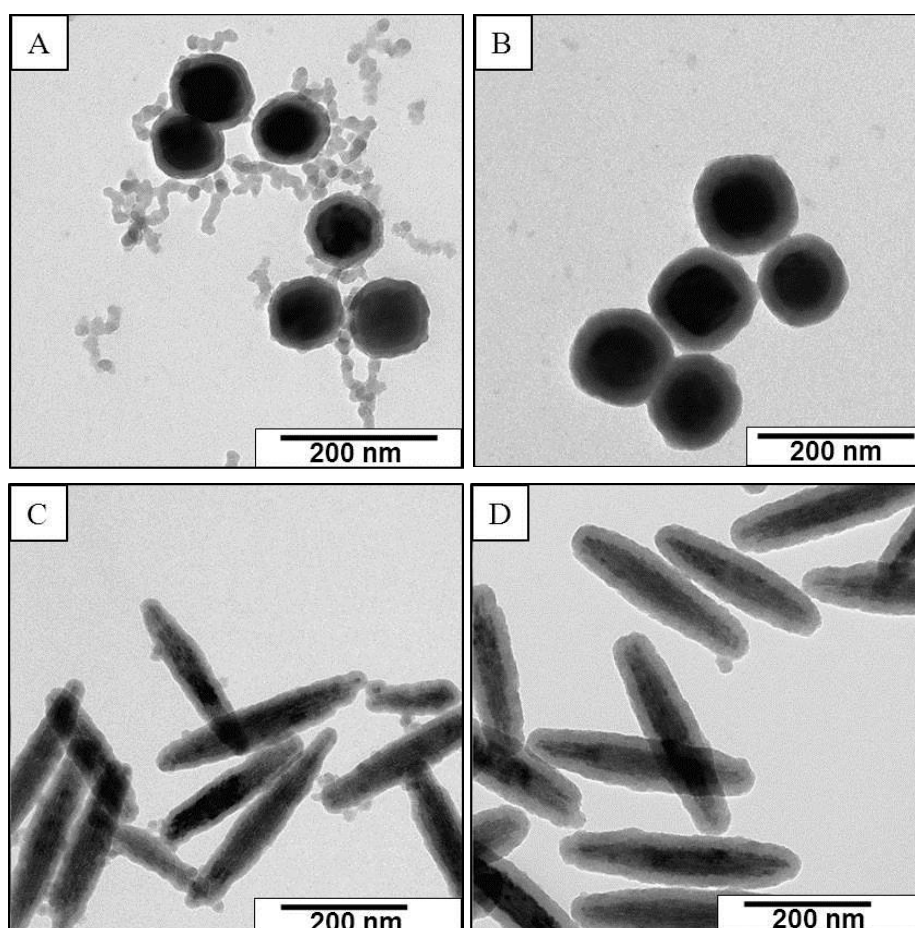


Figure 3.4. TEM images of spherical $\alpha\text{-Fe}_2\text{O}_3\text{-sp@PVP-10@SiO}_2$ after a) second ($\alpha\text{-Fe}_2\text{O}_3\text{-sp@PVP-10@SiO}_2\text{-2}$) and b) third ($\alpha\text{-Fe}_2\text{O}_3\text{-sp@PVP-10@SiO}_2\text{-3}$) coating cycle; and ellipsoidal $\alpha\text{-Fe}_2\text{O}_3\text{-el-1@PVP-10@SiO}_2$ NP after c) second ($\alpha\text{-Fe}_2\text{O}_3\text{-el-1@PVP-10@SiO}_2$) and d) third ($\alpha\text{-Fe}_2\text{O}_3\text{-el-1@PVP-10@SiO}_2$) coating cycle.

Parallel to the silica deposition on hematite nanoparticles, a second phenomenon occurred when the silica precursor concentration in the solution was too high. Above a certain concentration, silica was not deposited exclusively on the seed particles, but formation of secondary silica nanoparticles started. By keeping the all-over concentration low, this separate silica nucleation could be inhibited. Table 3.2 summarizes silica layer thickness values measured for spherical and ellipsoidal particles. With each coating step an increase of shell thickness of about 5-10 nm was measured independent of particle morphology.

Table 3.2. Silica shell thickness (t_{TEM}) for spherical and ellipsoidal nanoparticles measured with TEM after first, second and third coating cycles.

Sample	t_{TEM}	t_{TEM}	t_{TEM}
	1. coating cycle [nm]	2. coating cycle [nm]	3. coating cycle [nm]
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@PVP-10@SiO}_2$	-	12 ± 2	22 ± 2
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@PVP-40@SiO}_2$	-	17 ± 3	24 ± 4
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@PVP-55@SiO}_2$	-	15 ± 2	21 ± 3
$\alpha\text{-Fe}_2\text{O}_3\text{-el-1@PVP-10@SiO}_2$	-	13 ± 3	18 ± 2
$\alpha\text{-Fe}_2\text{O}_3\text{-el-1@PVP-40@SiO}_2$	-	13 ± 2	20 ± 2
$\alpha\text{-Fe}_2\text{O}_3\text{-el-1@PVP-55@SiO}_2$	-	15 ± 3	22 ± 3

3.2.3 Magnetic Properties $\alpha\text{-Fe}_2\text{O}_3\text{@SiO}_2$ Nanoparticles with Different Morphologies

Magnetic measurements were performed within the scope of a cooperation with Bilal Janjua from II. Physikalisches Institut A, RWTH Aachen University. More detailed measurements can be found in his dissertation.^[23] For this work, measurements were performed at room temperature for dried nanoparticle samples. $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3\text{@SiO}_2$ samples with different morphologies were investigated with reference to their magnetic properties. Figure 3.5 shows magnetization curves of three samples. In pure hematite nanoparticles, the magnetization rises with increasing magnetic field. Saturation of the magnetization was not achieved. A possible explanation might be that

in these nanoparticles there are some disordered and frustrated spins which try to align with the field as the external field increases. These observations are displayed in Figure 3.5a.

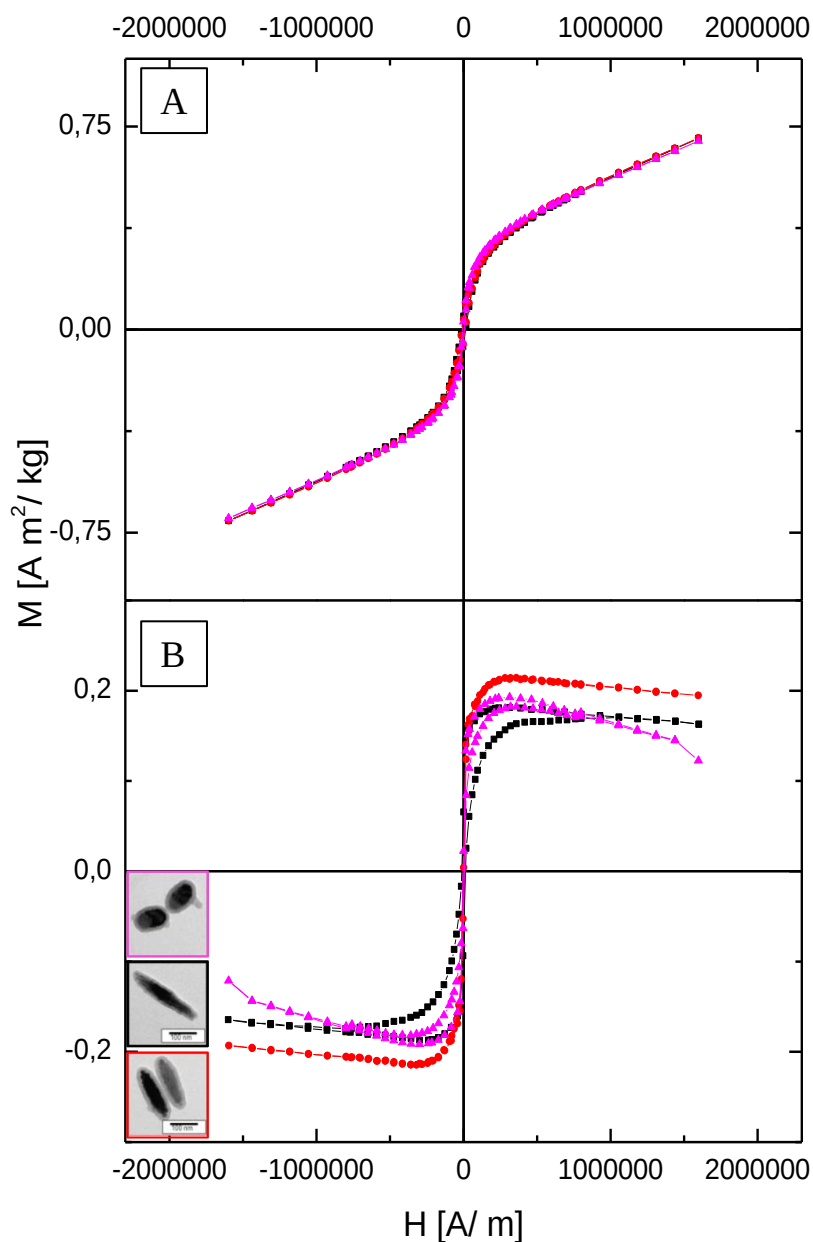


Figure 3.5. Magnetization curves of dried a) α -Fe₂O₃ nanoparticles: α -Fe₂O₃-el-1 (black); α -Fe₂O₃-el-2 (red); α -Fe₂O₃-el-4 (pink) and b) α -Fe₂O₃@SiO₂ samples with different morphologies at room temperature: α -Fe₂O₃-el-1@PVP-10@SiO₂-2 (black) α -Fe₂O₃-el-2@PVP-10@SiO₂-2 (red); α -Fe₂O₃-el-4@PVP-10@SiO₂-2 (pink).

Mass-related magnetizations were found to be smaller for silica-coated hematite nanoparticles (Figure 3.5b), indicating a noteworthy influence of silica part. Additionally, silica-coated hematite nanoparticles showed a different behavior in the magnetic field. Small diamagnetic properties are found at higher fields due to silica, which is known to be diamagnetic.

3.3 Silica Coating on Silver Chloride Nanoparticles with TEOS

The technology of silica coating by using TEOS as a precursor and PVP as adhesion promoter could be transferred successfully to silver chloride (AgCl) nanoparticles. Within the scope of the IGF-Forschungsvorhaben 16630N „Selbstregelnde Lichtdurchlässigkeit bei Fasermaterialien zur Licht- und Klimaregulierung“, the encapsulation of silver chloride nanoparticles was investigated. The aim of this work was the encapsulation of photo-switchable materials in order to enhance their stability against environmental influences.

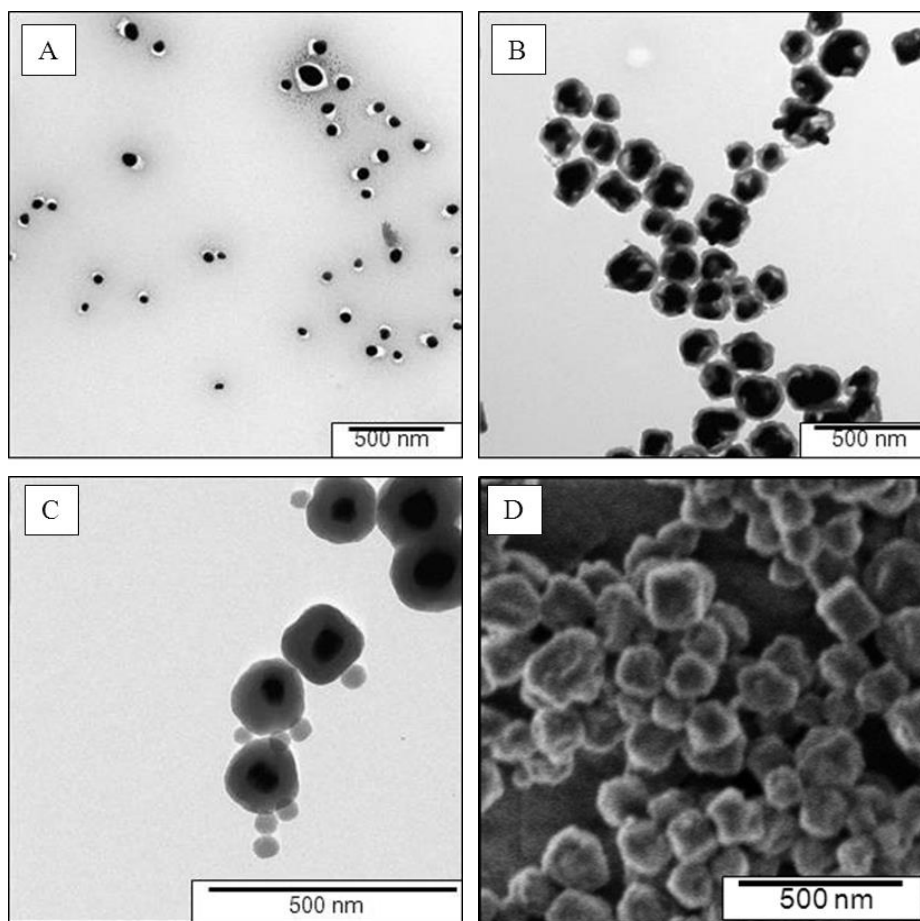
3.3.1 Investigation of AgCl and Silica Coated AgCl Nanoparticles using Electron Microscopy

A method for silver chloride nanoparticle synthesis in ethylene glycol was proposed by *S. Peng et al.*^[24] After synthesis, a silica coating was performed on the AgCl surface. TEM images of silver chloride and silica coated silver chloride (AgCl@SiO₂) nanoparticles are shown in Figure 3.6. Irradiation of the sample with an electron beam causes a reduction of silver chloride to silver. This can be found in Figure 3.6a and b. Obviously the particles shape was changed in TEM, but for Figure 3.6b the silica shell displays the former shape of the silver chloride nanoparticles. The silica shell was not affected by the electron beam, so it did not change in size and morphology. Shell thickness could be determined for the single silica coating steps by measuring the shell thickness with TEM. Silica shell was found to be 19 nm after the first coating and 45 nm after the second coating (Table 3.3).

Table 3.3. Particle radius (R_{TEM}) and silica shell thickness (t_{TEM}) of AgCl and AgCl@SiO₂ measured with TEM.

Sample	Coating step	R_{TEM} [nm]	t_{TEM} [nm]
AgCl	0	57 ± 12	-
AgCl@SiO ₂ -1	1	76 ± 17	19 ± 5
AgCl@SiO ₂ -2	2	121 ± 8	44 ± 2

Furthermore, FE-SEM investigations were performed on silica coated AgCl nanoparticles to obtain three dimensional images. Particles were found to be spherical or cubic in most cases. A FE-SEM image is displayed in Figure 3.6d.

**Figure 3.6.** TEM images of a) AgCl nanoparticles; b) Silica-coated AgCl nanoparticles after first coating (AgCl@SiO₂-1); c) Silica-coated AgCl nanoparticles after second coating (AgCl@SiO₂-2) and d) FE-SEM images of AgCl@SiO₂-2 nanoparticles.

3.3.2 Determination of Silica Shell Thickness and Surface Properties in Solution

Detailed investigations of particle size and shell growth during the coating steps were performed with DLS measurements in aqueous dispersion. Hydrodynamic diameters were found to increase with an increasing number of coating steps as to be expected (Table 3.4). Shell thickness could be calculated from DLS measurements to be 37 nm after the first coating and 83 nm after the second coating step. PDIs were found to stay nearly constant during the whole synthesis procedure.

Measured zeta potentials decreased with increasing silica shell thickness, as one would expect, indicating a successful silica coating. For nearly uncharged silver chloride nanoparticles covered with PVP, a zeta potential of -5.7 ± 7.9 mV was measured decreasing to -22.7 ± 7.1 mV after two silica coating steps. A zeta potential of around -20 mV is known to be typical for silica nanoparticles.

Table 3.4. Hydrodynamic radius (R_H), shell thickness (t_{DLS}), polydispersity index (PDI) and zeta potential (ζ) of different AgCl and AgCl@SiO₂ samples.

Sample	Coating step	R_H [nm]	t_{DLS} [nm]	PDI	ζ [mV]
AgCl	0	92.1	-	0.20	-5.7 ± 7.9
AgCl@SiO ₂ -1	1	128.7	36.6	0.16	-17.9 ± 6.9
AgCl@SiO ₂ -2	2	174.8	82.7	0.28	-22.7 ± 7.1

3.4 Water-Based Silica Coating Process with Functional Polyalkoxysiloxanes

The following results have already been published in part in *Particle & Particle Systems Characterization*, **2014**, 31, 365-373.^[1] In this paragraph, a water-based silica coating approach using reactive water-soluble polyalkoxysiloxanes (PEOS) is described. Coating hematite particles with silica using a water-based surfactant-free approach is of particular interest due to simplicity of this process. Using water as a solvent gives one the possibility to avoid multiple transfers of nanoparticle to different solvents. The

whole synthesis route can be performed in one solvent. Furthermore, water-soluble silica precursors, functionalized polyalkoxysiloxanes, work as source materials and adhesions promoters themselves. Silica precursors used here, polyalkoxysiloxanes, are hyperbranched polymers being hydrophobic in nature.^[25, 26] Water-solubility of the used PEOS is ensured by post-modification with poly(ethylene glycol) (PEG) chains.^[27, 28] Moreover it is possible to introduce further reactive groups, e.g. vinyl functionalities, during PEOS synthesis.^[27] In the following, PEG modified PEOS will be referred to as PEOS-PEG; vinyl and PEG modified PEOS will be referred to as PEOS-PEG-V. Figure 3.7 displays the chemical structure of PEOS-PEG-V.

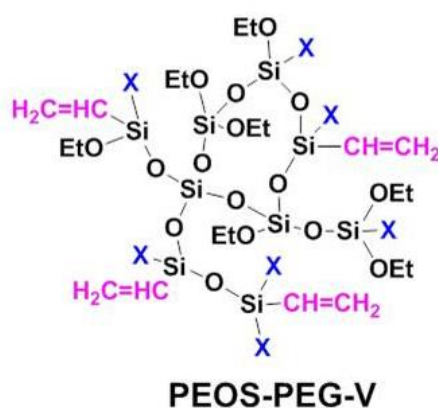
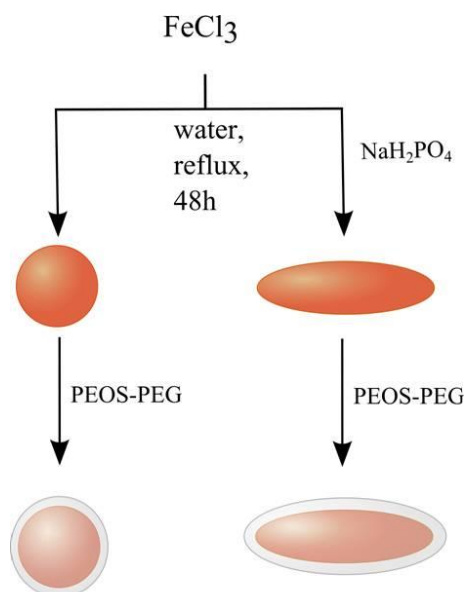


Figure 3.7. Chemical structure of functionalized hyperbranched polyalkoxysiloxane.^[1]

Dynamic light scattering experiments performed for the PEOS samples modified with vinyl and PEG functionalities showed no scattering, indicating the molecularly solubility of products. Modification degree with PEG of PEOS-PEG sample described in the following results is 20%. Modified PEOS-PEG-V sample shows 15% vinyl and 40% PEG functionalities.

In collaboration with Garima Agrawal, a reproducible synthesis of silica-coated functional hematite particles could be developed (Scheme 3.1).



Scheme 3.1. Hematite nanoparticle formation by following water-based surfactant-free silica coating process.

Simultaneous introduction of vinyl functionalities onto the silica shell is possible. The vinyl groups immobilized on the surface during formation of the silica shell are still reactive and accessible for further chemical modifications like thiol-en-click reactions.

3.4.1 Silica Coating of $\alpha\text{-Fe}_2\text{O}_3$ Nanoparticles with PEG-Functionalized Water-soluble PEOS

3.4.1.1 Size and Morphology Investigations

TEM investigations of hematite core silica shell nanoparticles synthesized in a water-based process using PEOS-PEG and PEOS-PEG-V as silica source showed exceptional shell formation on the particles. Shell formation depends on precursor concentration and hydrophobicity. In a step-by-step synthesis the shell growth was performed. To grow silica shell exclusively on hematite nanoparticles, polyalkoxysiloxane was added drop-by-drop keeping the over-all concentration of silica precursor in the solution low. The morphology, size and shell properties of core-shell nanoparticles were analyzed by using TEM (Figure 3.8a and b) and additionally DLS for spherical particles.

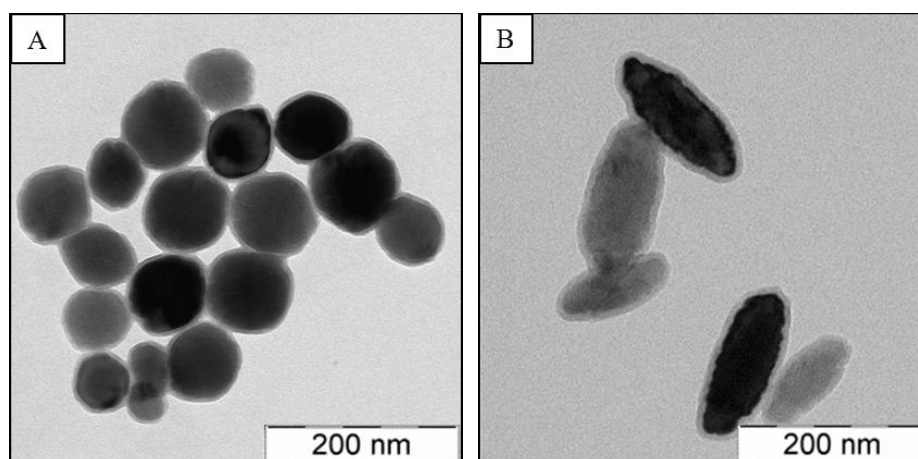


Figure 3.8. TEM pictures of a) spherical silica-coated hematite nanoparticles ($\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PP3}$) and b) ellipsoidal silica-coated hematite nanoparticles ($\alpha\text{-Fe}_2\text{O}_3\text{-el@SiO}_2\text{-PP3}$).

With TEM spherical hematite nanoparticles were found to have an average radius of 36 nm. An increase in size was measurable for particles coated with PEOS-PEG as a precursor. Moreover, silica appeared as a defined shell around the hematite particles due to different contrasts of both materials in TEM. The thickness of the silica shell was measured several times. Average results for shell thicknesses are mentioned in Table 3.5.

In addition to TEM measurements, light scattering methods offer the possibility to measure particle dimensions in dispersion excluding effects resulting from drying phenomena.

Table 3.5. Characteristic properties of spherical particles coated with PEOS-PEG; hydrodynamic radius (R_H) measured by DLS, particle radius obtained by TEM (R_{TEM}), thickness of SiO_2 layer (t_{TEM}).

Sample	R_H [nm]	R_{TEM} [nm]	t_{TEM} [nm]
$\alpha\text{-Fe}_2\text{O}_3\text{-sp}$	49	36 ± 2	-
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PP1}$	59	39 ± 4	2 ± 1
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PP2}$	60	42 ± 1	5 ± 1
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PP3}$	60	47 ± 5	10 ± 1

In DLS experiments performed in highly diluted aqueous dispersion, a hydrodynamic radius of 49 nm could be determined for the spherical hematite particles. After coating with silica, an average hydrodynamic radius of 60 nm was measured. Detailed information is summarized in Table 3.5.

Ellipsoidal particles were found to have a longitudinal axis of 134 nm and a transversal axis of 53 nm in TEM analysis. Particles appear very monodisperse having only a slight tendency to agglomerate. After coating hematite nanoparticles with silica using water-soluble PEOS-PEG, shell thickness of the layer could be measured with TEM for ellipsoidal as well as for spherical particles. Results are summarized in Table 3.6.

Table 3.6. Characteristic properties of ellipsoidal particles coated with PEOS-PEG; longitudinal axis (L_{TEM}) and transversal axis (T_{TEM}) measured by TEM, thickness of SiO_2 layer (t_{TEM}).

Sample	L_{TEM} [nm]	T_{TEM} [nm]	t_{TEM} [nm]
$\alpha\text{-Fe}_2\text{O}_3\text{-el-3}$	134 ± 3	53 ± 2	-
$\alpha\text{-Fe}_2\text{O}_3\text{-el-3@SiO}_2\text{-PP1}$	144 ± 6	63 ± 3	5 ± 1
$\alpha\text{-Fe}_2\text{O}_3\text{-el-3@SiO}_2\text{-PP2}$	155 ± 7	74 ± 7	11 ± 1
$\alpha\text{-Fe}_2\text{O}_3\text{-el-3@SiO}_2\text{-PP3}$	156 ± 4	75 ± 5	11 ± 1

Morphology of hematite particles does not seem to influence the coating process. A uniform coating irrespective of particle size and morphology together with a growth of shell thickness of about 2 to 6 nm per coating step were observed.

3.4.1.2 Investigation of Chemical Composition and Zeta Potential

After an investigation of size and morphology, further chemical and physical properties of core-shell nanoparticles were determined. FTIR spectroscopy and zeta potential measurements were used to verify the success of the surface modification of hematite nanoparticles by changes of surface properties detected by the two methods.

In FTIR spectra, characteristic signals for hematite were found at 584 and 482 cm^{-1} (Figure 3.9) known to be in compliance with other studies.^[29] In comparison to unmodified particles, FTIR spectrum for silica-coated particles show additional peaks

with respect to the modifying compound. $\alpha\text{-Fe}_2\text{O}_3@\text{SiO}_2$ hybrid samples show significant vibrational absorption of the asymmetric Si-O-Si vibration in the region between 1305 cm^{-1} and 1003 cm^{-1} .^[30] Another characteristic signal can be attributed to the -Si-OH vibration at 931 cm^{-1} .^[6, 30] $\alpha\text{-Fe}_2\text{O}_3@\text{SiO}_2\text{-V}$ samples show only slight differences compared to $\alpha\text{-Fe}_2\text{O}_3@\text{SiO}_2$. Characteristic bands for C=C-H and C-H bands in the region of $2900\text{-}3000\text{ cm}^{-1}$ are slightly increased.^[30]

Further information concerning the surface modification could be obtained by pH dependent zeta potential measurements. Hematite particles showed a strongly positive zeta potential in pH range between 3 and 7 (+17.2 mV till 0.1 mV) and negative values between 7 and 10 (0.1 mV till -41.2 mV). The isoelectric point (IEP) was to be found around pH 7. Zeta potentials for different spherical as well as ellipsoidal hematite particle species are summarized in Table 3.7.

Table 3.7. Zeta potential for spherical (ζ_{sp}) and ellipsoidal hematite nanoparticles (ζ_{el}) at pH 7.

Sample	Coating step	ζ_{sp} [mV]	$\zeta_{\text{el-3}}$ [mV]
$\alpha\text{-Fe}_2\text{O}_3$	0	3.1 ± 13.0	1.7 ± 8.0
$\alpha\text{-Fe}_2\text{O}_3@\text{SiO}_2\text{-PP1}$	1	-41.6 ± 6.3	-22.7 ± 7.7
$\alpha\text{-Fe}_2\text{O}_3@\text{SiO}_2\text{-PP2}$	2	-19.2 ± 9.8	-19.5 ± 6.1
$\alpha\text{-Fe}_2\text{O}_3@\text{SiO}_2\text{-PP3}$	3	-39.6 ± 8.8	-22.9 ± 3.2

Figure 3.10 shows pH dependent zeta potential curves for different nanoparticles species. Compared to non-coated particles,^[31] the surface charge of hybrid particles was strongly negative even for acidic pH range. For pH 3 zeta potential of silica-coated nanoparticles was slightly positive (+3.3 mV). The point of no charge could be determined at around pH 4. For alkaline pH values like pH 10, a strongly negative surface charge of around -32.0 mV was measured.^[32,33]

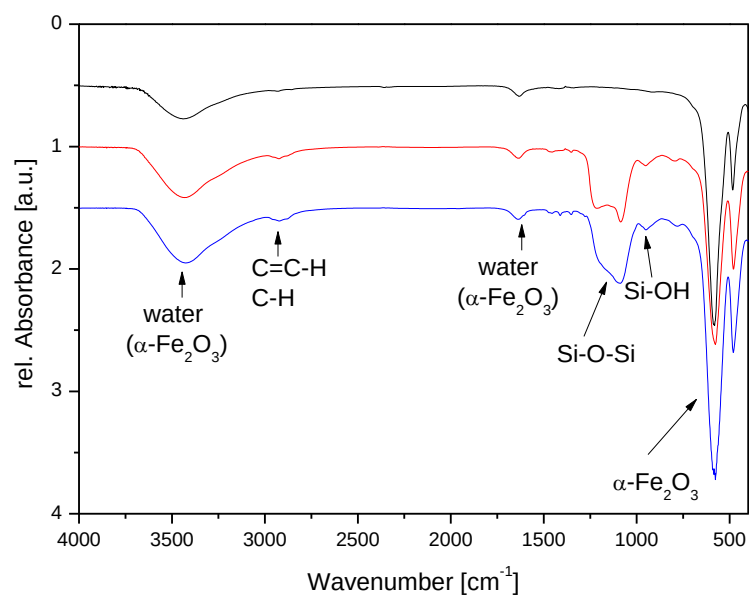


Figure 3.9. FTIR spectra of pure hematite particles, $\alpha\text{-Fe}_2\text{O}_3\text{-sp}$, (black) and silica-coated hematite particles, $\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PP1}$, (red) and hematite nanoparticles coated with vinyl-functionalized SiO_2 , $\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV}$, (blue).

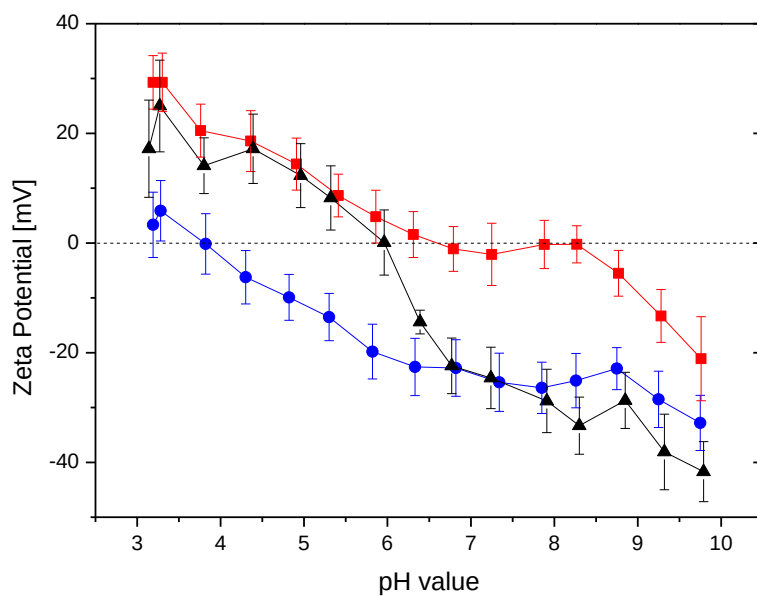


Figure 3.10. pH dependent zeta potential measurements for $\alpha\text{-Fe}_2\text{O}_3\text{-sp}$ (black), silica-coated $\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV}$ (blue) and cysteamine functionalized $\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV@Cys}$ nanoparticles (red).

3.4.2 Silica Coating of α -Fe₂O₃ Nanoparticles with Vinyl Pre-functionalized PEOS-PEG and Post-modification of Shell with Cysteamine

In another experiment, PEOS-PEG-V (PPV) was used for the coating of spherical hematite particles with vinyl functionalized silica. In this paragraph, I will show possibilities to prove that vinyl groups are accessible for further modifications. As model reaction, a photocatalytic reaction with cysteamine was performed.

3.4.2.1 Colloidal Stability Measurement for Different Modification Steps

To show reactivity of double bonds immobilized to the nanoparticle surface, pH dependent zeta potential measurements for non-coated hematite particles, silica-coated hematite nanoparticles before and after modification with cysteamine are shown in Figure 3.10. α -Fe₂O₃-sp@SiO₂-PPV@Cys particles showed a highly positive charged surface in the acidic pH range, +29.3 mV for pH 3, due to protonation of amine groups fixed on the surface. For alkaline pH values (pH 10), amine groups are deprotonated again and a negative zeta potential of -21.1 mV could be measured. Isoelectric point was found to be around pH 6.5.

Colloidal stability of α -Fe₂O₃-sp, α -Fe₂O₃-sp@SiO₂-PPV and α -Fe₂O₃-sp@SiO₂-PPV@Cys nanoparticle dispersions was compared by analyzing sedimentation behavior of nanoparticles for three different pH values by using an analytical centrifuge. An integrated optoelectronic sensor system allows spatial and temporal changes of light transmission to be detected during the rotation. The transmission increases with centrifugation duration since particles move to the bottom of the cell. Throughout the measurement, transmission profiles were recorded and the sedimentation process can be shown as a time course of relative position of the boundary between supernatant and sediment (Figure 3.11).

The slope of the linear regions for the curves presented in Figure 3.11 is equal to the sedimentation velocity of colloids. According to Stokes' Law, the sedimentation velocity for diluted samples is proportional to the square of the radius of the particles and their difference in density to the continuous phase

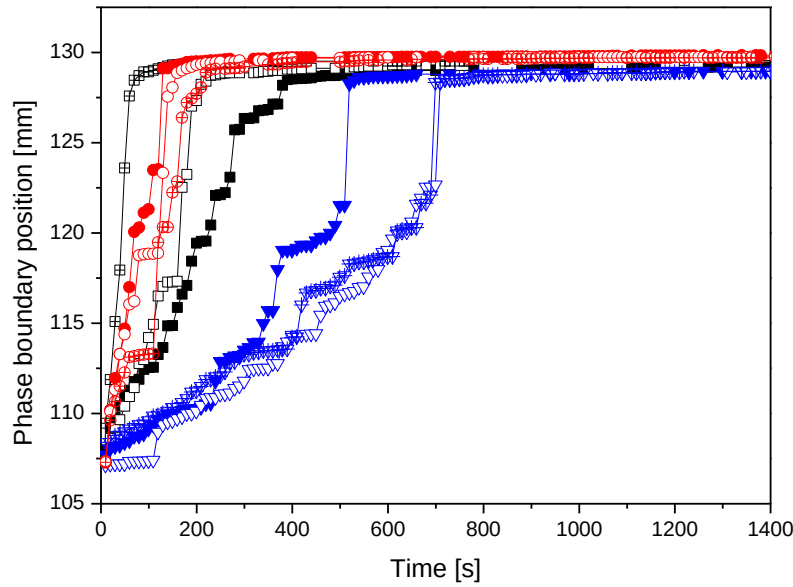


Figure 3.11. Sedimentation curves for different pH values (pH 5 solid symbols, pH 7 open symbols, pH 9 open symbols with cross) measured for non-coated $\alpha\text{-Fe}_2\text{O}_3\text{-sp}$ (black), silica-coated $\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV}$ (blue) and cysteamine functionalized $\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV@Cys}$ nanoparticles (red) (centrifugation speed: 1,000 rpm, 20°C).

Equation 2.1 (Paragraph 2.2.3) is an ideal model to describe the phenomenon of sedimentation influenced mainly by particle size, viscosity and centrifugal acceleration not considering any interparticle interactions. But also other factors influence the process of sedimentation, for example interparticle forces causing attraction and repulsion of particles. In this system, the size of the nanoparticles does not change considerably after coating with silica shell and modification with cysteamine. Therefore, the surface charge of the particles and magnetic attraction should be considered as strong influencing forces. Silica shells are known to reduce the interparticle magnetic attraction^[34] of particles avoiding clustering as could be shown in Paragraph 2.2.3.

The sedimentation curves, measured for pH 5, 7 and 9, showed minor sedimentation velocity for $\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV}$ in comparison to the two other particle species. The uncoated spherical hematite particles as well as cysteamine functionalized $\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV@Cys}$ particles show significantly higher sedimentation speed. Correlated with the pH dependent zeta potential measurements, it is possible to show that $\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV}$ nanoparticles offer a higher colloidal stability due to a very

efficient electrostatic stabilization over a pH range from pH 5 to 10. Comparing $\alpha\text{-Fe}_2\text{O}_3\text{-sp}$ and $\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV}$ at pH 9, a similar zeta potential was found but completely different sedimentation behavior was observed due to different surface properties of particles. The sedimentation velocities calculated for the pH values 5, 7 and 9 are summarized in Table 3.8.

Table 3.8. Sedimentation velocities for $\alpha\text{-Fe}_2\text{O}_3\text{-sp}$, silica-coated $\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV}$ and cysteamine functionalized $\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV@Cys}$ nanoparticles (centrifugation speed: 1,000 rpm, 20°C).

Sample	Sedimentation velocity [$\mu\text{m/s}$]			
	pH	5	7	9
$\alpha\text{-Fe}_2\text{O}_3\text{-sp}$		54.9 ± 1.3	90.2 ± 9.3	154.8 ± 5.4
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV}$		27.2 ± 2.6	17.6 ± 0.9	17.3 ± 0.9
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV@Cys}$		170.9 ± 10.9	137.3 ± 7.3	93.9 ± 7.5

It was found that sedimentation speed for highly charged $\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV}$ nanoparticles is significantly lower for all three pH values than for the other two samples. $\alpha\text{-Fe}_2\text{O}_3\text{-sp}$ nanoparticles showed a high tendency to agglomerate at pH 9, therefore sedimentation occurs faster. But as discussed earlier, the sedimentation velocity of a nanoparticle is not only influenced by the zeta potential but also by other attractive and repulsive forces. The reduction of magnetic interactions caused by the silica shell might be an explanation for the higher stability of $\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV}$ in comparison to $\alpha\text{-Fe}_2\text{O}_3\text{-sp}$ even if the zeta potential of both species is similar at pH 9.

3.4.2.2 UV-VIS and Fluorescence Spectroscopic Analysis of Fluorescence Labeled Nanoparticles ($\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV@RITC}$)

Functionalization of amino groups with the fluorescence dye rhodamine B is a common way to make amino functionalities visible for UV-VIS spectroscopy. The reaction of amino-functionalities with isothiocyanate modified rhodamine B (RITC) is a well-known and easy reaction, which offers the possibility for an indirect proof of reactive amino groups on the particles surface in this case.

For analysis, UV-VIS absorption spectra were normalized by intensity of the most intense band. Figure 3.12 shows UV-VIS spectra of cysteamine functionalized nanoparticles ($\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV@Cys}$) as well as RITC-labeled particles ($\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV@RITC}$).

The signals found at 260 nm and 410 nm are known to be the main absorption bands for nanosized hematite nanoparticles, reported previously by *Chernyshova et al.*^[35] Those two signals were found to be strong for the cysteamine functionalized hematite nanoparticles. For RITC-labeled hematite nanoparticles, an additional absorption band was found at 522 nm which clearly refers to RITC.

A difference spectrum was calculated from the two spectra shown in Figure 3.13 to reduce the influence of the hematite nanoparticles absorption. The difference spectrum calculated was compared to a spectrum measured for pure RITC (Figure 3.13). The RITC reference spectrum shows a very strong characteristic peak for 550 nm which was found to be red shifted in the spectra for immobilized RITC to the particle surface.

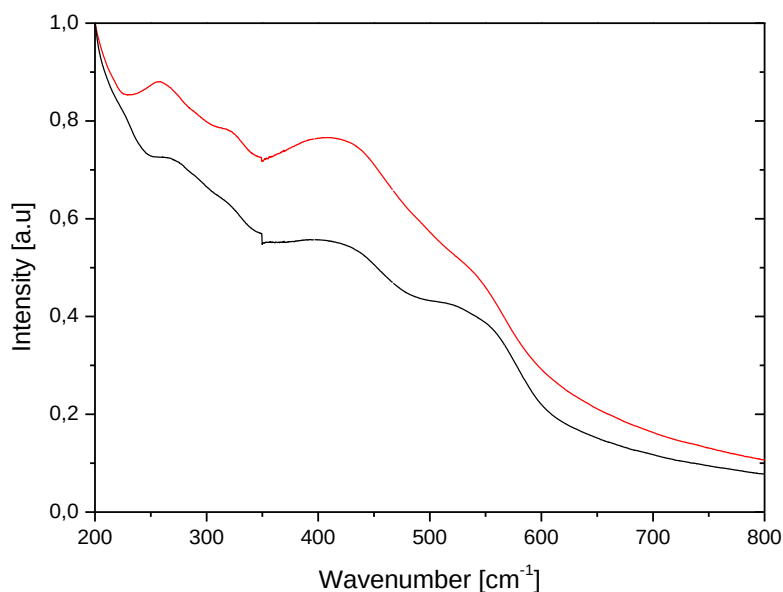


Figure 3.12. UV-VIS spectra for $\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV@Cys}$ (red) and $\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV@RITC}$ (black).

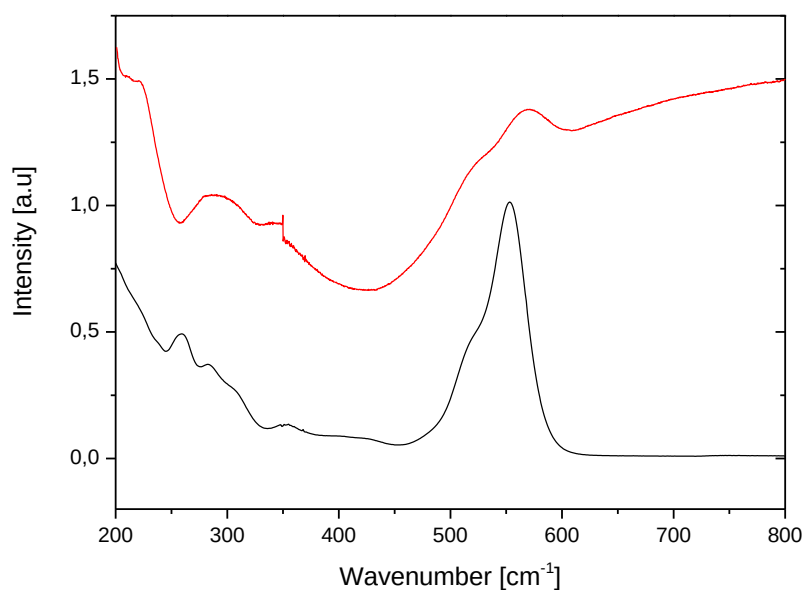


Figure 3.13. UV-VIS spectrum for rhodamine B isothiocyanate as reference (black) and difference spectrum calculated from Figure 3.12 (red).

Besides its UV-VIS absorption properties, rhodamine B shows fluorescence properties. For the RITC-labeled hybrid nanoparticles, excitation and emission spectra were measured by fluorescence spectroscopy; moreover, the spectra were normalized for further analysis (Figure 3.14). A very characteristic peak is known to be found at 500 nm in excitation spectra for RITC. For immobilized RITC mentioned maximum is shifted to 450 nm. A shift to lower wavelength could also be observed for the emission spectra. The characteristic maximum for RITC was found at 580, but at 535 nm for immobilized RITC.^[36]

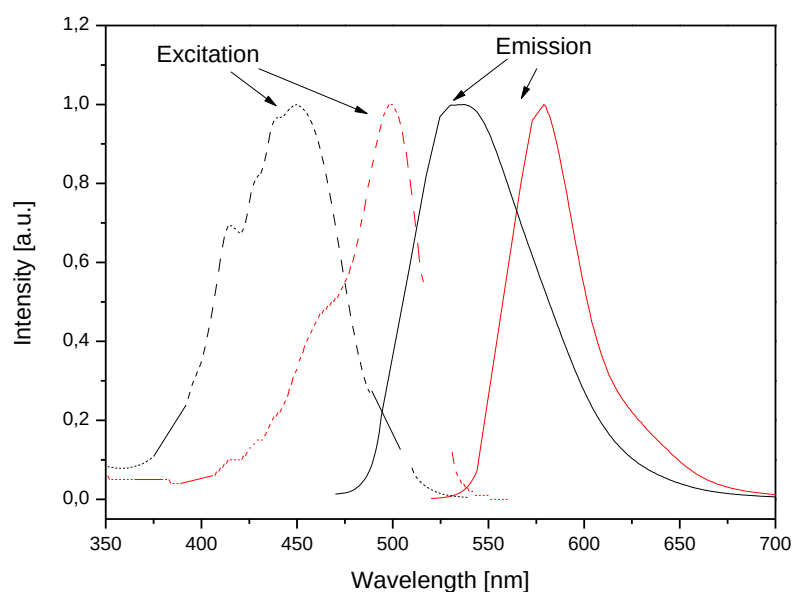


Figure 3.14. Fluorescence spectra of RITC (black) and $\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV@RITC}$ (red) (excitation spectra dashed line, emission spectra drawn line).

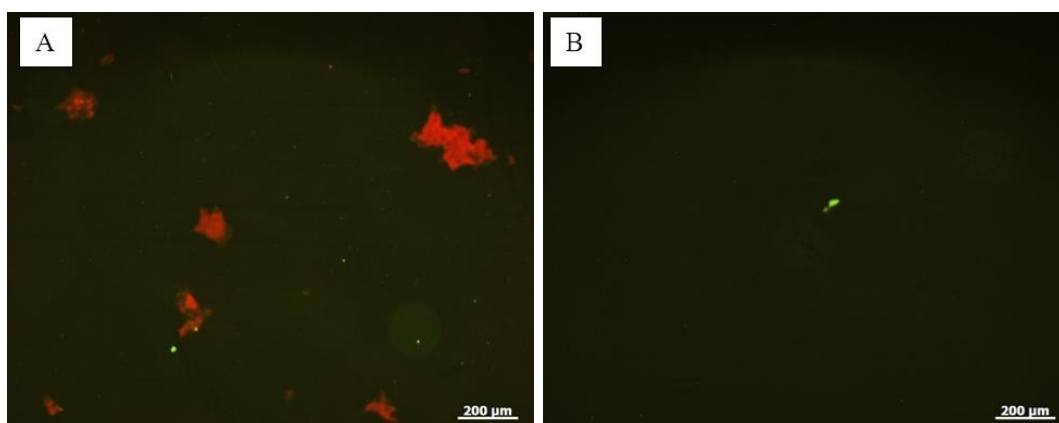


Figure 3.15. Fluorescence microscopic images for a) rhodamine B labeled hematite particles ($\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV@RITC}$) and b) not labeled hematite nanoparticles ($\alpha\text{-Fe}_2\text{O}_3\text{-sp@SiO}_2\text{-PPV@Cys}$).

Figure 3.15a shows a fluorescence micrograph of agglomerates of rhodamine B labeled hematite particles showing red fluorescence due to the RITC immobilization to the surface. Single particles cannot be displayed due to the deficient resolution of the optical microscope. As a reference, particles having no RITC-label were measured showing no red fluorescence.

3.5 Summary

In the first part of the chapter it could be shown that there is only a marginal influence of molecular weight of PVP on the coating process within the range of 10 to 55 kg · mol⁻¹. The hematite particles used here could be coated by using TEOS as a silica source in the classical method. The increase of the silica shell was followed by TEM, DLS and USAXS. For all methods a growth of the shell was found in the range of approximately 5 to 10 nm per coating step. For method described, it is necessary to transfer hematite nanoparticles pre-functionalize with PVP from water to ethanol as solvent.

Therefore, it could be shown that this method could be successfully transferred to AgCl nanoparticles. AgCl nanoparticles were synthesized having a radius of 57 nm. Shell growth was investigated with TEM and DLS. For TEM measurements an increase of approximately 20 nm per coating step was measured. In DLS experiments a nearly doubled value was determined. It should be noticed that here the hydrodynamic radius is measured which normally appears to give higher values than TEM measurements. Additionally zeta potential was measured. AgCl nanoparticle showed nearly no charge on the surface, while the zeta potential dropped strongly after silica coating.

In contrast to the classical methods described previously, addition of adhesion promoters and stabilizers, such as surfactants or polymers, is avoided using pre-functionalized water-soluble PEOS-PEG and PEOS-PEG-V as silica sources. This approach is described in the second part of the chapter. The development of an easy and efficient water-based synthetic route to obtain functional and stable silica-coated hematite particles was performed successfully. The method displayed allows simultaneous formation of the silica shell around hematite core as well as incorporation of reactive groups, here vinyl groups, on the surface of core shell nanoparticles. The reactivity of surface-immobilized vinyl groups was proven by modifying the surface with cysteamine in a thiol-ene reaction followed by labeling with rhodamine B isothiocyanate. Another convincing advantage of a water-based coating process with PEOS-PEG is the avoidance of solvent transfer during particles synthesis and coating process.

For these samples, the shell growth was also studied with methods such as TEM and DLS. An increase of 2 to 5 nm per coating step was measured. Zeta potential measurements and FTIR spectra also proved the presence of SiO₂ on the particle surface. In a pH range of 3 to 10, three different samples were analyzed regarding their surface charges. For pure hematite nanoparticles, a positive zeta potential was found in a range of pH 3 to 7. Below that (pH 7 to 10), negative zeta potentials were measured. For hematite nanoparticles with SiO₂ a negative zeta potential was measured over almost the whole pH range. With an amination of the vinyl groups using cysteamine, an indirect proof of the reactivity of the vinyl groups was given. The zeta potentials measured strongly increased for this sample and were found to be positive over nearly the whole pH range. Further modification of these amino groups with rhodamine B isothiocyanate (RITC) offered a detection of these groups with UV-VIS and fluorescence spectroscopy.

3.6 Experimental

3.6.1 Synthesis of $\alpha\text{-Fe}_2\text{O}_3\text{@SiO}_2$ using TEOS as Precursor and PVP as Adhesion Promoter

Spherical and ellipsoidal hematite nanoparticles were synthesized as described in Chapter 2. Before silica coating can be performed particles need to be pre-functionalized with PVP. Therefore 7.9 g PVP was dissolved in 120 mL and stirred overnight. On the following day, 45.57 mg of hematite nanoparticles were mixed with the PVP solution for 24 h after which the particles were sedimented by centrifugation and directly redispersed in 12 mL ethanol. To the ethanolic dispersion of pre-functionalized hematite nanoparticles 80 mL ethanol, 7 mL water and 1 mL of tetramethylammonium hydroxide (TMAH) solution (1% v/v aqueous solution) were added. After 15 min, the addition of a TEOS/ethanol mixture (ratio 2:1) was started. Using a peristaltic pump, 0.2 mL of the mixture was added every 20 min until a total volume of 1.2 mL TEOS had been added. The dispersion was purified by repeated centrifugation and washing with ethanol. For a step-by-step growth of the silica shell, the coating was repeated up to five times analogous to the method described above.

3.6.2 Synthesis of AgCl@SiO_2 using TEOS Precursor and PVP as Adhesion Promoter

Silver chloride nanoparticle synthesis was performed according to a method proposed by S. Peng *et al.*^[24] In a typical synthesis, sodium chloride (70.2 mg, 1.20 mmol) and poly(vinylpyrrolidone) ($M_w = 10$ kg/mol) (30.0 mg, 0.003 mmol) were dissolved in 33 mL ethylene glycol and heated to 60°C. For a second solution, silver nitrate (153 mg, 0.90 mmol) was dissolved in 3 mL ethylene glycol. Upon reaching a stable temperature the second solution was added to the first solution rapidly. The solution turned turbid immediately after the addition. The reaction was heated to 60°C for a further 30 min. Later the dispersion was cooled down to room temperature. Finally 10 mL water was added and the dispersion was purified by repeated centrifugation and washing with aqueous PVP solution. First time dispersion was centrifuged for 30 min with a

centrifugation speed of 7,000 rpm. This step was followed by two washing steps with 15 mL aqueous PVP solution (5.0 wt-%). In between each washing step, the sample was centrifuged for 10 min with a centrifugation speed of 7,000 rpm. Afterwards, AgCl nanoparticles were redispersed in 30 mL ethanol by ultrasonification. Silver chloride nanoparticles were kept in darkness to avoid reduction to silver by light.

The following steps need all to be performed without exposure of the sample to light. For the silica coating, silver chloride nanoparticles were diluted with ethanol to a total volume of 244 mL. 21 mL distilled water and 3 mL of an aqueous TMAH solution (1% v/v) were added. Using a peristaltic pump, 0.6 mL of a ethanolic TEOS solution (ratio TEOS/EtOH 2:1) were added every 10 min until a total volume of 4.8 mL TEOS had been added. Reaction was stirred overnight at room temperature. For purification, coated silver chloride particles were sedimented by centrifugation (7,000 rpm, 10 min) and washed with distilled water three times. Afterwards, particles were dispersed in 5 mL distilled water. Silica shell thickness could be increased by repeating the coating process several times.

3.6.3 Silica Coating of α -Fe₂O₃ Nanoparticle using PEOS-PEG as Silica Precursor

Spherical as well as ellipsoidal hematite silica core-shell nanoparticles were prepared in an aqueous solution using PEOS-PEG as a silica precursor. PEOS-PEG was synthesized by Garima Agrawal. Experimental details can be found in her dissertation.^[37] Spherical and ellipsoidal hematite particles were coated using a step-by-step base catalyzed condensation reaction PEOS-PEG to obtain a silica shell. Therefore 10 mL distilled water was added to 45 mg of hematite particles. As a catalyst, 1 mL of ammonia solution (25% aqueous solution) was added to the dispersion. By using a syringe pump, 0.6 mL PEOS-PEG was added whilst stirring with a constant rate for over 30 min followed by further stirring for 3 h until the condensation reaction was completed. Purification of the particles was performed by repeated centrifugation followed by washing three times with distilled water using an ultrasonic bath for redispersion of the particles. To increase the shell thickness the whole coating procedure was repeated up to three times.

3.6.4 Silica-Coating of α -Fe₂O₃ Nanoparticles using PEOS-PEG-V as Silica Precursor

By using vinyl-functionalized water-soluble PEOS-PEG (PEOS-PEG-V) as a precursor, spherical hematite nanoparticles modified with additional functional vinyl groups on the surface (α -Fe₂O₃-sp@SiO₂-PPV) were synthesized analogous to the method described above. For the synthesis, PEOS-PEG-V was used which was functionalized with vinyl groups as well as PEG functionalities.

3.6.5 Amination of α -Fe₂O₃@SiO₂-PPV Nanoparticle Surface with Cysteamine by Thiol-ene Click Reaction and Labeling with RITC

In a photocatalytic thiol-ene click reaction, the amination of α -Fe₂O₃-sp@SiO₂-PPV was performed by clicking cysteamine to the vinyl groups. To perform the reaction, 69 mg cysteamine and 23 mg 2,2-dimethoxy-2-phenylacetophenone (DMPAP) were dissolved in 50 mL distilled water. 25 mg α -Fe₂O₃-sp@SiO₂-PPV was added to this aqueous solution. Reaction was carried out for 3 h during UV irradiation with a wavelength of 356 nm. Following, for purification of the obtained α -Fe₂O₃-sp@SiO₂-PPV@Cys, particles were centrifuged and washed with distilled water for three times.

After amination of the particle surface, a labeling with the fluorescent dye RITC was performed. For the labeling 44 mg rhodamine B isothiocyanate (RITC) were solved in 7.5 mL distilled water. Following 5 mL particles dispersion containing 4 mg α -Fe₂O₃-sp@SiO₂-PPV@Cys were added. Dispersion was stirred overnight at room temperature. Afterwards, the product (α -Fe₂O₃-sp@SiO₂-PPV@RITC) was centrifuged and washed with distilled water for five times followed by further purification by dialysis against water for four days.

3.6.6 Sample Preparation and Measurement Conditions

The device designations of instruments used for the measurements can be found in the Appendix I.

For the preparation of the TEM samples a drop of the particle dispersion was trickled on a piece of formvar and carbon coated copper grid. Before being placed into the TEM specimen holder, the copper grid was air-dried under ambient conditions.

For FE-SEM measurements, the sample was dropped onto a thin layer of aluminum foil. After drying the foil was transferred to a sample holder.

ImageJ[®] and WinTEM[™] software was employed to process the TEM digital images to analyze the particle size and morphology. At least 100 particles were measured.

For DLS one drop of the dispersion is diluted with 5 mL of distilled water. For measurements 1 mL of the diluted dispersion was used.

For pH dependent zeta potential measurements one drop of the dispersion was diluted in 2 mL of distilled water. For further measurements one drop of this diluted dispersion is dropped into 1 mL of a solution with a pH ranging from 3 to 11. 0.8 mL of this dispersion was used for the measurements.

USAXS measurements were performed for diluted samples. Therefore, one drop of the dispersion was diluted with 5 mL of distilled water. Afterwards, the dispersion was filled in a capillary with a diameter of 1.5 mm.

For UV-VIS and fluorescence spectroscopy one drop of the dispersion was diluted with 5 mL of distilled water. Afterwards, the measurements were performed for 1 mL of the dispersions.

For sample preparation of IR measurements, samples were dried and few mg of the sample was measured in KBr.

For fluorescence microscopy the dispersion was dropped on a glass waver. After drying the waver was measured with the fluorescence microscope.

The sedimentation velocities were determined for dispersions as prepared. Therefore, 0.4 mL dispersion was filled in a special cuvette. The centrifugation speed was chosen to be 1,000 rpm.

3.7 References

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4 Asymmetric Multi-Compartment Nanoparticles

4.1 Introduction

Bottom-up synthesis of multi-compartment nanoparticles has been in the focus of scientists for many years now.^[1] A lot of work has been done in this field to design small size building blocks offering multi-functionalities which can find applications in the fields of electronics, catalysis, sensor technology and biomedicine.^[2, 3] Especially the design of more complex nano-architectures obtained directly from solution and further scaling-up the synthesis are very challenging tasks.^[4, 5] For the formation of Janus-type nanoparticles several mechanisms have been proposed, including selective surface modification^[6], polymer-based direct synthesis^[4, 7] as well as phase separation on particle surface^[8]. Among spherical or core-shell particles, nanoparticles with less symmetry, e.g. lemon-shaped particles or dumbbells^[9, 10], are of particular interest. All methods proposed so far to synthesize dumbbell structures describe a preferential asymmetrical overgrowth of a second component on a previously formed seed particle.^[11] It seems trivial, but this asymmetric growth needs to be energetically favored above symmetric growth or a separate nucleation.^[11]

Besides the direct contact of two or more components providing multiple chemical functionalities, dumbbell-shape nanoparticles offer additional features due to their special shape. In several studies it was shown that asymmetric multi-compartment nanoparticles can be assembled into even more complex structures.^[12, 13]

However, easy and reproducible synthetic approaches which enable up-scaling for those building blocks are still rarely found in the literature. In this chapter I will establish a simple method for building up lemon-shape and dumbbell-like nanoparticles from solution.

4.2 Hematite Nanoparticle – Asymmetric Coating with Different Copolymers

Asymmetric multi-compartment particle synthesis was performed on the basis of work previously reported by Feyen *et al.* in 2010.^[4] In a seeded emulsion polymerization process starting from an oil-in-water emulsion induced by pre-functionalized ellipsoidal hematite nanoparticles^[14], asymmetric multi-compartment nanoparticles are synthesized. For pre-functionalization, 16-heptadecenoic acid (HAD, Figure 4.1) is used.

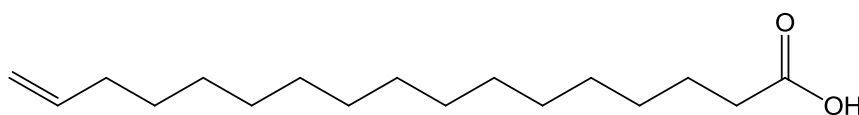


Figure 4.1. Chemical structure of 16-heptadecenoic acid.

A broad variety of copolymers with variation of molar ratios and hydrophobicity is attached to the hematite nanoparticles surface. In this chapter, different copolymers consisting of varying compositions of the monomers styrene, divinylbenzene (DVB), glycidyl methacrylate (GMA) and *N*-vinylcaprolactam (VCL) (Figure 4.2) were considered.

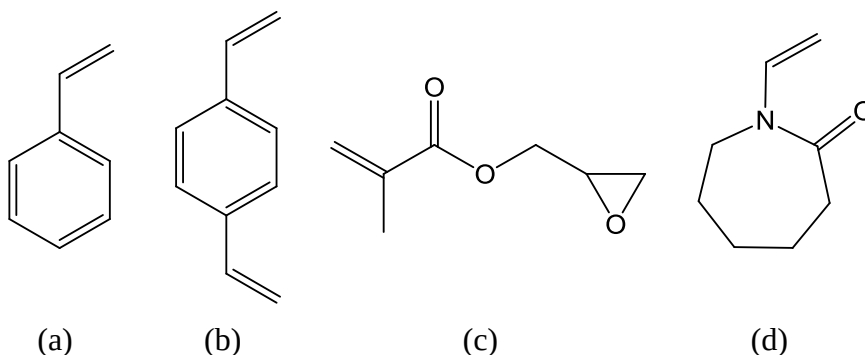


Figure 4.2. Chemical structures of the monomers a) styrene, b) divinylbenzene, c) glycidyl methacrylate and d) *N*-vinylcaprolactam.

4.2.1 Asymmetric Coating of Hematite Nanoparticles with PS-co-GMA-co-DVB

4.2.1.1 Step-by-Step Growth of PS-co-GMA-co-DVB Polymer Shell- Investigation with TEM, TGA and FTIR

In this paragraph, the step-by-step increase of polymer shell on the hematite particles is shown. This method offers the possibility to increase shell thickness. After the first coating it is clearly visible from Figure 4.3a, that an asymmetric polymer coating could be deposited onto the ellipsoidal hematite nanoparticle. The tips of the ellipsoids seem to stay uncoated. This sample is called $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-SW-1}$ for further reference; the sample after the second coating step is called $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-SW-2}$.

As can be seen from the TEM image in Figure 4.3b, the shell thickness was increased a number of times comparing coating step one to coating step two. The polymer shell growth predominantly perpendicular to the longitudinal axis of the nanoparticles, but the tips of the ellipsoids now seem to be completely covered with polymer now. Furthermore, it can be observed, that the surface of the polymer layer becomes rougher in comparison to the sample which was only coated once.

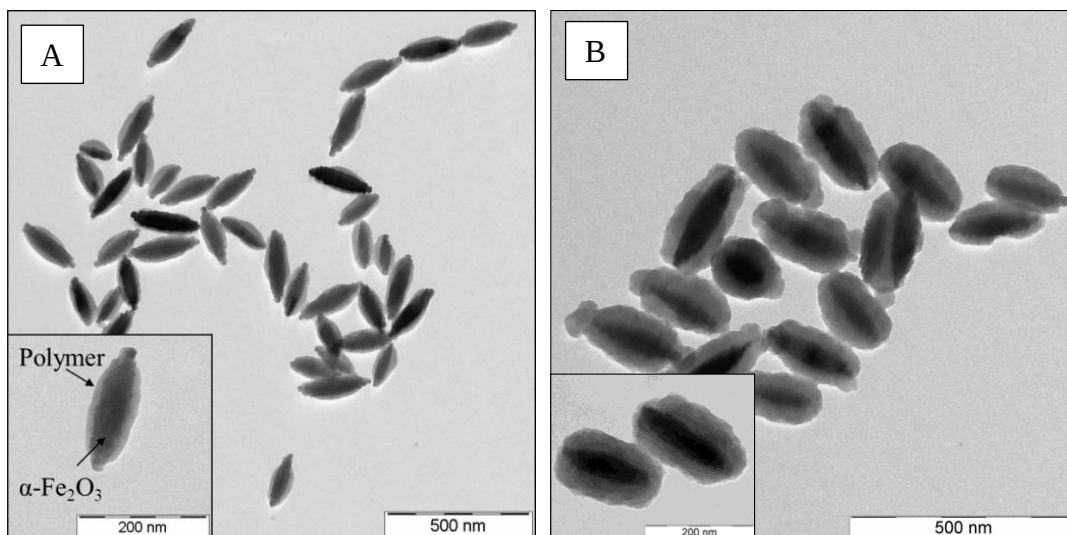


Figure 4.3. TEM images of $\alpha\text{-Fe}_2\text{O}_3\text{@PS-co-GMA-co-DVB}$ after a) first coating ($\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-SW-1}$) and b) second coating ($\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-SW-2}$).

TG analysis was used to measure the ratio of hematite to polymer for the step-by-step growth (Figure 4.4). The copolymer was combusted within a range of 30 to 500 °C and only inorganic material, here $\alpha\text{-Fe}_2\text{O}_3$, remained. The weight loss correlates to the

polymer mass in the sample. The initial weight loss, region $T < 120$ °C, is due to loss of a small water amount from the composite. The thermal decomposition of the C–C backbone and complete polymer degradation takes place within the region from 120 to 500 °C. The residual mass remaining after heating of the samples to 500 °C can be related to the α -Fe₂O₃ nanoparticles which remain undecomposed under these conditions.

Comparing TGA measurements performed for a sample coated once and the same sample coated twice, the increase of polymer coating has been found to be tripled after the second coating step. The polymer mass in the sample was increased from 16% to 51%.

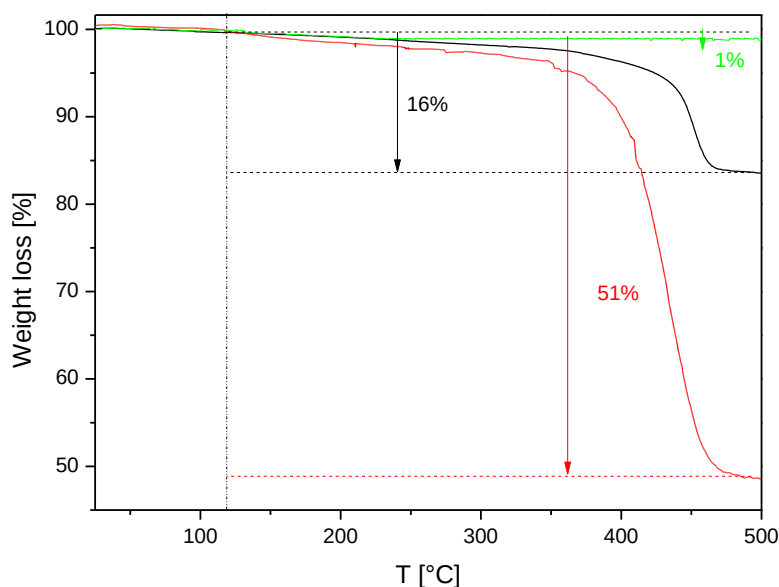


Figure 4.4. TGA measurements for a sample after first (α -Fe₂O₃@PSGD-SW-1, black) and second (α -Fe₂O₃@PSGD-SW-2, red) polymer coating and pure hematite nanoparticles (α -Fe₂O₃, green) (N₂ atmosphere, heating rate: 10 K/min).

It can therefore be concluded that the polymer shell applied during the first coating works properly as an anchorage for the following polymerization. Monomer diffuses into the already attached polymer shell and starts polymerizing there. This process is continued the surface of the polymer layer leading to a strong increase of the polymer layer as well as surface roughness.

The increase of polymer shell thickness described can also be followed by FTIR spectroscopy (Figure 4.5). Characteristic signals for hematite as well as for the copolymer were detected. For comparison all spectra were normalized to the characteristic peaks of hematite in the fingerprint region. The intensity of characteristic peaks for the polymer was found to become stronger after the second coating. The strongest peaks can be assigned to functional groups of the polymer shell. Peaks in the region from 3083 to 3023 cm^{-1} can be assigned to the C-H stretching of the benzene rings referring to styrene and divinylbenzene. Further stretching vibrations were found for the CH_3 group at 2925 and 2852 cm^{-1} . A very small peak was detected at 1727 cm^{-1} . This peak is related to the C=O stretching of the carbonyl group referring to GMA. A broad peak around 1630 cm^{-1} also refers to the aromatic rings, but is typical for hematite, too. Presumably several peaks are overlaid in this part of the spectrum making the detection of characteristic groups challenging in this region. CH_2 vibrations were found in the region around 1500 cm^{-1} . Typical peaks for ring deformation of aromatic rings with various numbers of substituents were found in the region of 900 to 700 cm^{-1} . Peaks at lower wavenumbers can be clearly assigned to hematite.^[15]

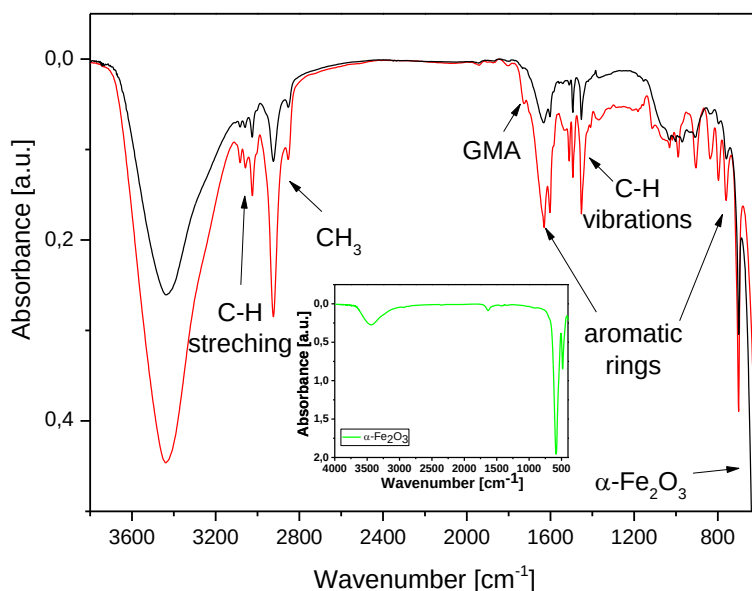


Figure 4.5. FTIR spectra of $\alpha\text{-Fe}_2\text{O}_3\text{@PS-co-GMA-co-DVB}$ after the first coating ($\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-SW-1}$, black) and after the second coating ($\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-SW-2}$, red), inset: FTIR spectrum of $\alpha\text{-Fe}_2\text{O}_3$ (green).

4.2.2 Influence of Monomer Concentration on the Asymmetric Coating Process

4.2.2.1 Investigation of Shell Growth with TEM, IR and TGA

In a series of three different concentrations, the influence of the monomer to hematite nanoparticle ratio on the asymmetric polymer coating was investigated. Figure 4.6 illustrates how a low monomer concentration (sample $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-C-1}$) results in an island formation of polymer on the hematite seed. An increase of the monomer concentration (sample $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-C-2}$) leads to asymmetric coated multi-compartment particles with free tips. Further increase of the monomer concentration leads to the formation of core-shell particles with complete coverage of the $\alpha\text{-Fe}_2\text{O}_3$ core.

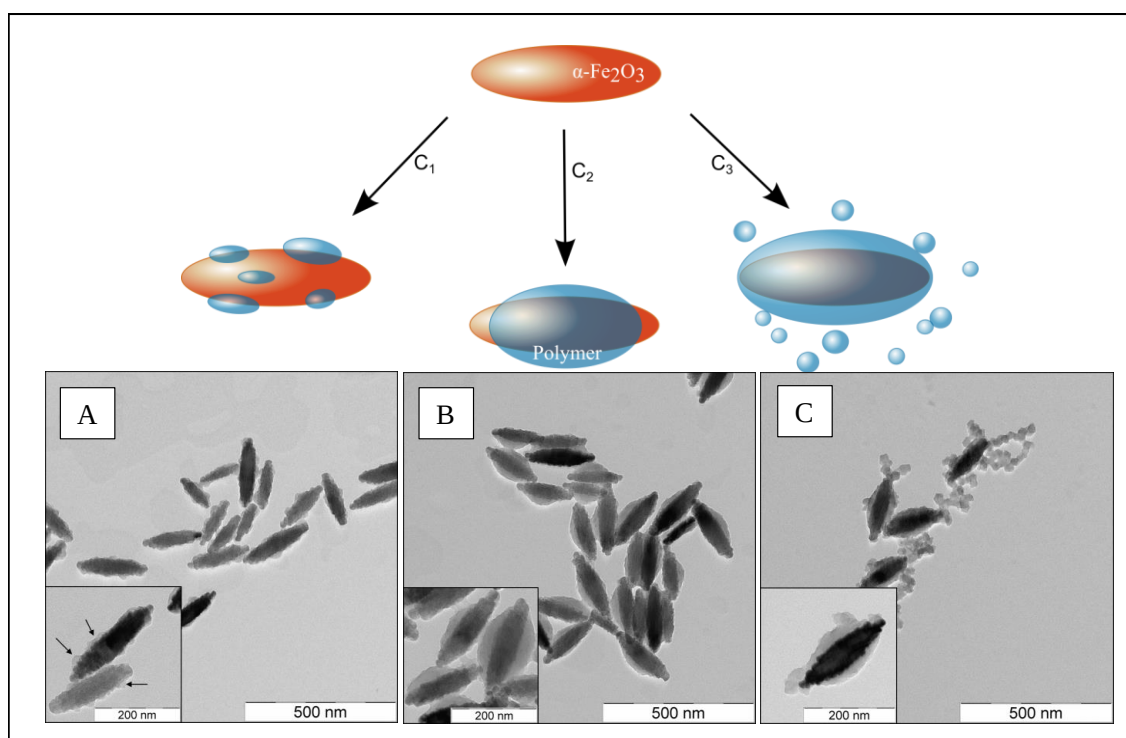


Figure 4.6. Dependence of monomer concentration on asymmetric polymer coating process of ellipsoidal hematite nanoparticles: from left to right $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-C-1}$; $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-C-2}$ and $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-C-3}$.

In addition, exceeding a critical concentration, as shown for sample $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-C-3}$, lead to a strong secondary particle formation. The polymer layer becomes more and rougher. It was not observed that the polymer shell thickness increases significantly

when comparing samples $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-C-2}$ and $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-C-3}$. It is assumed that there is a critical monomer concentration during the synthesis that limits the polymer deposition onto the ellipsoidal hematite nanoparticles. A further increase of the concentration leads to a preferred secondary particle formation instead of continuous growth of polymer shell.

Besides the proof of chemical composition, FTIR spectroscopy, which was shown in Figure 4.5, can also give an indication of the hematite to polymer ratio attached to the nanoparticle surface. The FTIR spectra displayed in Figure 4.7 were normalized to a typical hematite peak in the fingerprint region for more exact comparability of the peak intensities. In the concentrations series displayed in the graph below, it was found that the peak intensity increases with increasing polymer concentration. These increases can be followed especially for peaks around 2900 cm^{-1} , 1630 cm^{-1} and 1500 cm^{-1} indicating an increase in polymer containing aromatic rings as they are found in styrene and DVB.^[15]

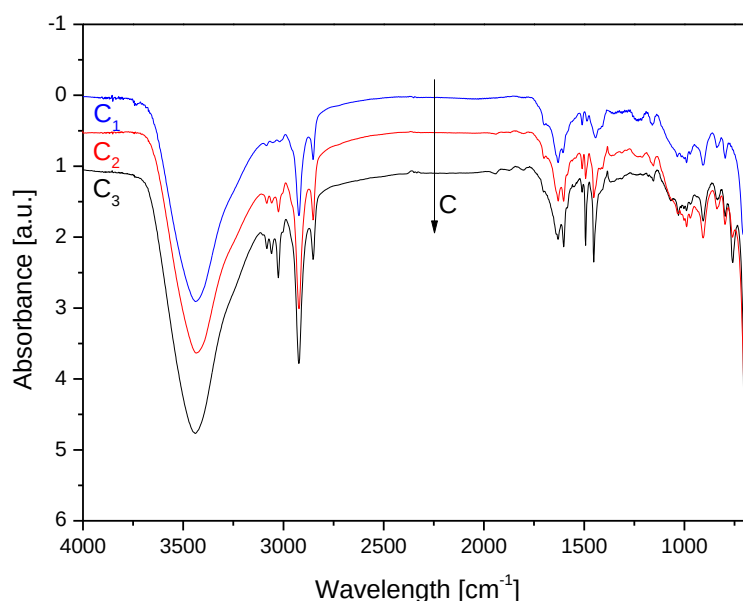


Figure 4.7. IR spectra of $\alpha\text{-Fe}_2\text{O}_3\text{@PS-co-GMA-co-DVB}$ samples with three different hematite to polymer ratios: $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-C-1}$ (blue); $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-C-2}$ (red) and $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-C-3}$ (black).

The observations from IR spectra are confirmed by the TGA results (Figure 4.8). Here an increase in the hematite to polymer ratio was detected. For concentrations from

sample $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-C-1}$ to $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-C-3}$ a gradual increase of polymer from 15% to 33% was observed.

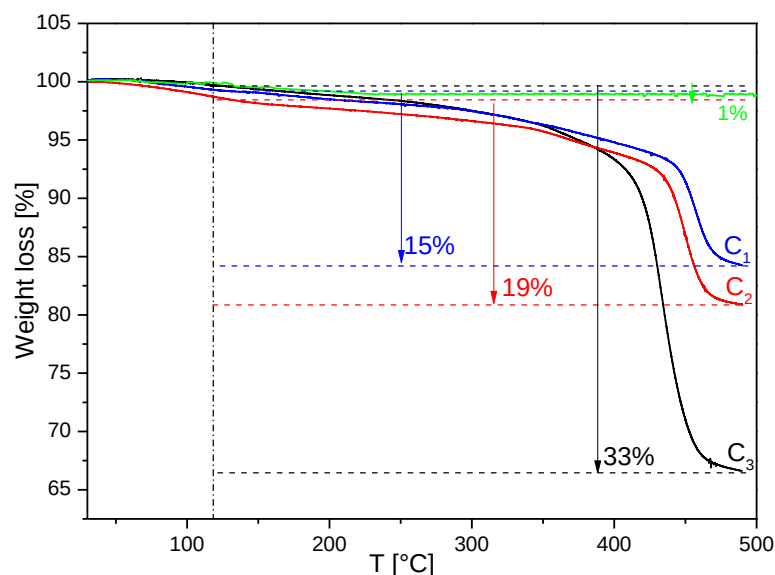


Figure 4.8. TGA spectra of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles (green), $\alpha\text{-Fe}_2\text{O}_3\text{@PS-co-GMA-co-DVB}$ samples with three different hematite to polymer ratios: $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-C-1}$ (blue); $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-C-2}$ (red) and $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-C-3}$ (black) (N_2 atmosphere, heating rate: 10 K/ min).

All three analysis methods are consistent with concerning the results. The TGA curve of sample $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-C-3}$ indicates that there is a maximum amount of polymer which can be deposited on the hematite particle surface during one coating process. A further increase of the monomer concentration leads to a strong formation of secondary polymer particles in solution, which have to be removed in several washing steps.

4.2.3 Influence of Monomer Hydrophilicity on Polymer Shell Structure

After changing the copolymer composition to more hydrophilic monomers, a change in the shell structure can be observed. The shell becomes less asymmetric as observed for lemon-shaped nanocomposites with very hydrophobic copolymers. But functional monomers like *N*-vinylcaprolactam (VCL) offer some interesting properties e.g.

biocompatibility and temperature sensitivity. Three dimensional cross-linked networks containing a remarkable amount of VCL as a copolymer are known to show a volume phase transition (VPT) for a certain temperature. Nanocomposites presented here show less asymmetry as systems described above, but offer a good possibility of a hard core and a soft shell with a tunable shell thickness depending on temperature.

4.2.3.1 Cryo-TEM and TEM Investigation on Thermosensitive $\alpha\text{-Fe}_2\text{O}_3\text{@PS-co-VCL-co-DVB}$ Nanocomposites

To obtain nanocomposites with a more hydrophilic polymer shell GMA, was exchanged with *N*-vinylcaprolactam (VCL). The TEM image for sample $\alpha\text{-Fe}_2\text{O}_3\text{-el@PSVD}$ (Figure 4.9a) show that the nanocomposites are not lemon-shaped anymore like sample $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-C-2}$ with the more hydrophobic polymers. But the TEM image also show a non-symmetric growth of the shell around the particles. For the longitudinal axis of the core-shell nanoparticle an average value of 257 ± 32 nm and a transversal axis of 174 ± 11 nm was determined.

In Figure 4.9b, a cryo-TEM image of the same sample is displayed showing the core-shell nanocomposite in the swollen state. It seems that there is not a significant difference between dried state and swollen state. A closer look shows that the shell decreases slightly in the dried state. The shell thickness is increased, so the total size of the nanocomposite has grown to 282 ± 21 nm for the longitudinal axis and to 192 ± 12 nm for the transversal axis. That is a difference of about 25 nm for the longitudinal axis and about 18 nm for the transversal axis.

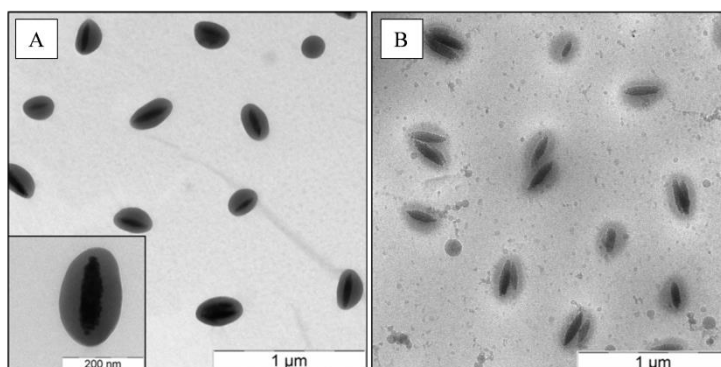


Figure 4.9. a) TEM image and b) cryo-TEM image of ellipsoidal $\alpha\text{-Fe}_2\text{O}_3\text{-el@PSVD}$ nanoparticles (molar ratio of styrene to VCL 1:1).

For further investigations of e.g. temperature sensitivity of the functional shell, a sample with an spherical hematite core and an identical copolymer shell as in sample $\alpha\text{-Fe}_2\text{O}_3\text{-el@PSVD}$ was synthesized (Figure 4.10b). Furthermore, two more samples are shown here with different polystyrene to PVCL ratios. Figure 4.10 shows the respective TEM image for sample $\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-3}$, $\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-1}$ and $\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-0.5}$. The numbers at the end of the sample names indicate the molar ratio of PVCL. E.g. sample $\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-3}$ has a molar ratio of PS to PVCL of 1 to 3.

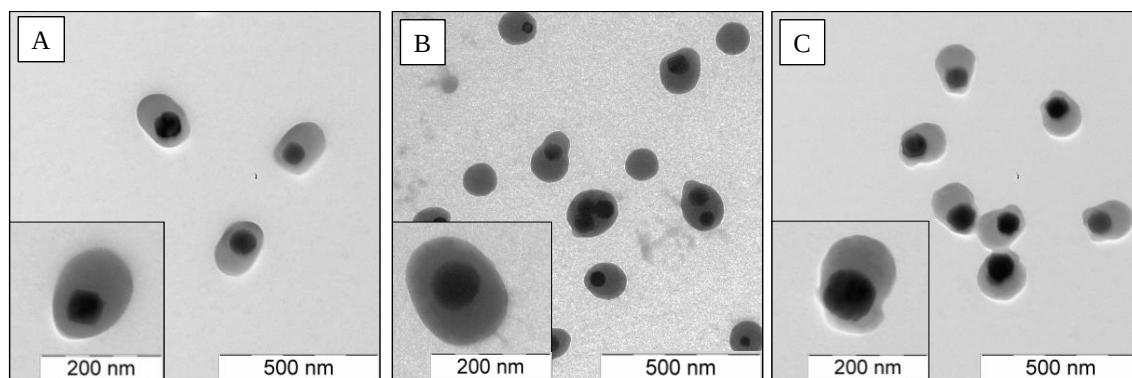


Figure 4.10. TEM image of spherical $\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-3}$ (molar ratio of PS to PVCL 1:3), $\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-1}$ (molar ratio of PS to PVCL 1:1). $\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-0.5}$ (molar ratio of PS to PVCL 1:0.5).

4.2.3.2 IR and TGA Investigation on Thermosensitive $\alpha\text{-Fe}_2\text{O}_3\text{@PS-co-VCL-co-DVB}$

As already shown in the previous paragraphs, IR investigations give a detailed insight in the chemical composition of the multi-compartment particles. The spectrum displayed below (Figure 4.11) for sample $\alpha\text{-Fe}_2\text{O}_3\text{-el@PSVD}$ shows characteristic peaks for the CH_2 vibration in the polymer backbone and aromatic rings around 2900 cm^{-1} indicating a successful polymerization of the monomers. Additionally, signals for C-H vibration in aromatic rings, as are found in the structures of styrene and DVB, can be found between 700 and 800 cm^{-1} . Another very strong peak can be determined at 1639 cm^{-1} . This peak can be assigned to the C=O vibration of VCL.^[15]

Additionally to the chemical composition investigated by IR spectroscopy, the ratios of hematite to polymer were determined with TG analysis (Figure 4.12). Both samples analyzed were prepared identically.

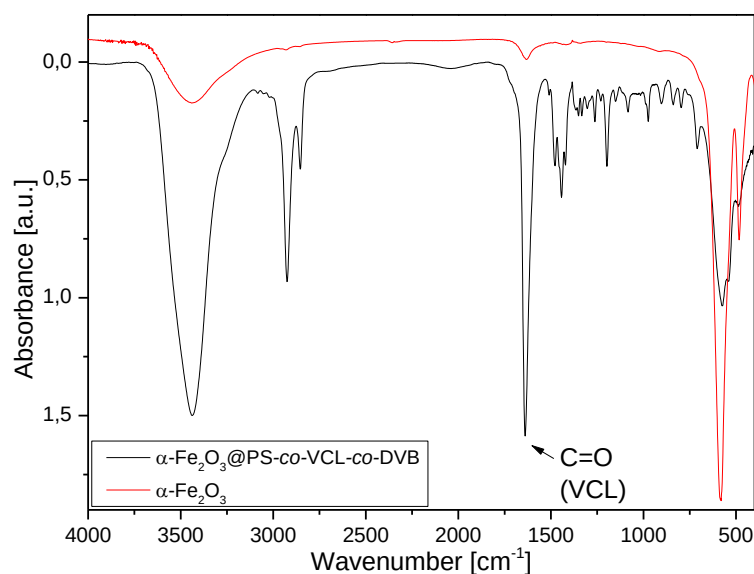


Figure 4.11. IR spectra for $\alpha\text{-Fe}_2\text{O}_3\text{-el@PS-co-VCL-co-DVB}$ nanoparticles ($\alpha\text{-Fe}_2\text{O}_3\text{-el@PSVD}$, black) and hematite nanoparticles ($\alpha\text{-Fe}_2\text{O}_3\text{-el}$, red).

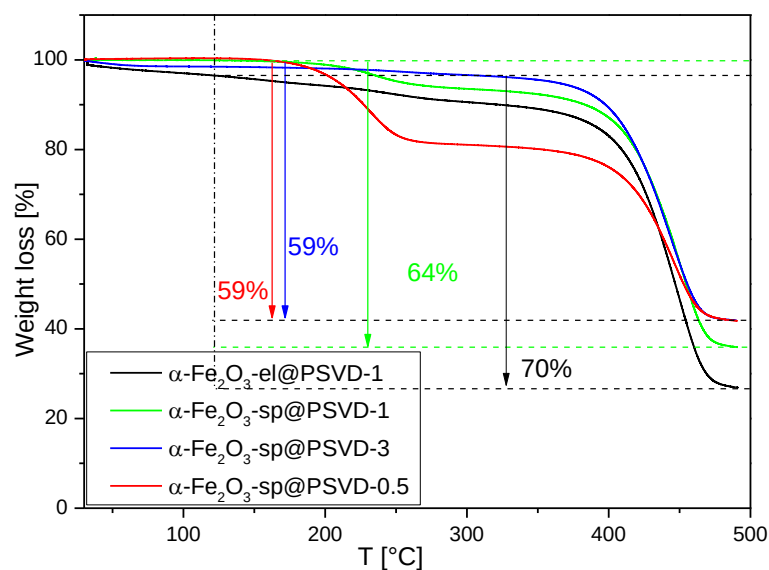


Figure 4.12. TGA spectra of $\alpha\text{-Fe}_2\text{O}_3\text{@PSVCL}$ samples with an ellipsoidal core ($\alpha\text{-Fe}_2\text{O}_3\text{-el@PSVD-1}$, black) and spherical cores ($\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-1}$, green; $\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-3}$, blue; $\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-0.5}$, red) and hematite core (N_2 atmosphere, heating rate: 10 K/ min).

Only the shape of the core was varied. It was found that the polymer coating was almost identical. Polymer content in both samples was found to be 70% for ellipsoidal particles

(α -Fe₂O₃-el@PSVD-1). For samples with spherical cores, namely α -Fe₂O₃-sp@PSVD-3, α -Fe₂O₃-sp@PSVD-1 and α -Fe₂O₃-sp@PSVD-0.5 the weight losses were found to be very similar for all samples ranging from 60 to 64%. These results are found to be as expected because only the ratios of monomers not the total amounts were varied during the synthesis.

4.2.3.3 Temperature Dependent DLS Investigations on Thermosensitive α -Fe₂O₃@PS-co-VCL-co-DVB

Three dimensional cross-linked polymers made from VCL, so-called PVCL microgels, are known to show a volume phase transition for moderate temperatures around 30°C. Not only homopolymers, but also copolymers are known to show VPT in aqueous dispersion.

In order to investigate the thermosensitive behaviour of the composite system in dispersion, spherical nanoparticle are more suitable. DLS measurements for more complex geometric objects are not trivial and the ellipsoidal shape of the nanoparticle strongly influences the results of the DLS measurements. So the temperature-sensitivity measurements were performed for spherical objects in order to reduce the deviation due to differences in diffusion depending on the shape. In general, all previous results indicate also these results can be transferred to ellipsoidal system as well.

Instead of ellipsoidal α -Fe₂O₃-el@PSVD nanoparticles, nanocomposites with identical composition were analyzed having spherical hematite core (α -Fe₂O₃-sp@PSVD) (Figure 4.10).

Figure 4.13 shows the temperature dependent DLS measurements for sample α -Fe₂O₃-sp@PSVD-3, α -Fe₂O₃-sp@PSVD-1 and α -Fe₂O₃-sp@PSVD-0.5 in a temperature range of 15 to 45°C. The curves for α -Fe₂O₃-sp@PSVD-3 and α -Fe₂O₃-sp@PSVD-1 show a high swelling of the polymer shell for 15°C followed by a deswelling with increasing temperature. For low temperatures the shell was found to swell 1.7 to 2.0 times more than for high temperatures. From the first derivative of the fitted curve, a volume phase transition temperature (VPTT) of 27°C was determined for both samples. This VPTT was found to be slightly lower than for pure VCL microgels which is known to be around 30°C^[16]. The shift of the VPTT is because of the hydrophobicity of polystyrene

segments inserted into the hydrogel layer. The presence of the hydrophobic polystyrene segments induces the collapse of the polymer network at lower temperatures due to the low solvation of polymer chains by water molecules. For sample $\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-0.5}$ only a slight decrease in size was determined. The properties of hydrophobic polystyrene segments are predominant reducing the temperature-sensitivity of the polymer shell strongly.

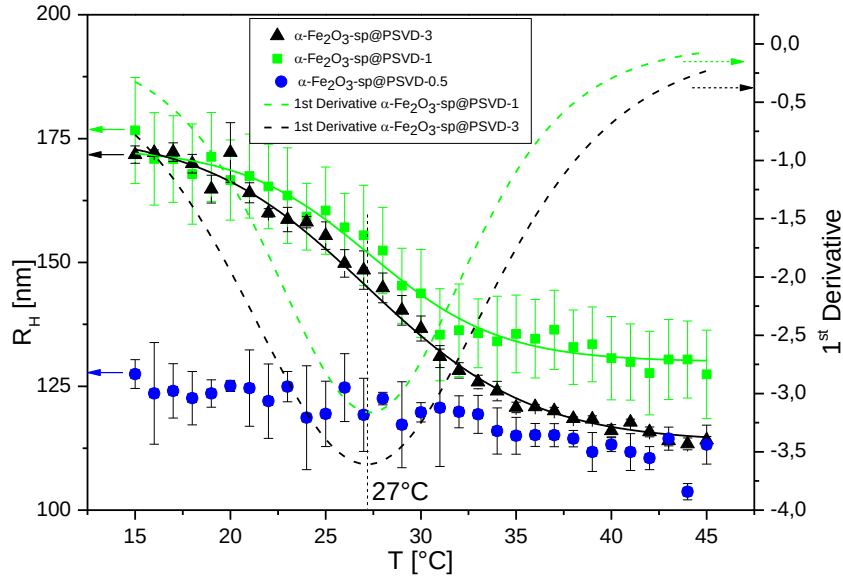


Figure 4.13. Temperature dependent DLS measurements of $\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-3}$ (black), $\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-1}$ (green) and $\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-0.5}$ (blue).

To analyze the data measured in more detail, the shell thickness was determined for the swollen state at 15°C and for the collapsed shell at 45°C with the Equations 4.1 and 4.2:

$$t_{15^\circ\text{C}} = R_{H,\text{sample}}^{15^\circ\text{C}} - R_{H,\alpha\text{-Fe}_2\text{O}_3}^{15^\circ\text{C}} \quad (4.1)$$

$$t_{45^\circ\text{C}} = R_{H,\text{sample}}^{45^\circ\text{C}} - R_{H,\alpha\text{-Fe}_2\text{O}_3}^{45^\circ\text{C}} \quad (4.2)$$

From these values the swelling ratio σ could be calculated with Equation 4.3.

$$\sigma = \frac{t_{15^{\circ}\text{C}}}{t_{45^{\circ}\text{C}}} \quad (4.3)$$

The values measured and calculated values for sample $\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD}$ can be found in Table 4.1. Additionally, the radius measured with TEM was added to the table to compare the values. The TEM results were found to be in consistency with the values derived from DLS.

Table 4.1. Hydrodynamic radii (R_H) and shell thickness (t) for 15 and 45°C, swelling ratio (σ) and average radii determined with TEM (R_{TEM}) for a reference sample $\alpha\text{-Fe}_2\text{O}_3\text{-sp}$ and $\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-3}$, $\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-1}$ and $\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-0.5}$.

Sample	$R_H^{15^{\circ}\text{C}}$ [nm]	$R_H^{45^{\circ}\text{C}}$ [nm]	$t_{15^{\circ}\text{C}}$ [nm]	$t_{45^{\circ}\text{C}}$ [nm]	σ	R_{TEM} [nm]
$\alpha\text{-Fe}_2\text{O}_3\text{-sp}$	52 ± 5	53 ± 7	-	-	-	36 ± 7
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-3}$	172 ± 2	114 ± 1	120	61	2.0	145 ± 12
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-1}$	177 ± 11	127 ± 9	125	74	1.7	151 ± 23
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-0.5}$	128 ± 2	113 ± 2	76	60	1.2	138 ± 25

4.2.4 Discussion of Formation Mechanism

Summarizing all the previous observations, the following mechanism can be proposed for the asymmetric polymer coating (Figure 4.14). In a first step, hematite spindles were functionalized with 16-heptadecenoic acid. Here a double layer of deprotonated surfactant was applied to the hematite surface in basic medium. The particles were electrostatically stabilized by repulsion of same charges on the particle surfaces. After addition of the monomers, the outer surfactant layer diffused to the monomer-water interface and started stabilizing the monomer droplet around the hematite particle. This mechanism was proposed by M. Feyen^[19] in 2010. The addition of the water-soluble initiator starts the radical formation in water. The radicals diffuse into the monomer

layer where the polymerization is started. A solid polymer is formed which is attached to the hematite nanoparticle surface.

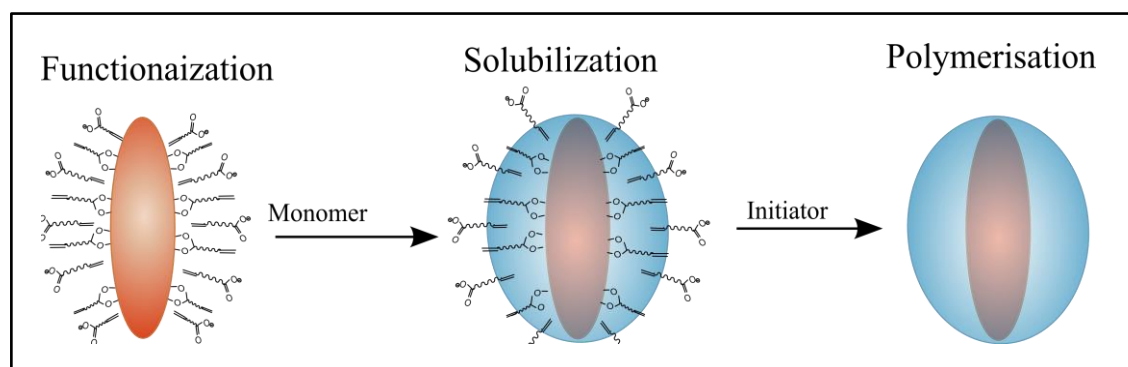


Figure 4.14. Scheme of the formation mechanism of asymmetric hematite/polymer nanoparticles proposed here.

An explanation of the limitation of the monomer volume solubilized by the hematite spindle can be found in the work done by *Scanna et al.* They proposed a new type of particle-stabilized emulsion in 2007.^[14] The emulsification of the oil seems to be inverted in contrast to Pickering emulsion meaning that the inorganic particle is located inside the oil droplet. It was observed that a volume of oil which can be emulsified by one ellipsoidal hematite nanoparticle is limited. It corresponds to a sphere with the radius equal to the major spindle semi-axis. This is the reason for the formation of secondary polymer particles when the monomer concentration is too high.

By combining both works, an explicit insight into the mechanistic details can be given.

4.3 Selective Silica Growth on Asymmetric Hematite Polymer Hybrid Nanoparticles

Starting from the asymmetric hematite-polymer nanoparticles mentioned in the previous paragraph, a formation of dumbbell-type nanoparticles is described here. I will show that silica can be grown selectively on the free edges of the hybrid particles.

4.3.1 TEM Investigations of Dumbbell-Shape Multi-Compartment Nanoparticles

In the following experiments the special characteristics of silica were used to create nanoparticles which were even more asymmetric than those described in the previous paragraph. Silica is known to have a high affinity to oxidic surfaces.^[17] But it shows a minor tendency to grow on hydrophobic polymer surfaces consisting of styrene and styrene-copolymers without any anchor group.^[18] If both surfaces are present in the system, silica is expected to start growing on the oxidic surface. This assumption could be proved by TEM images presented in Figure 4.15 showing precisely all three different materials combined to dumbbell shape multi-compartment nanoparticles. The ellipsoidal hematite cores show the highest contrast in TEM due to their high density. The polymer shell appears lighter around the longitudinal axis of the cores. Silica can be clearly distinguished from the polymer shell because of its darker color. It is located at the edges of the particles appearing to be more or less spherical.

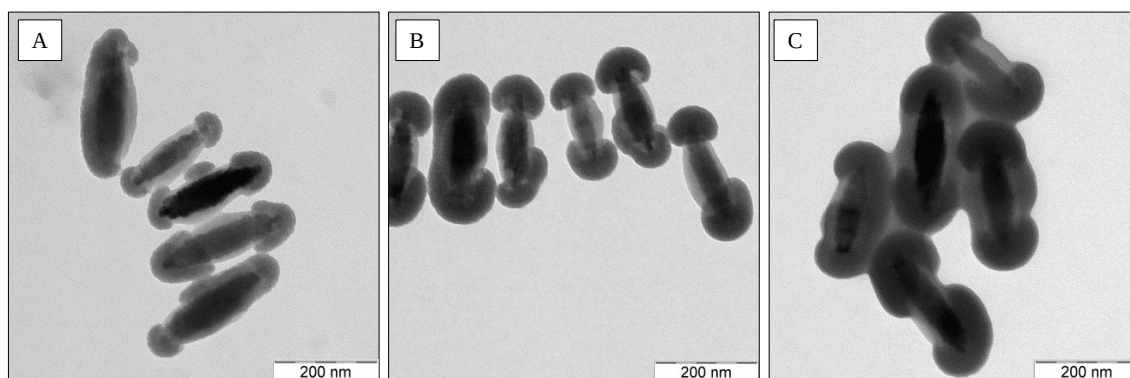


Figure 4.15. TEM images of hematite-polymer hybrid particles coated with different amounts of silica: a) $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD@SiO}_2\text{-C1}$; b) $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD@SiO}_2\text{-C2}$ and c) $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD@SiO}_2\text{-C3}$.

4.3.2 FE-SEM and EDX Analyses of Dumbbell Shape Multi-Compartment Nanoparticles

Dumbbell-shaped structures were analyzed simultaneously by FE-SEM, STEM and EDX analysis. Figure 4.16a shows a FE-SEM overview image of the sample $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD@SiO}_2\text{-C1}$. It is clearly visible that almost all multi-compartment

particles are dumbbell-shaped. A closer look is given by Figure 4.16b-d showing FE-SEM and STEM images as well as EDX mapping for the same image. The combination of the three methods give information about the three dimensional shape (FE-SEM), as well as the distribution of materials (STEM and EDX). The EDX image clearly shows where the three main elements iron (yellow), silicon (red), and carbon (blue) used are located.

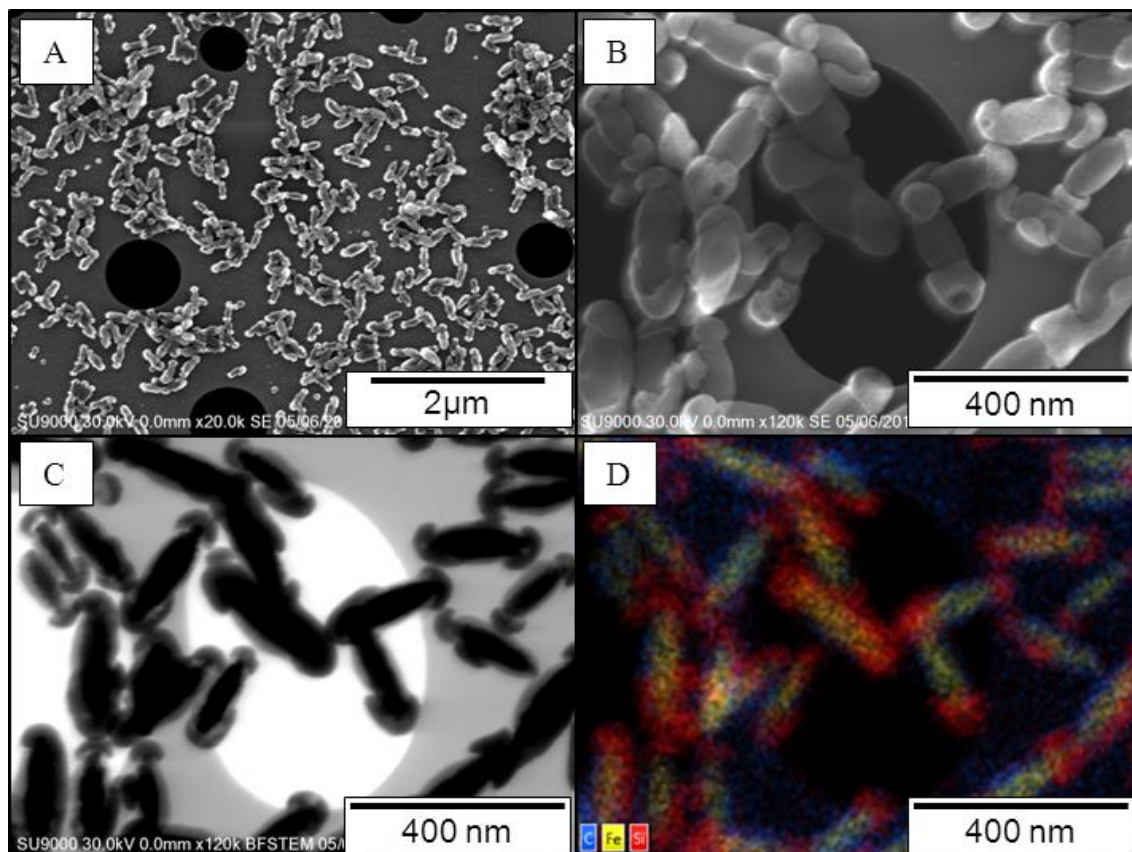


Figure 4.16. FE-SEM of $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD@SiO}_2\text{-C1}$ a) overview; b) detailed FE-SEM image; c) STEM image and c) EDX mapping.

4.3.3 FTIR Investigations of Chemical Composition of $\alpha\text{-Fe}_2\text{O}_3\text{@PS-co-GMA-co-DVB@SiO}_2$ Nanoparticles

Additionally to the morphology, the chemical composition of multi-compartment particles was investigated with FTIR spectroscopy. Figure 4.17 shows FTIR spectra comparing samples of $\alpha\text{-Fe}_2\text{O}_3$, $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-C2}$ and $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD@SiO}_2\text{-C1}$. It was found that silica deposition was successful, which is indicated by the strong peak at 1099 cm^{-1} . Furthermore, all characteristic peaks for hematite and the polymer coating

can also be found in the spectra. Due to the high intensity of the Si-O-Si vibration band, all other characteristic peaks decrease strongly.

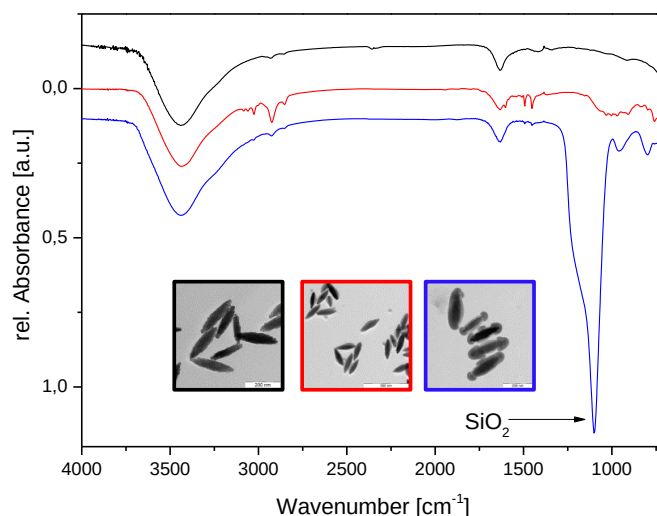


Figure 4.17. FTIR spectra of α -Fe₂O₃ (black), α -Fe₂O₃@PSGD-C2 (red) and α -Fe₂O₃@PSGD@SiO₂-C1 (blue).

4.3.4 TGA and Zeta Potential Analyses on Dumbbell Shape Multi-Compartment Nanoparticles to Investigate SiO₂ Content

To determine the SiO₂ content deposited on the multi-compartment particles, TGA measurements have been performed. Exemplary one sample was measured before and after silica deposition (Figure 4.18).

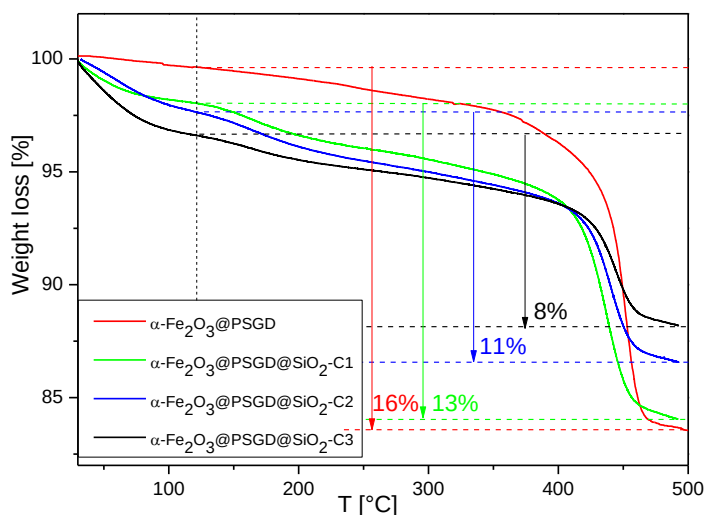


Figure 4.18. TGA measurements for α -Fe₂O₃@PSGD (red) and α -Fe₂O₃@PSGD@SiO₂-C1 (green), α -Fe₂O₃@PSGD@SiO₂-C2 (blue) and α -Fe₂O₃@PSGD@SiO₂-C3 (black) (N₂ atmosphere, heating rate 10 K/ min).

Before the silica coating was performed, a ratio of 16% polymer to 84% hematite was determined to be 0.19. The equations below show the way calculations are performed.

$$r_{\frac{polymer}{hematite}} = \frac{wt_{polymer}[\%]}{wt_{hematite}[\%]} = \frac{16\%}{84\%} = 0.19 \quad (4.4)$$

Assuming that only the polymer decomposes during the measurement, a composition of 8% polymer and 92% inorganic material, here hematite and silica, was measured. Furthermore, it is known that the ratio between polymer and hematite has not been changed. Accordingly, the hematite amount of sample $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD@SiO}_2\text{-C1}$ can be calculated with the Equation 4.5 and was found to be 42%.

$$wt_{hematite}[\%] = \frac{wt_{polymer}[\%]}{0.19} = 68\% \quad (4.5)$$

Knowing the percentage weight of polymer and hematite, the weight of silica could be calculated as followed:

$$wt_{silica}[\%] = wt_{total}[\%] - wt_{polymer}[\%] - wt_{hematite}[\%] = 19\% \quad (4.6)$$

Contents of hematite, polymer and silica are summarized in Table 4.2. for samples $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD@SiO}_2\text{-C1}$, $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD@SiO}_2\text{-C2}$ and $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD@SiO}_2\text{-C3}$.

Table 4.2. Weight content of hematite ($Wt_{\alpha\text{-Fe}_2\text{O}_3}$), polymer ($Wt_{polymer}$) and silica (Wt_{SiO_2}) and zeta potential (ζ) of lemon-shaped and dumbbell-shaped particles

Sample	$Wt_{\alpha\text{-Fe}_2\text{O}_3}$ [%]	$Wt_{polymer}$ [%]	Wt_{SiO_2} [%]	ζ [mV]
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSGD}$	84	16	0	-38.6 ± 5.5
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSGD@SiO}_2\text{-C1}$	68	13	19	-42.4 ± 10.3
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSGD@SiO}_2\text{-C2}$	58	11	31	-50.2 ± 9.9
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSGD@SiO}_2\text{-C3}$	42	8	50	-54.9 ± 12.8

Zeta potential measurements are in good consistency with the TGA results which show a continuous increase of the silica content. The measured zeta potentials show a decrease, as expected, with increasing silica amount (Figure 4.19). The zeta potential

decreases continuously from -38.6 mV for sample $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD-C2}$ to -54.9 mV for sample $\alpha\text{-Fe}_2\text{O}_3\text{@PSGD@SiO}_2\text{-C3}$.

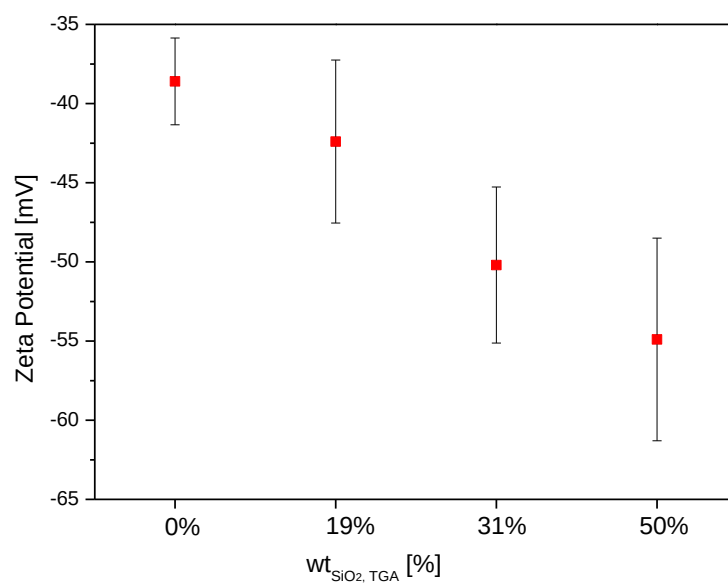


Figure 4.19. Zeta Potential measurements as a function of silica content in the samples (T: 20°C, pH 7).

4.4 Summary

In this chapter, the syntheses of multi-compartment nanoparticle with extraordinary shapes were developed. A new method for the targeted deposition of polymers onto an ellipsoidal hematite template was established. With this method, lemon-shaped or dumbbell-shaped colloids were obtained.

In the first part of this chapter, the gradual growth of an asymmetric coating of poly(styrene-*co*-glycidyl methacrylate-*co*-divinylbenzene) was reported. The question as to whether it would be possible to obtain an asymmetric polymer shell with tunable thickness was addressed. It was found that after the first coating step, asymmetric shells were obtained resulting in lemon-shaped colloids. A further coating step multiplied the shell thickness, but the polymer shell was found to be less asymmetric and rougher. The increase was followed visually by TEM. In IR spectra, the increases in intensity of the characteristic polymer peaks indicated an increase of the polymer to hematite ratio. These hints were quantified by using TGA. The polymer amount was found to be enhanced from 16 to 51%.

In order to investigate the influence of monomer to hematite amount during the synthesis thoroughly, a concentration series was performed. In TEM it was found that very low concentrations lead to some form of island formation of polymer onto the hematite spindles. A higher concentration results in the formation of lemon-shaped particles as desired. A further increase does not result in a thicker polymer shell but in the formation of free secondary particles in solution. Again IR spectra showed the increases in intensity of the characteristic polymer peaks indicated with increasing polymer content. TG analyses showed absolute values of 15, 19, and 33% for three concentrations.

Furthermore, the influence of the hydrophilicity of the monomers on the asymmetric coating process was investigated. The deposition of poly(styrene-*co*-*N*-vinylcaprolactam-*co*-divinylbenzene) was found to result in core-shell geometry and no longer in lemon-shaped particles anymore. The polymer amount was found to be doubled compared to the copolymers previously used. Additionally, temperature

dependent DLS measurement showed temperature-responsive behavior of the composites.

Therefore, silica could be deposited onto the free edges of the lemon-shaped nanocomposites. Afterwards dumbbell-shaped structures were displayed with TEM. The success of silica deposition was proved by IR spectroscopy. In TGA the composites were found to consist of 42% hematite, 8% polymer and 50% silica.

4.5 Experimental

4.5.1 Step-by-Step Growth of PS-co-GMA-co-DVB on Hematite Nanoparticles

In a coating process, nanoparticles are coated with an asymmetric polymer shell. In order to increase the polymer coating, the experiment was repeated a second time using hematite nanoparticles already coated as described above. However, only the polymerization reaction was performed leaving out the functionalization of the particles.

Asymmetric particles were synthesized in a seeded emulsion polymerization. Before the polymerization was performed, the particles were functionalized with 16-heptadecenoic acid. For the functionalization, 66 mg of ellipsoidal hematite nanoparticles were dispersed in 14 mL aqueous ammonia solution (1.3 vol-%) and 80 mg of 16-heptadecenoic acid were added. The dispersion was continuously stirred under nitrogen atmosphere at 50 °C for 30 min. Then the monomers were added and stirred for a further minute. Afterwards, the dispersion was further diluted 142 mL of warm aqueous ammonia solution. The initiator was dissolved in 1 mL distilled water and rapidly added to the dispersion. The reaction was stirred at 70°C for 5 h. A purification of the samples was performed by repeated centrifugation (10,000 rpm, 10 min) and washed with distilled water up to five times.

In order to increase the polymer shell thickness even more, hematite nanoparticles already coated were coated again by further repetition of this procedure described above. The amount used of monomers can be found in Table 4.3.

Table 4.3. Amounts of monomers and initiator needed for stepwise growth of PS-co-GMA-co-DVB onto hematite nanoparticles.

Sample	GMA	Styrene	DVB	KPS
	[mmol]	[mmol]	[mmol]	[mmol]
α -Fe ₂ O ₃ @PSGD-SW-1	2.32	23.56	5.9	0.17
α -Fe ₂ O ₃ @PSGD-SW-2	2.32	23.56	5.9	0.17

4.5.2 Coating of PS-co-VCL-co-DVB onto Hematite Nanoparticles

For synthesis of sample $\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD}$ respectively $\alpha\text{-Fe}_2\text{O}_3\text{-el@PSVD}$ 22 mg of hematite nanoparticles (spherical respectively ellipsoidal) are functionalized with HDA by adding 5 mL distilled water and 1 mL ammonia solution (1.3 vol-%) and 27 mg HDA. The dispersion was heated to 50°C for 30 min to finish the functionalization.

The following reaction was performed under nitrogen atmosphere. For the shell coating with polymer, appropriate amounts of styrene and VCL (Table 4.4) as well as 256 mg (1.96 mmol) DVB were added to the solution. After 1 min of moderate stirring, the reaction mixture was diluted with 46 mL of warm distilled water, after which it was heated up to 70°C. After 30 min the initiator, AMPA, was dissolved in 1 mL distilled water and added to start the reaction. The reaction was stirred at 70°C for 3 h. After 3 h the dispersion was cooled down to room temperature and was stirred overnight.

Table 4.4. Experimental details for synthesis of $\alpha\text{-Fe}_2\text{O}_3\text{@PSVD}$ nanoparticles with different PS to PVCL ratios

Sample	styrene [mg]	styrene [mmol]	VCL [mg]	VCL [mmol]
$\alpha\text{-Fe}_2\text{O}_3\text{-el@PSVD-1}$	391	3.75	600	4.3
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-3}$	191	1.83	800	5.73
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-1}$	391	3.75	600	4.3
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@PSVD-0.5}$	591	5.67	400	2.87

In order to increase the dispersion stability, some droplets of ammonia solution were added the next day after which the particles were purified by repeated centrifugation as well as washing with water. A centrifugation speed of 10,000 rpm was applied for 10 min. Afterwards, the particles were redispersed in 20 mL water. This procedure was repeated up to five times. In a last step, particles were redispersed in a volume of 20 mL water.

4.5.3 Selective Silica Deposition on $\alpha\text{-Fe}_2\text{O}_3\text{@PS-co-GMA-co-DVB}$

In a typical procedure, 2.5 mL of an aqueous solution containing 8.3 mg $\alpha\text{-Fe}_2\text{O}_3\text{@PS-co-GMA-co-DVB}$ was mixed with 1.55 mL ammonia solution (1.2 vol-%) and 1.55 mL ethanol for 1 h. Later, 6.25 mL ethanol were mixed with 0.29 mL ammonia solution (25 vol-%) and were added to the reaction mixture. Furthermore, a solution of 31 μL of TEOS in 4.4 mL ethanol was added rapidly to the dispersion. The reaction was stirred for 24 h at room temperature. Samples were purified by repeated centrifugation and washing with distilled water. Experimental details for other samples can be found in Table 4.5.

Table 4.5. Experimental details for synthesis of $\alpha\text{-Fe}_2\text{O}_3\text{@PS-co-GMA-co-DVB@SiO}_2$ particles with different SiO_2 amounts.

Sample	$\alpha\text{-Fe}_2\text{O}_3\text{@PS-co-GMA-co-DVB}$ [mg]	TEOS [mg]	TEOS [μL]
$\alpha\text{-Fe}_2\text{O}_3\text{@PS-co-GMA-co-DVB@SiO}_2\text{-1}$	8.3	29.1	31
$\alpha\text{-Fe}_2\text{O}_3\text{@PS-co-GMA-co-DVB@SiO}_2\text{-2}$	8.3	55.6	59
$\alpha\text{-Fe}_2\text{O}_3\text{@PS-co-GMA-co-DVB@SiO}_2\text{-3}$	8.3	88.8	94

4.5.4 Sample Preparation and Measurement Conditions

The device designations of instruments used for the measurements can be found in the Appendix I.

For the preparation of the TEM samples a drop of the particle dispersion was trickled on a piece of formvar and carbon coated copper grid. Before being placed into the TEM specimen holder, the copper grid was air-dried under ambient conditions. For cryo-TEM the sample was quickly frozen in liquid nitrogen.

Field emission scanning electron microscopy (FE-SEM) images and energy dispersive X-ray spectroscopy (EDX) analysis were obtained in a Hitachi SU9000 (Tokyo, Japan) electron microscope using a beam voltage of 30 kV and AZtec control software (Version 2.2, Oxford Instruments GmbH). The EDX maps were recorded with acquisition times larger than 30 min. A BF-STEM detector and a SE detector were used parallel to detect SEM and TEM images at the same time. For sample preparation one droplet of the dispersion was applied onto a copper grid which was covered with a perforated carbon film.

ImageJ[®] and WinTEM[™] software was employed to process the TEM digital images to analyze the particle size and morphology. At least 100 particles were measured.

For temperature dependent DLS, one drop of the dispersion is diluted with 5 mL of distilled water. For measurements 1 mL of the diluted dispersion was used. The samples were measured in a range from 15 to 45°C. Temperature was increased with 1°C per step.

For sample preparation of IR measurements, samples were dried and few mg of the sample was measured in KBr.

For TGA 5 to 10 mg of the dried sample was measured in a temperature range from 30 to 500°C.

4.6 References

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5 PVCL-Microgel Hybrid Nanoparticles

5.1 Introduction

In recent years, highly functional microgel nanoparticles have been found to be available as containers for inorganic nanoparticles e.g. metal or metal oxides. These nanocomposites are of increasing interest due to their extraordinary characteristics. By the combination of two materials completely new properties of the hybrid material are created.^[1, 2]

On the one hand, the hybrid materials show properties related to the microgel network. Microgels are polymeric colloids with a cross-linked and hairy structure. Size and morphology as well as porosity can be easily tailored.^[2-4] Furthermore, microgels provide an opportunity of enormous diversity regarding chemical functionalization. The nature, degree and distribution of functionalities in the microgels can be customized.^[5, 6] For example many reactive monomers e.g. glycidyl methacrylate (GMA) can be incorporated into the polymer network. In the following section, detailed studies of nanocomposites based on poly(*N*-vinylcaprolactam) (PVCL) microgels are presented. PVCL microgels are known to be soluble in water as well as in some organic solvents e.g. THF.^[7] Another outstanding characteristic of microgels is their responsiveness to external stimuli, including temperature and pH, resulting in a change of dimension.

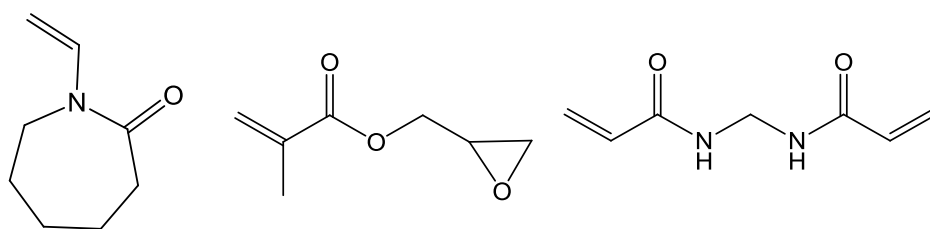


Figure 5.1. Monomers of microgel; from left to right: *N*-Vinylcaprolactam (VCL); Glycidyl methacrylate (GMA); *N,N'*-Methylenebisacrylamide (BIS).

On the other hand well known properties of the embedded metal or metal oxide nanoparticles contribute strongly. Many of those nanoparticles are known not to be

colloidally stable in water.^[8] One possibility for stabilization in water is the coating of these structures with water-soluble polymers.^[9] But here the aim is the incorporation of e.g. magnetic or catalytic nanoparticles into the microgel network. Afterwards the hybrid microgels will respond to a magnetic field or work as a catalyst.^[10, 11]

During numerous studies, several techniques have been developed to obtain microgel nanocomposites. In general, two routes for preparing nanocomposites exist. For the first route, one component needs to be synthesized in a separate step followed by the hybrid material formation in a second synthetic step. Either the nanoparticle formation is performed in-situ, meaning inside the previously formed microgel^[12] or microgels are formed in a co-precipitation process in presence of already existing inorganic nanoparticles.^[13] In this case the nanoparticles are used as nucleation sites for the precipitation of the hydrogel shell. The second route can be considered as a diffusion-based synthesis. Initially both microgels and nanoparticles are synthesized separately. Subsequently inorganic nanoparticles are loaded into the microgels.^[7]

The following chapter deals with two different synthesis strategies to obtain PVCL microgels with inorganic iron-based nanoparticles incorporated into the polymer network. The hybrid materials obtained offer new properties due to characteristics of both materials. A synthetic route for $\alpha\text{-Fe}_2\text{O}_3\text{@PVCL}$ core-shell nanocomposites as well as loading of microgels with separately synthesized FePt nanoparticles is presented here. For the synthesis of $\alpha\text{-Fe}_2\text{O}_3\text{@PVCL}$ nanocomposites, the polymer shell was grafted onto the pre-functionalized hematite cores. For the diffusion-based loading of microgels, FePt nanoparticles have been chosen as they exhibit excellent monodispersity, strong superparamagnetic properties as well as needed hydrophobic surface modification.^[14, 15]

5.2 Thermoresponsive PVCL Core-Shell Nanoparticles with $\alpha\text{-Fe}_2\text{O}_3$ Core

For encapsulation of $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles with PVCL shell, a surface modification with vinyl groups onto the particles surface needs to be performed first. Here the same surfactant was used as described in Chapter 4. The carboxylic group of

16-heptadecenoic acid adsorbs onto the oxidic surface of the particle.^[16] Also the vinyl group is displayed by this molecule. Once the surface of the particles is functionalized with anchor groups, the grafting of PVCL hydrogel onto the particle can be performed. Therefore, the nanoparticles are dispersed in aqueous mixture of VCL and BIS, where the polymerization is initiated at 70°C by adding a water soluble initiator. The composite material obtained combines properties of hematite and PVCL. As PVCL microgels are known to be temperature-sensitive, I expect the nanocomposites to also show different swelling behavior depending on temperature.

5.2.1 Investigation of Size, Structure and Volume Phase Transition of the PVCL Shell

In this part I report on core-shell particles with hematite core and PVCL shell. Samples with different PVCL hydrogel to hematite ratios have been obtained.

5.2.1.1 TEM Investigations

The thickness of the PVCL shell has been determined by TEM measurements. The TEM images below show four samples with different hematite to polymer ratios. Due to the differences in contrasts, hematite and hydrogel can be clearly distinguished. Hematite has a high density, it appears very dark in TEM, while the PVCL hydrogel has a lower density. Therefore, the shell appears as a lighter corona around the core. From Figure 5.2a to d the shell was found to increase continuously. On the images, some particles appear to be agglomerated which might be related to the drying process during sample preparation. In DLS measurements it could be shown that these phenomena do not occur in solution (Figure 5.4).

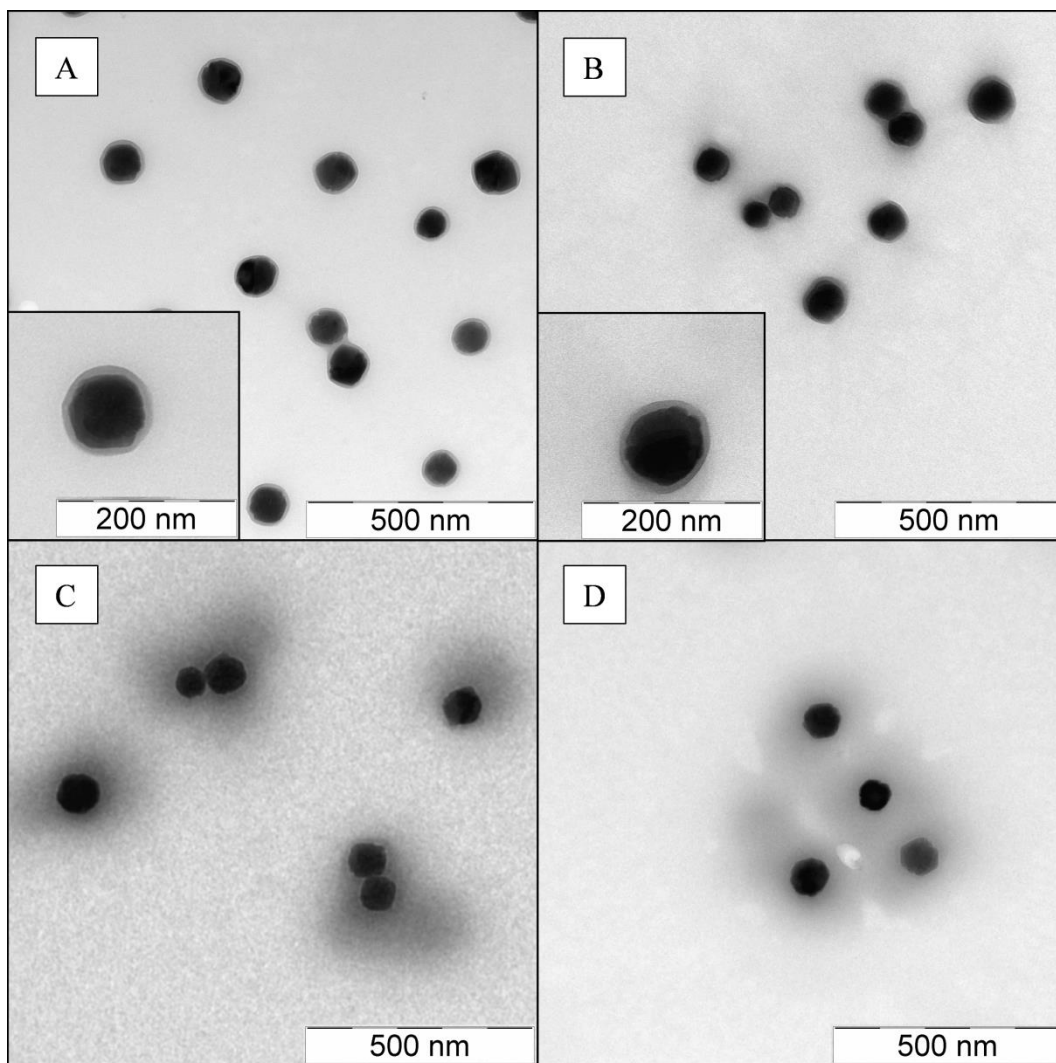


Figure 5.2. TEM images of $\alpha\text{-Fe}_2\text{O}_3$ @MG for different polymer to hematite ratios: a) $\alpha\text{-Fe}_2\text{O}_3$ @MG-1; b) $\alpha\text{-Fe}_2\text{O}_3$ @MG-2; c) $\alpha\text{-Fe}_2\text{O}_3$ @MG-3 and d) $\alpha\text{-Fe}_2\text{O}_3$ @MG-4.

5.2.1.2 Influence of pH on Size and Electrophoretic Mobility

Size and electrophoretic mobility of $\alpha\text{-Fe}_2\text{O}_3$ @MG was found to be strongly influenced by pH. Figure 4.3a shows the pH dependence of all samples measured at 20°C. The samples analyzed showed an increase in hydrodynamic radius from pH 4 to pH 10. Only sample $\alpha\text{-Fe}_2\text{O}_3$ @MG-1, which is the sample with the thinnest PVCL shell, exhibits a different behavior. The increase of hydrodynamic radii can be explained by a swelling of the PVCL hydrogel shell due to repulsion of equal charges in the polymer. With increasing pH, the carboxylic acid groups are increasingly deprotonated resulting

in a more negative electrophoretic mobility and an increase in size due to repelling charges. The network is expanded due to the additional exertion of the forces described.

For reasons already described, the electrophoretic mobility becomes increasingly negative with increasing pH (Figure 5.3b). It can be observed that the electrophoretic mobility is slightly more negative for particles with a PVCL microgel shell. Only the surfactant 16-heptadecenoic acid can be considered as reasonable source of negative charge. An excess of surfactant seems to be incorporated into the PVCL network during synthesis. Table 5.1 summarizes the absolute values displayed in Figure 5.3a.

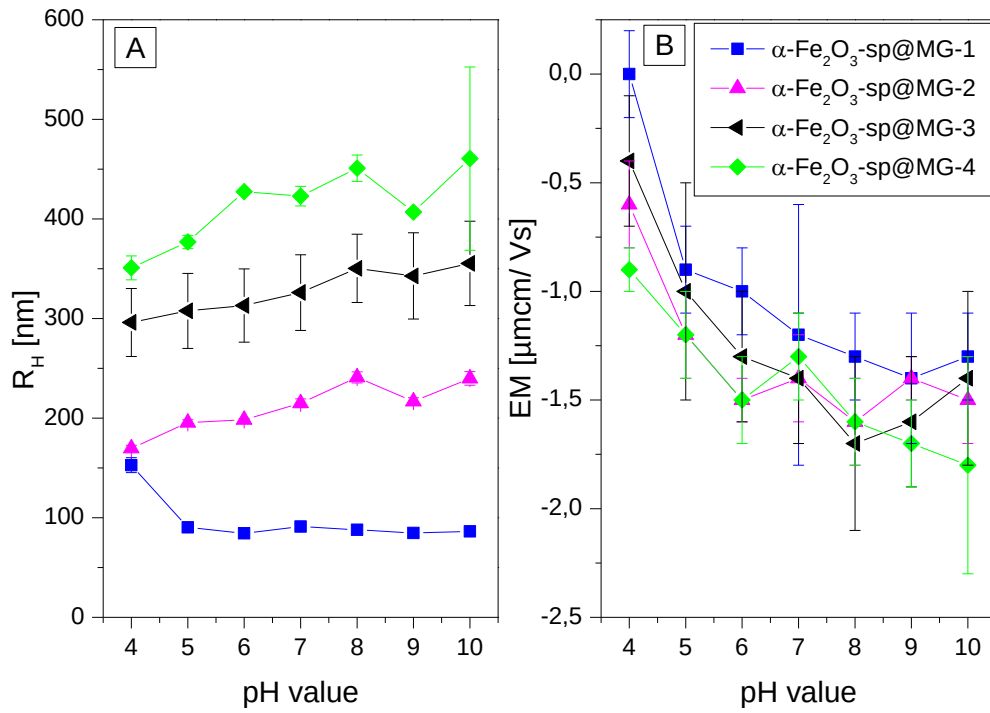


Figure 5.3. pH dependence of a) hydrodynamic radius (R_H) and b) electrophoretic mobility of (at 20°C).

Swelling ratios can be calculated from the hydrodynamic radii obtained for different pH values. Swelling ratios σ between pH 4 and pH 10 have been calculated using following Equation 5.1:

$$\sigma_{pH} = \frac{R_H^{pH 10}}{R_H^{pH 4}} \quad (5.1)$$

For samples $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-2}$ to $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-4}$ the σ_{pH} was calculated to be between 1.2 and 1.4. It can be concluded that the swelling is similar for all samples depending on the pH value. This observation is not surprising as the HAD concentration as well as the cross-linking degree was kept constant for all samples. For sample $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-1}$ all hydrodynamic radii stay constant. It is slightly increased for pH 4. Maybe the sample agglomerated slightly at that pH.

Table 5.1. pH dependent hydrodynamic radii (R_{H}) of different core-shell $\alpha\text{-Fe}_2\text{O}_3\text{@MG}$ nanocomposites.

	$\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-1}$	$\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-2}$	$\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-3}$	$\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-4}$
pH value	R_{H} [nm]	R_{H} [nm]	R_{H} [nm]	R_{H} [nm]
4	153 ± 8	170 ± 3	296 ± 34	351 ± 12
5	90 ± 2	196 ± 3	308 ± 38	377 ± 7
6	84 ± 2	198 ± 2	313 ± 37	428 ± 2
7	91 ± 1	215 ± 4	326 ± 38	423 ± 10
8	88 ± 4	241 ± 6	350 ± 34	451 ± 13
9	85 ± 1	217 ± 4	343 ± 43	407 ± 3
10	86 ± 2	240 ± 7	355 ± 42	461 ± 92

Table 5.2 compares electrophoretic mobilities of sample $\alpha\text{-Fe}_2\text{O}_3\text{-sp}$ with $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG}$ samples in a pH range of 4 to 10. While $\alpha\text{-Fe}_2\text{O}_3\text{-sp}$ shows a positive mobility in a pH range of 4 to 7 and a negative mobility from 7 to 10, all other samples show a negative electrophoretic mobility over the whole pH range. From sample $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-1}$ to $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-4}$ a steady decrease can be observed for all pH values. As already explained, the carboxylic acid groups offered by HDA seem to be partially incorporated into the PVCL network providing the negative charges in the pH range analyzed.

Table 5.2. pH dependent electrophoretic mobility (EM) of different core-shell α -Fe₂O₃@MG nanocomposites.

pH value	α -Fe ₂ O ₃ -sp EM [μ mcm/Vs]	α -Fe ₂ O ₃ -sp @MG-1 EM [μ mcm/Vs]	α -Fe ₂ O ₃ -sp @MG-2 EM [μ mcm/Vs]	α -Fe ₂ O ₃ -sp @MG-3 EM [μ mcm/Vs]	α -Fe ₂ O ₃ -sp @MG-4 EM [μ mcm/Vs]
4	3.3 $\pm$ 0.4	0.0 $\pm$ 0.2	-0.6 $\pm$ 0.2	-0.4 $\pm$ 0.3	-0.9 $\pm$ 0.1
5	1.3 $\pm$ 0.4	-0.9 $\pm$ 0.2	-1.2 $\pm$ 0.2	-1.0 $\pm$ 0.5	-1.2 $\pm$ 0.2
6	1.1 $\pm$ 0.2	-1.0 $\pm$ 0.2	-1.5 $\pm$ 0.1	-1.3 $\pm$ 0.3	-1.5 $\pm$ 0.2
7	0.1 $\pm$ 0.2	-1.2 $\pm$ 0.6	-1.4 $\pm$ 0.2	-1.4 $\pm$ 0.3	-1.3 $\pm$ 0.2
8	-0.8 $\pm$ 0.3	-1.3 $\pm$ 0.2	-1.6 $\pm$ 0.2	-1.7 $\pm$ 0.4	-1.6 $\pm$ 0.2
9	-1.3 $\pm$ 0.4	-1.4 $\pm$ 0.3	-1.4 $\pm$ 0.1	-1.6 $\pm$ 0.3	-1.7 $\pm$ 0.2
10	-2.0 $\pm$ 0.3	-1.3 $\pm$ 0.2	-1.5 $\pm$ 0.2	-1.4 $\pm$ 0.4	-1.8 $\pm$ 0.5

5.2.1.3 Temperature Dependent DLS Measurements

In temperature dependent DLS measurement hybrid nanocomposites have shown thermo-sensitive behavior (Figure 5.4). All samples have been measured at pH 8 to ensure that they are all highly charged. In a range of 15 to 50°C the PVCL shell swells and de-swells depending on temperature. With increasing temperature the polymer chains start to collapse on the hematite nanoparticles surface. For all samples the typical VPT behavior of microgels could be observed. The VPTT was calculated for α -Fe₂O₃-sp@MG-2, α -Fe₂O₃-sp@MG-3 and α -Fe₂O₃-sp@MG-4 from the first derivative of the fitted curves. For sample α -Fe₂O₃-sp@MG-2 the VPTT was found to be 25°C, which seems to be a little too low. But maybe the further differences in shrinkage were too low to follow them properly via DLS (Table 5.3). For the samples α -Fe₂O₃-sp@MG-3 and α -Fe₂O₃-sp@MG-4, VPTT was found to be around 30°C which correlates nicely with VPTT of pure PVCL microgels.^[17] Additional to the temperature dependent DLS curves, swelling ratios and shell thicknesses in swollen respectively deswollen state were calculated. Results can be found in Table 5.3.

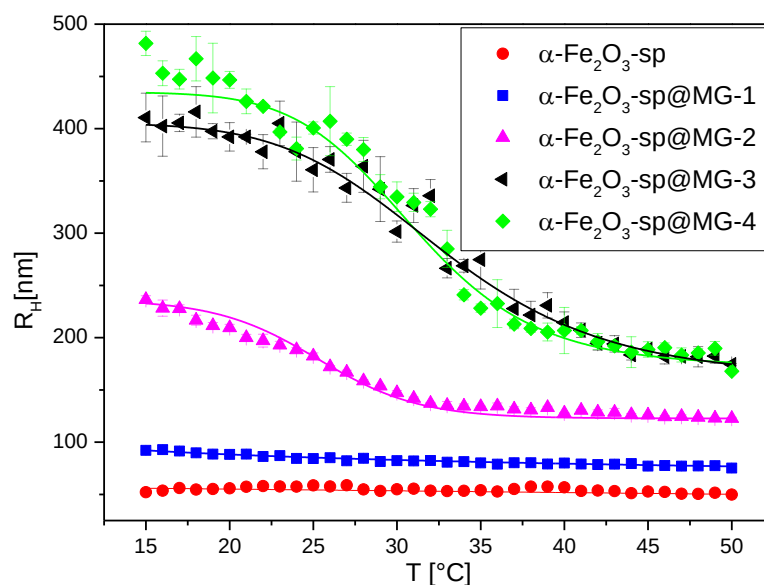


Figure 5.4. Temperature dependent DLS measurements for different $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG}$ samples with different shell thicknesses at pH 8.

From sample $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-1}$ to $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-4}$, a strong increase in shell thicknesses, in swollen as well as deswollen state, was measured. Also the swelling ratio increases linearly from 1.7 to 3.6. All results are displayed in the graphs in Figure 5.6. Noticeable is the similarity of the behavior of sample $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-3}$ and $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-4}$. It is assumed that there is a maximum amount of PVCL shell that can be grown onto the hematite particle surface. A further increase of the monomer concentration in the reaction solution leads to secondary particle formation (Figure 5.5).

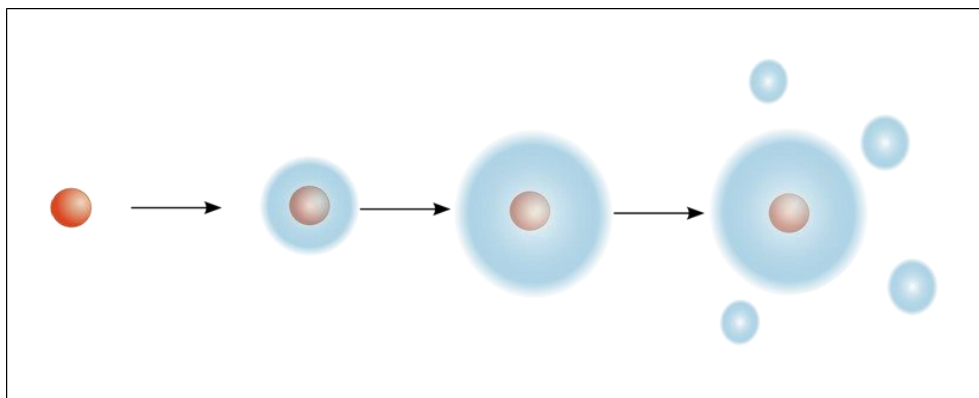


Figure 5.5. Schematic illustration of the PVCL shell growth. An increase of the monomer concentration results in a secondary particle formation.

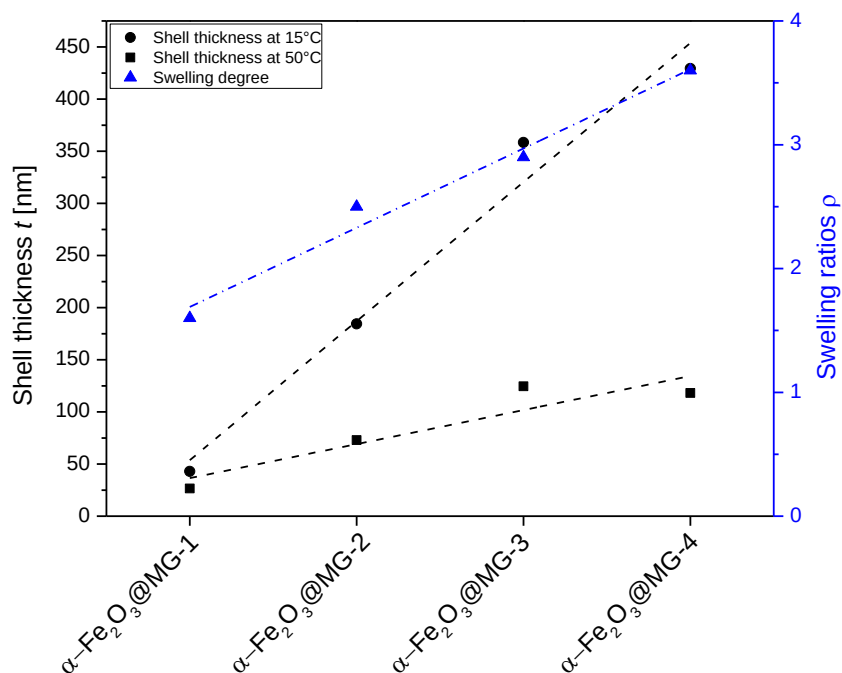


Figure 5.6. Linear increase of the PVCL shell thickness for 15°C (black circle) and 50°C (black squares) as well as linear increase in swelling ratio (blue triangles) for samples α -Fe₂O₃-sp@MG-1, α -Fe₂O₃-sp@MG-2, α -Fe₂O₃-sp@MG-3 and α -Fe₂O₃-sp@MG-4.

Table 5.3. Hydrodynamic radii (R_H) for 15°C and for 50°C, shell thickness (t) for 15°C and for 50°C, swelling ratio (σ) and volume phase transition temperature (VPTT).

Sample	$R_H^{15^\circ\text{C}}$ [nm]	$R_H^{50^\circ\text{C}}$ [nm]	$t_{15^\circ\text{C}}$ [nm]	$t_{50^\circ\text{C}}$ [nm]	σ	VPTT [°C]
α -Fe ₂ O ₃ -sp	52 ± 1	50 ± 1	-	-	-	-
α -Fe ₂ O ₃ -sp@MG-1	95 ± 3	76 ± 1	43	26	1.7	-
α -Fe ₂ O ₃ -sp@MG-2	237 ± 4	123 ± 1	185	73	2.5	25
α -Fe ₂ O ₃ -sp@MG-3	411 ± 23	174 ± 1	359	124	2.9	31
α -Fe ₂ O ₃ -sp@MG-4	482 ± 12	168 ± 3	430	118	3.6	30

5.2.1.4 Determination of Hematite Nanoparticle to PVCL Ratio with TGA

To determine the ratio between hematite nanoparticles to PVCL shell for all samples, TGA was performed in a temperature range between 30 and 500°C. Figure 5.7 displays the percentage weight loss of the sample plotted against the temperature. The weight loss correlates to the polymer mass, which is combusted at high temperatures. Sample

$\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-1}$ shows a very high content of hematite compared to the polymer amount measured in the sample. For samples $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-2}$, $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-3}$ and $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-4}$, the polymer content exceeds the hematite amount. It is assumed that after the washing procedure some free polymer remained in the sample which might explain the similar polymer content for samples $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-2}$, $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-3}$ and $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-4}$. In all cases hematite to polymer ratio was much less than expected. Furthermore, it is assumed that TGA does not give exact results for this system measured here.

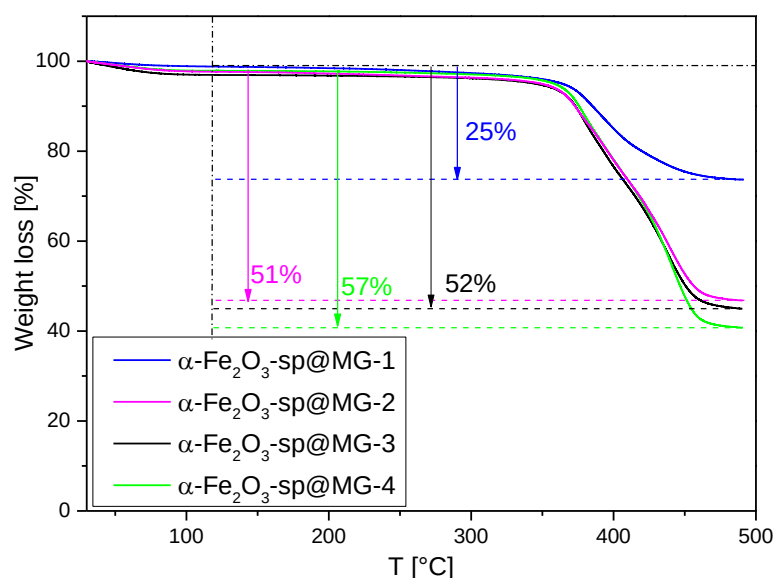


Figure 5.7. TGA graphs for determination of hematite to polymer ratio for $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG}$ samples: $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-1}$ (blue); $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-2}$ (violet); $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-3}$ (black) and $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-4}$ (green).

In Figure 5.8 all hematite to polymer ratios and shell thicknesses are plotted. It can be seen that the amount of polymer increases constantly. But from sample $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-2}$ onwards, it seems that a plateau is reached. In the beginning there is only a small amount of polymer bound to the surface of the hematite nanoparticles, but starting from a ratio of nearly 1:1 it seems that no more PVCL shell is formed on the surface. It is assumed that the competitive reaction of free polymer formation in solution is predominant. The maximum ratio of hematite to polymer is 1 to 1.4. Values are calculated from equation 5.2:

$$r_{poly/Fe_2O_3}^{TGA} = \frac{m_{polymer}}{m_{Hematite}} \quad (5.2)$$

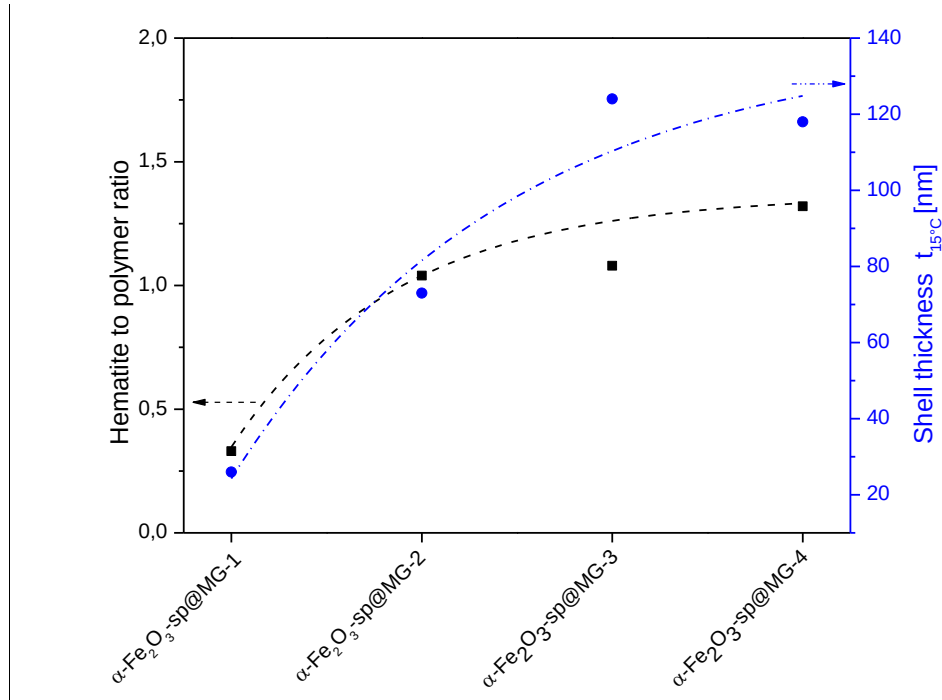


Figure 5.8. Hematite to polymer ratios (black squares) and shell thickness (blue circles) for samples $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-1}$, $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-2}$, $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-3}$ and $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-4}$.

5.2.1.5 IR Investigations for Determination of Chemical Composition

IR spectroscopy was used to determine the chemical composition and ratio between polymer and hematite. In Figure 5.9 the spectra of the four samples are displayed. All spectra have been normalized to the band at 578 cm^{-1} which is known to belong to hematite only.

The spectra of nanocomposites show characteristic peaks for hematite as well as for PVCL microgel shell. It was found that the typical peaks for C=O vibration of PVCL, mainly the one around 1637 cm^{-1} , increase in intensity with increasing polymer content.

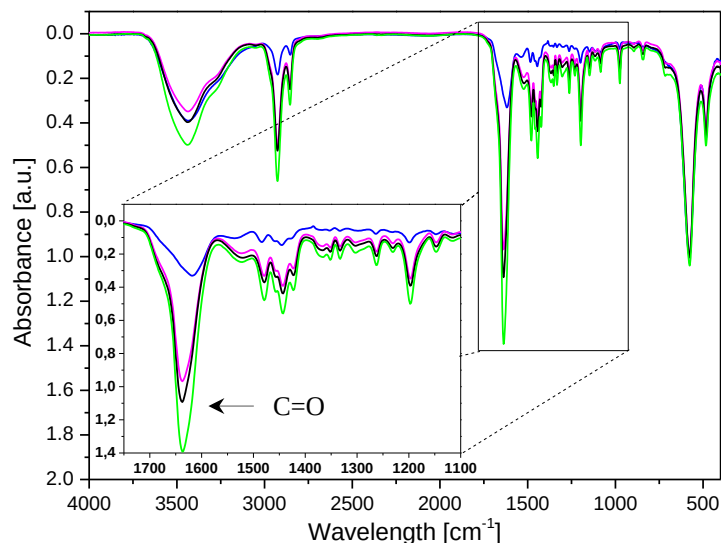


Figure 5.9. IR spectra for $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG}$ samples: $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-1}$ (blue); $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-2}$ (pink); $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-3}$ (black) and $\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-4}$ (green).

From increase in intensity described, the hematite to polymer ratio can be calculated by integration of the PVCL peak at 1637 cm^{-1} since the hematite peak has already been set to one value during the normalization.^[18] Comparison of the integrals of the peak at 1637 cm^{-1} for the different polymer contents give proportions, which are in nice consistency to values obtained by TGA. Results for both methods are given in Table 5.4.

Table 5.4. Hematite to polymer ratios calculated from TGA (Figure 5.8) and IR measurements for samples.

Sample	$r_{poly/Fe2O3}^{IR}$	$r_{poly/Fe2O3}^{TGA}$
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-1}$	0.46	0.34
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-2}$	1.00	1.09
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-3}$	1.11	1.15
$\alpha\text{-Fe}_2\text{O}_3\text{-sp@MG-4}$	1.39	1.40

5.3 Loading of FePt Nanoparticles in PVCL Microgels by Solvent Exchange Method

In this work I report on the successful synthesis of hybrid microgel particles loaded with small magnetic ion platinum particles (FePt NP) by using a solvent exchange method (Figure 5.10).^[19]

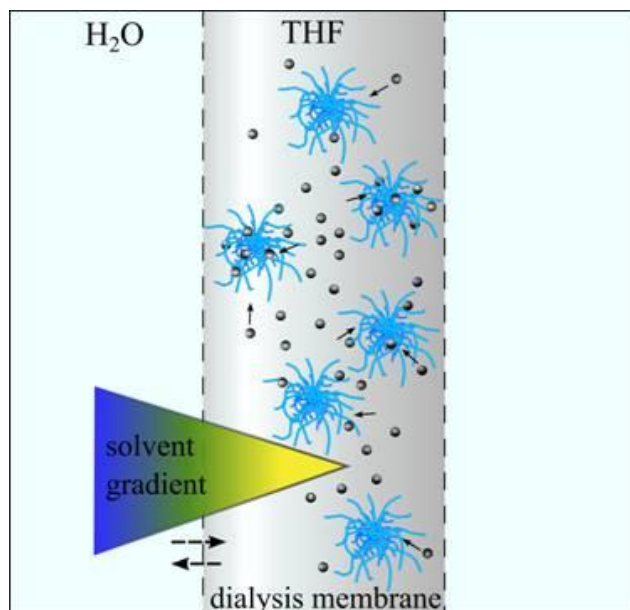


Figure 5.10. Schematic representation of solvent exchange method performed via dialysis process; situation at the beginning of the process.

Outstanding for this hybrid system is the combination of two fundamentally different chemical components. The combination of hydrophilic PVCL-based microgels, which were synthesized in water, and very hydrophobic alloy FePt nanoparticles, which are dispersed in organic media, was realized.

Figure 5.11 gives an overview about the synthetic procedure. To obtain a situation as described before, poly(*N*-vinylcaprolactam) microgels were transferred from water into tetrahydrofuran (THF) solution in a first step. The separately synthesized FePt nanoparticles with a diameter of $8.8 \text{ nm} \pm 0.6 \text{ nm}$ are known to be very hydrophobic due to the presence of oleyl amine and oleic acid ligands on their surface.^[20] The covering on the surface leads to a sterical stabilization of the particle in organic solvents. The FePt system could also be transferred in THF. Both components were mixed and by

exchanging the surrounding solvent from THF to water again, the FePt nanoparticles were forced to migrate into the microgels.

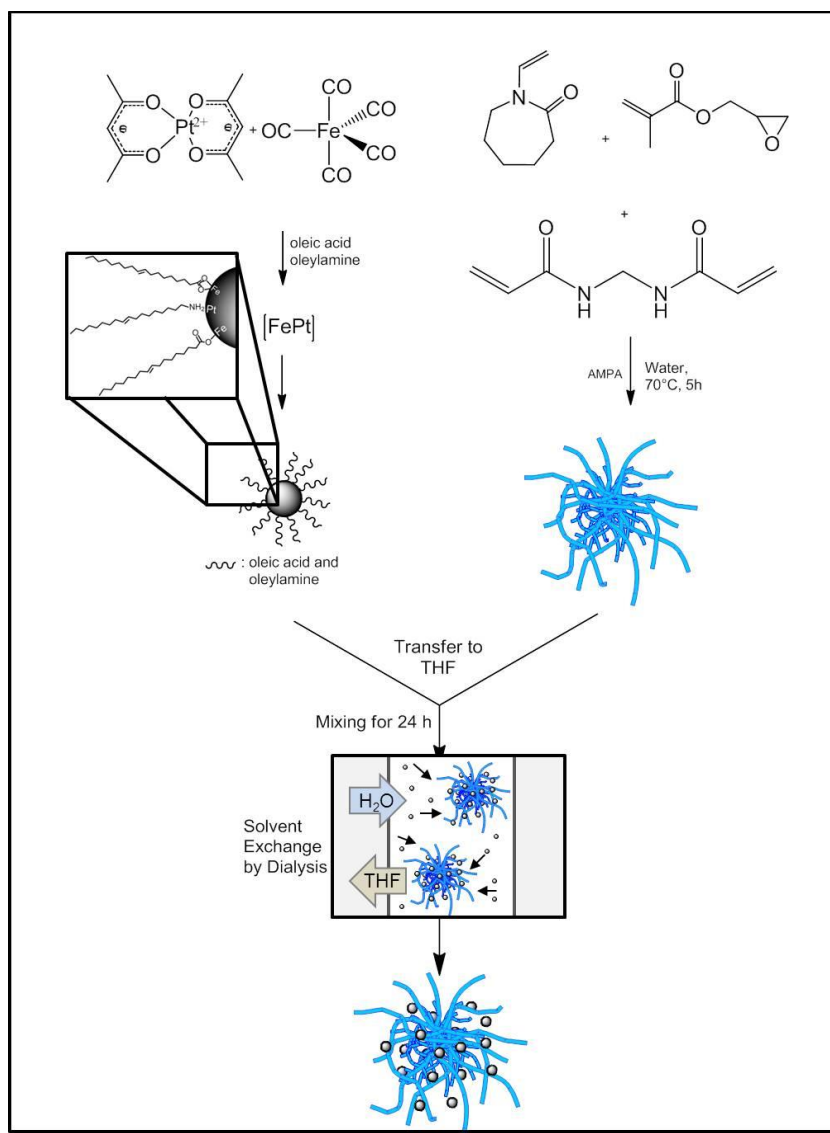


Figure 5.11. Reaction scheme for the preparation of microgel FePt hybrid particles.

These composite hybrid materials were colloidally stable in water and exhibited similar thermal responsiveness to un-loaded microgels. Furthermore, not only polymer features but also magnetic characteristics provided by FePt nanoparticles could be observed for the hybrid material. Therefore, it could be observed by eye that loaded microgels are responsive to a magnetic field and move toward a permanent magnet within minutes (Figure 5.12.).

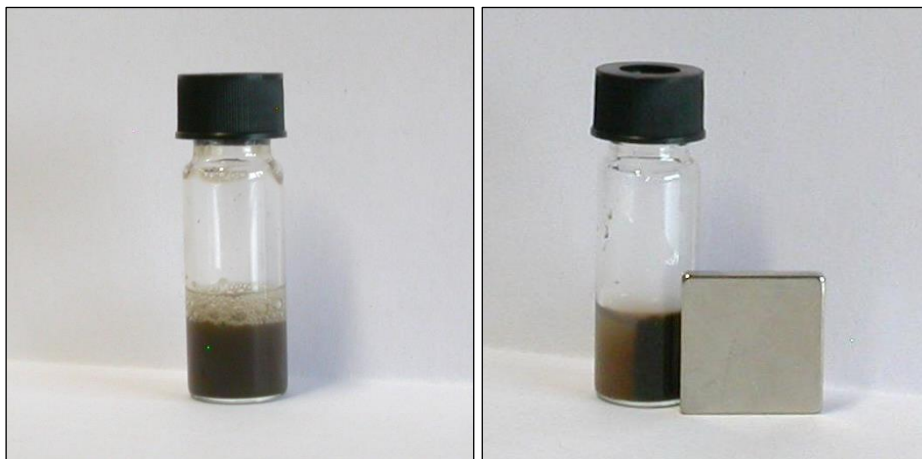


Figure 5.12. Photographes of MG@FePt-3 dispersion without (left) and with magnet (right).

5.3.1 Determination of Loading Degree and FePt Nanoparticle Distribution in Microgels

5.3.1.1 TEM and cryo-TEM Investigations on Microgel FePt Hybrid Materials

The quality of loading, particularly the distribution, of FePt nanoparticles in microgels has been investigated by TEM. Figure 5.13 shows samples with different concentrations of FePt nanoparticles incorporated. All samples showed a very good contrast. It was found that some microgels are heavily loaded and some appear to be empty (MG@FePt-1 and MG@FePt-2). For samples MG@FePt-3 to MG@FePt-5, no microgels without loading were detected.

For sample MG@FePt-1, which was the sample with the lowest loading, many empty microgels can be found (Figure 5.13b), whereas most of the microgels seem to be loaded for Mg@FePt-2 (Figure 5.13c). A loading as obtained for sample MG@FePt-3 seems to be almost optimal. As displayed in Figure 5.13d, the FePt nanoparticles are well distributed over the whole microgel. No empty microgels can be determined anymore. Only small clusters can be found consisting of a few FePt nanoparticles. Besides single FePt nanoparticles and small agglomerates in the microgels, strong tendency to clustering was observed for higher loadings, e.g. sample MG@FePt-4 and MG@FePt-5. Above a critical concentration of FePt nanoparticles with respect to microgel large agglomerates of FePt nanoparticles are formed displayed in Figure 5.13e and f.

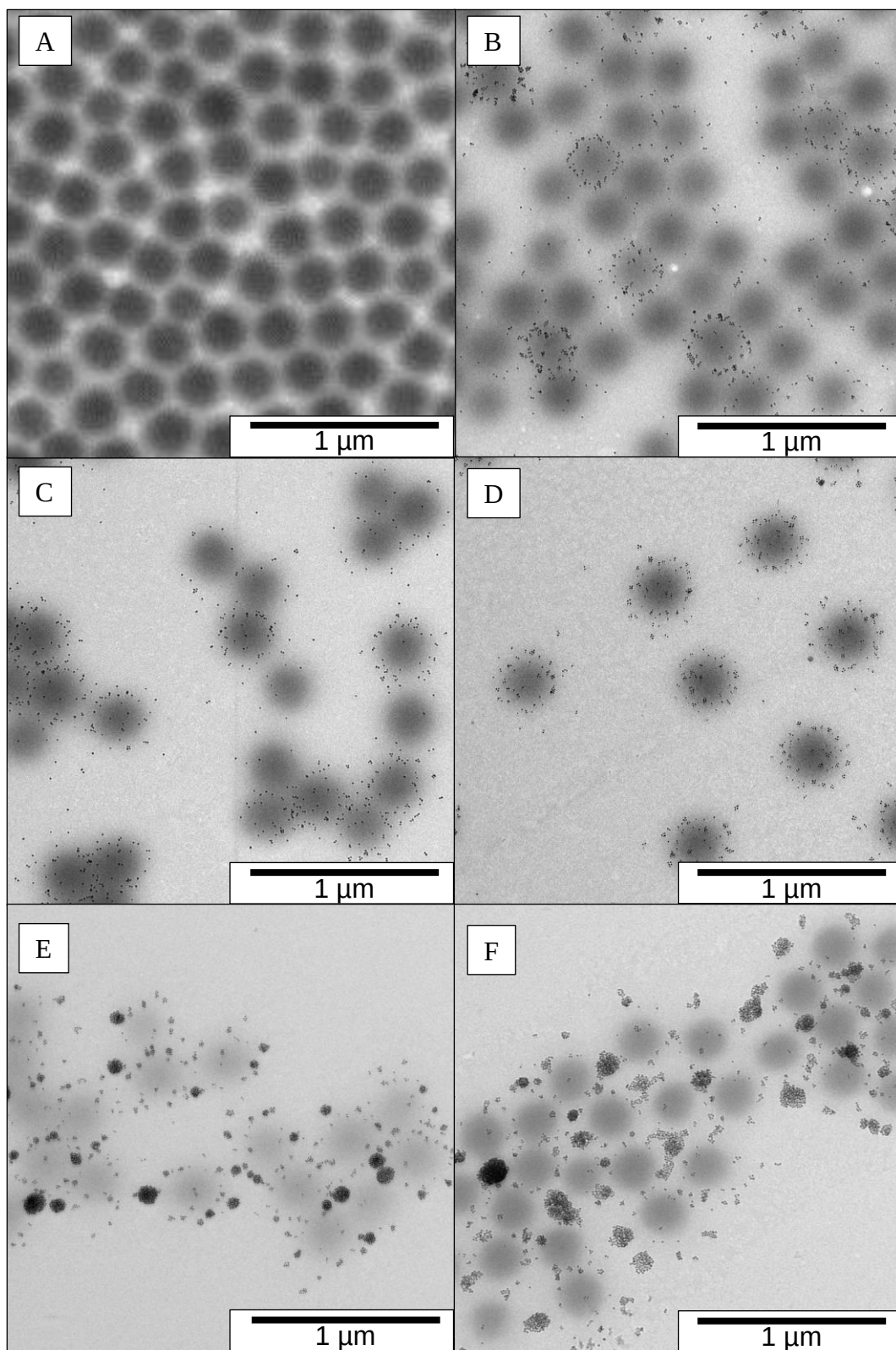


Figure 5.13. TEM images of microgels loaded different amounts of FePt nanoparticles: a) microgel reference (MG); b) MG@FePt-1; c) MG@FePt-2; d) MG@FePt-3; e) MG@FePt-4 and f) MG@FePt-5.

The incorporation of the FePt nanoparticles into the microgel was furthermore confirmed by cryo-TEM (Figure 5.14). For sample preparation, microgels were quickly frozen and investigated in the swollen state. It was found that the particles were well dispersed all over the microgel. Therefore, an assembly of FePt nanoparticles around the microgel due to some drying effects could be excluded.

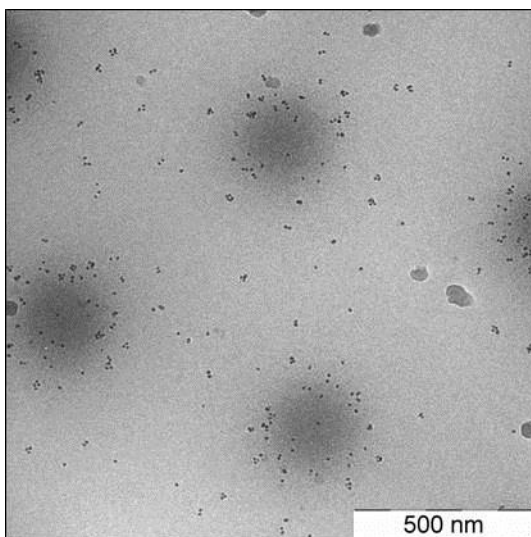


Figure 5.14. cryo-TEM image of loaded microgels in the swollen state (MG@FePt-3).

5.3.1.2 TGA Investigations for Determination of Loading Degree

To determine the amount of FePt nanoparticles incorporated into the microgel particles, TGA measurements were performed for different loading degrees. A gradual increase of FePt nanoparticles for higher loadings was measured as expected. In Figure 5.15 percentage weight loss is plotted against temperature.

In a range of 25 to 500 °C, the most part of the microgel polymer was combusted and only inorganic material, in this case FePt, remained. The spectra obtained can be divided into two distinct regions depending on the loss of weight during heating. The initial weight loss (region A; $T < 120$ °C) is due to the loss of a small amount of water from the composite. In region B (from 120 to 480 °C), the thermal decomposition of the C–C backbone and complete polymer degradation take place. The residual mass remaining after heating of the samples to 500 °C can be related to the FePt

nanoparticles, which remain undecomposed under these conditions. Table 5.5 summarizes the results measured with TGA. It could be shown that loadings could be varied between 14 and 30 wt-% of FePt. A reference measurement for pure FePt nanoparticles shows a slight weight loss of 20%, which is due to the decomposition of the stabilizing ligands oleyl amine and oleic acid. It could be shown that there is no oxidation of the FePt particles under conditions used, otherwise an increase in weight would have been expected for this measurement. Another reference measurement showed that microgels are decomposed almost completely, i.e. up to 91%.

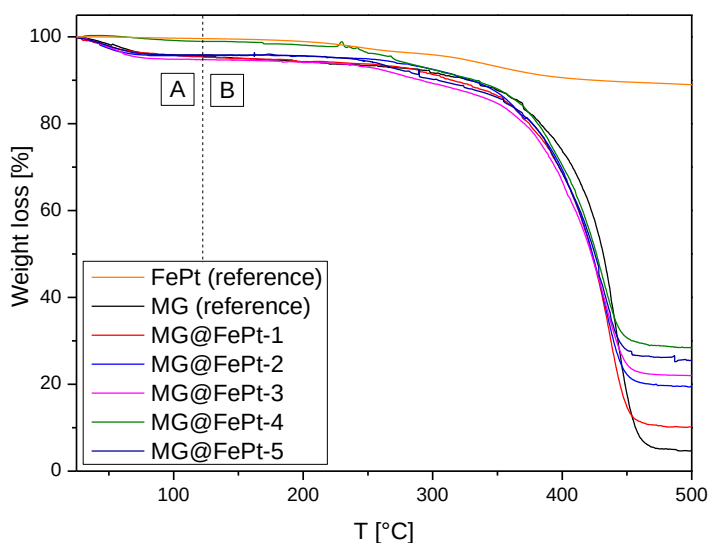


Figure 5.15. TGA measurements for microgel FePt hybrid particles with different loadings (heating rate: 10°C/ min, N₂ atmosphere).

Table 5.5. TGA data obtained by a temperature; weight loss between 25- 500°C (*wt loss*), weight left for 500°C (*wt₅₀₀*).

Sample	wt loss [%]	wt ₅₀₀ [%]
FePt	20	80
MG (reference)	91	9
MG@FePt-1	86	14
MG@FePt-2	76	24
MG@FePt-3	73	27
MG@FePt-4	71	29
MG@FePt-5	70	30

5.3.1.3 Temperature Behavior of Microgel FePt Hybrid Particles in Dispersion

PVCL microgel particles are known to have a volume phase transition temperature (VPTT) around 30 to 35 °C. They show a characteristic curve for a temperature trend measurement between 20 and 45 °C. For 20°C the particles are completely swollen with water and start to collapse with increasing temperature until they are completely shrunken. The microgels loaded with FePt nanoparticles preserve their temperature sensitivity (Figure 5.16). All samples with a homogenous distribution of FePt nanoparticles show a standard temperature trend curve, as could be measured for a reference sample without FePt-loading. With higher temperatures, the microgels collapse due to destruction of hydrogen bonds within the polymer network which oppose the hydrophobic attraction forces. It seems that the loading of FePt NPs has no appreciable influence on the mobility of the polymer chains above the VPTT as long as the FePt nanoparticles are well dispersed in the polymer network. Starting from the samples with higher loadings (MG@FePt-4 and MG@FePt-5), the behavior starts to deviate from the former results (Table 5.6). For these samples, a strong clustering of the FePt nanoparticles was observed in TEM measurements. For temperature dependent DLS measurements, the hydrodynamic radii in the swollen state were found to be higher and also radii for collapsed particles increase. The phenomenon described here increases the higher the loadings due to aggregation.

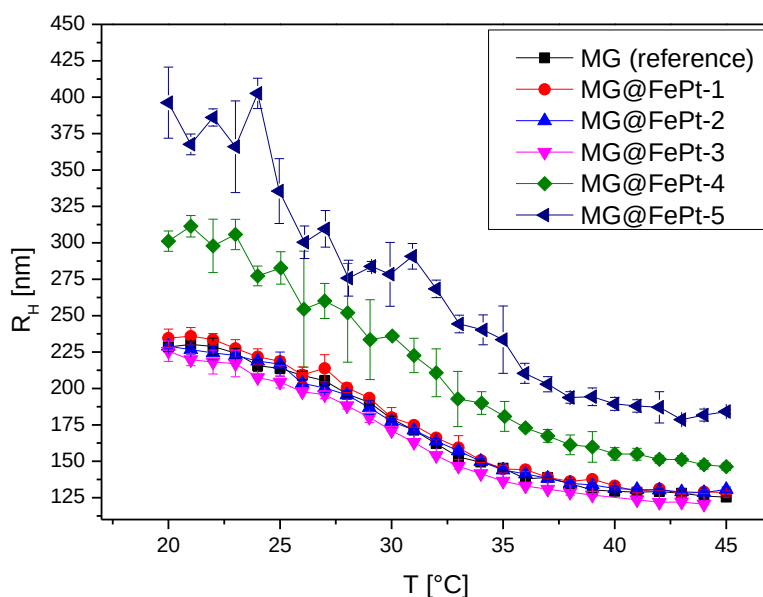
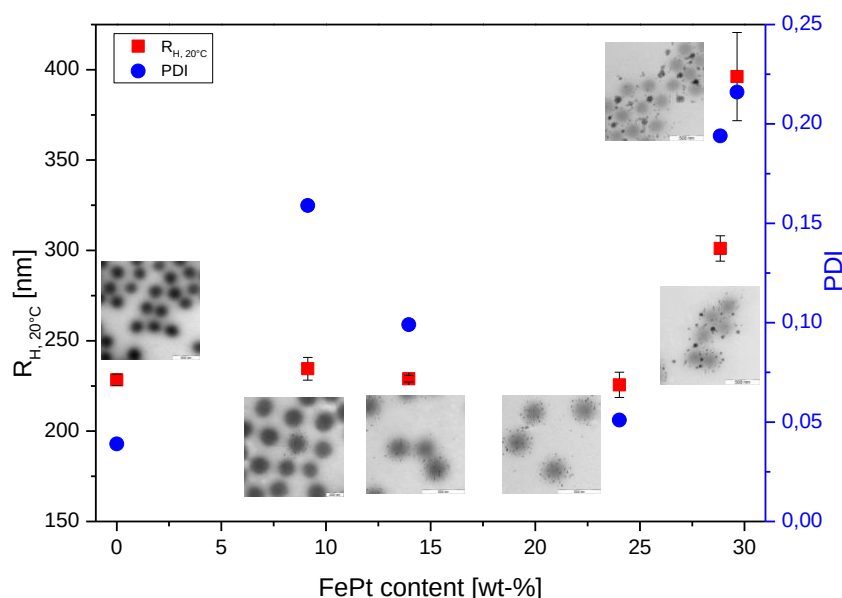


Figure 5.16. Temperature dependent DLS measurements of FePt-loaded microgels.

Table 5.6. VPTT for microgel samples with different degree of FePt-loading calculated from temperature dependent DLS measurement curves (Figure 5.16).

Sample	VPTT [°C]
MG (reference)	30.1
MG@FePt-1	29.8
MG@FePt-2	29.7
MG@FePt-3	30.1
MG@FePt-4	30.6
MG@FePt-5	28.5

Besides the increasing hydrodynamic radii as a function of FePt content, a rise of the PDI is also observed (Figure 5.17). This increase indicates dimerization and slight aggregate formation leading. The loading of the microgel particles is controlled by diffusion of the particles into the microgel. Most of the FePt nanoparticles are expected to be in the shell of the microgel due to the higher crosslinking density in the microgel core.

**Figure 5.17.** The hydrodynamic radii ($R_{H, 20^{\circ}\text{C}}$, red squares) and polydispersity index (PDI, blue circles) of hybrid microgels as a function of FePt content.

This leads to the conclusion that the higher the concentration of FePt, the higher the interactions between FePt and polymer chains are resulting in a reduction of steric stabilization provided by the hydrophilic microgel outer layer.

5.3.1.4 Colloidal stability of Microgel FePt Hybrid Particles in Dispersion

The colloidal stability of microgel dispersions loaded with different amounts of FePt nanoparticles was measured with an analytical centrifuge. The sedimentation behavior was analyzed and compared. The measurements are performed with an integrated optoelectronic sensor system, which allows detection of spatial and temporal changes in transmission of light during the rotation. As a result of accelerating the dispersion in the centrifuge, the phase boundary position between supernatant and sediment is shifted since the particles move in the direction of the cell bottom. To follow the sedimentation processes throughout the measurement, transmission profiles are recorded. The sedimentation behavior of the samples was found to be polydisperse according to differences in size or density. As microgels are known to be very monodisperse, differences in size can be excluded as a possible explanation for the deviations of the sedimentation. Variations in density, meaning non-uniform loading of FePt nanoparticles inside the microgels, seem to be more reasonable as already indicated by the TEM. An additional aspect to this explanation might be an increase in attraction due to magnetic interactions of the loaded microgels leading to slight agglomeration.

For sample MG@FePt-3 transmission profiles are displayed exemplarily for all samples. Figure 5.18 shows the polydisperse sedimentation towards the cuvette bottom. Obviously there are two particle fractions. The dash line indicates the border between the fractions. The first fraction, as shown by the upper part of the graph, consists of slowly settling particles. In the second fraction the particles settle much faster. I assume that in the first fraction consists of well dispersed hybrid microgels, while the second fraction might consist of highly loaded or slightly agglomerated microgel hybrid particles.

In order to determine the sedimentation velocities, the time courses of relative positions of the phase boundaries for the two fractions are thoroughly analyzed. The sedimentation velocity of individual samples can be calculated from the slope of the

linear regions. According to Stokes' law, the sedimentation velocity for diluted samples is proportional to the square of the radius of the particles and their difference in density to the continuous phase (Paragraph 2.2.3 Equation 2.1).

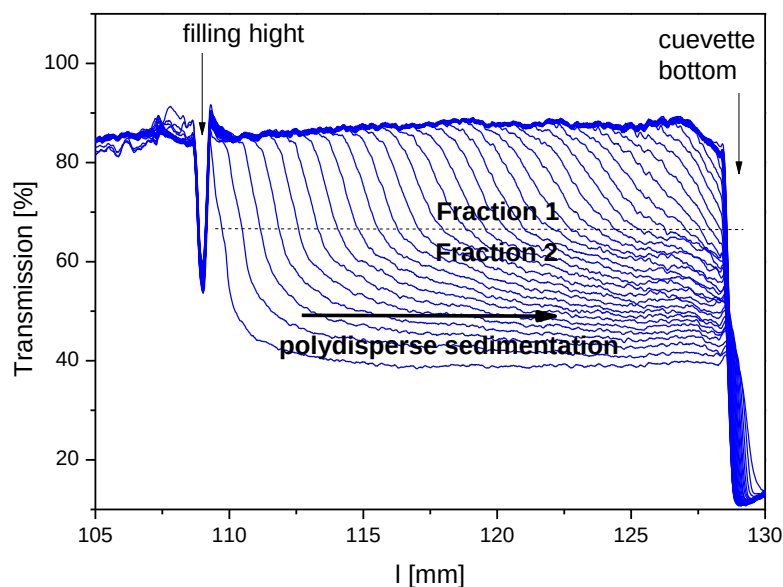


Figure 5.18. Transmission profiles for sample MG@FePt-3 for determination of sedimentation behavior.

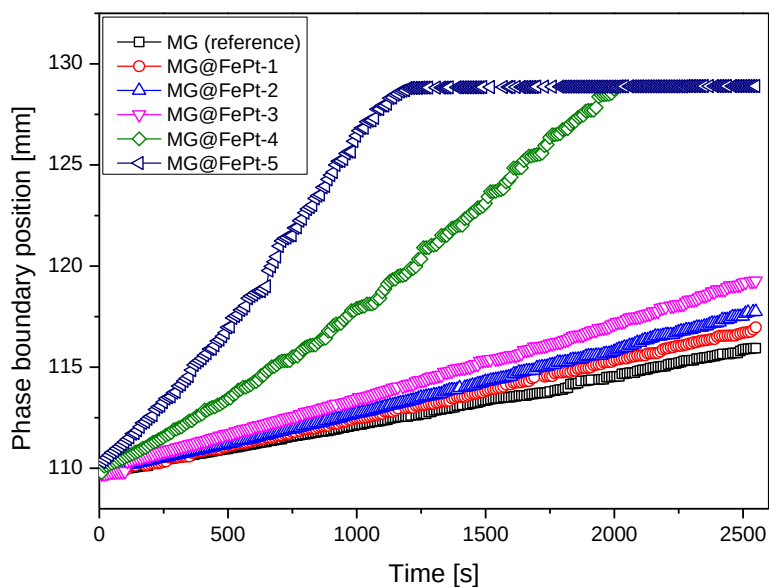


Figure 5.19. Sedimentation curves for fraction 2 of microgel FePt hybrid particles with different loadings (centrifugation speed: 1,000 rpm, temperature 20°C).

Figure 5.19 shows the time courses of relative position of the phase boundary for the second fractions. A consistent decrease in colloidal stability with increasing FePt loading in the microgels can be observed. For microgels with the highest loading, MG@FePt-5, the sedimentation is almost finished after 1,000 seconds. For sample MG@FePt-4 the sedimentation is slower, but is also completed after 2,000 seconds. The sedimentation for all other samples, including the reference microgel and samples MG@FePt-1 to MG@FePt-3 was still in progress as the measurement was finished. For these four samples slight deviances in the sedimentation velocities can be found. As can be seen, the degree of loading influences the colloidal stability.

Detailed analysis of the sedimentation velocity for fraction one, analyzed for all samples, showed that particles in these fraction have nearly the same sedimentation velocity as pure microgels ($2.33 \pm 0.01 \mu\text{m} \cdot \text{s}^{-1}$). Absolute values for all samples range between 2.60 ± 0.02 and $3.37 \pm 0.04 \mu\text{m} \cdot \text{s}^{-1}$. On the lower part of the graph fraction two can be found to settle much faster, indicating a higher density including a higher loading of FePt nanoparticles. The sedimentation velocities measured, as summarized in Table 5.7, show a continuous increase the higher the loading. For the sample Mg@FePt-5, the highest sedimentation of $30.36 \pm 1.42 \mu\text{m} \cdot \text{s}^{-1}$ was determined. This value is 13 times higher than for pure microgels.

Table 5.7. Sedimentation velocity for FePt loaded microgel samples (centrifugation speed: 1,000 rpm, temperature: 20°C).

Sample	$V_{\text{sed, fra1}}$	$V_{\text{sed, fra2}}$
	$[\mu\text{m} \cdot \text{s}^{-1}]$	$[\mu\text{m} \cdot \text{s}^{-1}]$
MG (reference)	2.33 ± 0.01	-
MG@FePt-1	2.60 ± 0.02	5.58 ± 0.19
MG@FePt-2	2.72 ± 0.01	4.53 ± 0.09
MG@FePt-3	3.28 ± 0.01	6.89 ± 0.29
MG@FePt-4	3.27 ± 0.01	15.08 ± 0.60
MG@FePt-5	3.37 ± 0.04	30.36 ± 1.42

5.4 Summary

Two types of hybrid PVCL-microgel based nanocomposites have been presented in this chapter. The successful synthesis of hematite core PVCL shell nanoparticles has been shown in the first part. The PVCL shell was found to be adjustable in thickness during the synthesis. Furthermore, the PVCL shell was found to be effected by external stimuli like pH and temperature. It was observed that changes in pH cause an increase of hydrodynamic radii going from acidic to basic pH. At the same time the electrophoretic mobilities were found to become increasingly negative. As already explained in paragraph 4.2.4, the functionalization reagent HDA diffuses to the monomer/water interface during the solubilization step of the monomer. Afterwards the polymerization is started fixing the charges on the polymer surface. Without HDA only slightly positive charges would be expected on the surface of a PVCL shell due to the positively charged initiator. The increase of number of charges in the microgel shell leads to a strong repulsion of the same. The exertion of additional force on the network leads to a stronger swelling the higher the pH.

A decrease in size was found in a temperature range from 15 to 45°C for all samples. VPTTs were found to be around 30°C. These values are in good consistency to the VPTT of pure PVCL microgels at 32°C. As hydrodynamic radii at 15 and 45°C have been compared, a linear increase in the swelling ratios has been found to increase from 1.7 to 3.6.

TG and IR analysis has given further proofs that PVCL was grafted onto the hematite surface and that the hematite to polymer ratio could be varied with in a range of 0.3 to 1.4.

In the second, part the successful loading of FePt nanoparticles with a diameter of 8.8 nm into PVCL-co-GMA microgels by a solvent exchange method has been shown. Outstanding for this system is the combination of very hydrophobic FePt nanoparticles with hydrophilic, water-soluble microgels. Samples with different degrees of loading have been obtained. (cryo-)TEM images visualized the different degrees of loading and the distribution of nanoparticles in the microgel notably. The distribution for sample

MG@FePt-3 was extraordinarily, as all microgels were loaded with an equal amount of nanoparticles and the distribution of the same is homogeneous.

The absolute amounts of inorganic to organic material could be followed by TG analysis. Loadings of 9 up to 30 wt-% FePt in the samples could be detected.

Surprisingly, the FePt nanoparticles were not found to influence the volume phase transition behavior of the microgels significantly. Temperature dependent DLS measurement showed the characteristic behavior of PVCL microgels. The microgels progressively shrink to a minimum size with increasing temperature within a temperature range between 15 and 45°C. From these curves the VPTTs for the hybrid microgels were determined. All the values around 30°C almost perfectly match the VPTT of the reference microgel (not loaded).

Measurements of the colloidal stability indicate a very good stability of the dispersions showing low tendency for agglomeration and following precipitation. Nevertheless, also these measurements indicate a further need to optimize the loading. It seems that all the samples still contain small amounts of exiguously loaded microgels.

As a general conclusion it can be said that both systems show excellent properties related to the inorganic nanoparticles (e.g. magnetic responsiveness) as well as to the properties of PVCL-based microgels (e.g. temperature-sensitivity). In the future, the targeted stimulations combining these external stimuli might be used in technical (e.g. as micro valves) or medical (e.g. as contrast agent for magnetic resonance imaging) applications.

5.5 Experimental

5.5.1 Synthesis of α -Fe₂O₃ Core PVCL Shell Nanoparticles

Before encapsulation of spherical hematite nanoparticle into PVCL hydrogel, 0.6 mL (22 mg) of α -Fe₂O₃ was pre-functionalized. Therefore, the amount of dispersion needed was mixed with 5 mL water and 0.1 mmol (27 mg) of 16-heptadecenoic acid. Afterwards, 1 mL of ammonia solution (1.3% v/v) was added. The mixture was heated up to 50°C for 30 min.

The encapsulation reaction was carried out under nitrogen atmosphere. For sample α -Fe₂O₃-sp@MG-1, the following procedure was performed. After functionalization of α -Fe₂O₃ nanoparticles, 330 mg VCL and 15 mg BIS were added to the dispersion and the reaction mixture was diluted with 45 ml of warm distilled water and then heated to 70°C. After 30 min, 11.2 mg AMPA, which were dissolved in 1 mL distilled water, were added to the reaction. The reaction was carried out for 3.5 h. For purification, reaction mixture was centrifuged up to five times until the supernatant was clear. The particles were centrifuged at 10,000 rpm for 10 min and washed with 20 mL distilled water per washing step. The particles were washed up to five times. The amounts needed to prepare the other samples can be found in Table 4.8.

Table 4.8. Amounts of chemicals for encapsulation of hematite nanoparticles with a PVCL shell.

Sample	α -Fe ₂ O ₃ -sp [mg]	VCL [mg]	BIS [mg]	AMPA [mg]	H ₂ O [mL]
α -Fe ₂ O ₃ -sp@MG-1	22.0	330.0	15.0	11.2	45
α -Fe ₂ O ₃ -sp@MG-2	22.0	385.0	17.5	13.1	45
α -Fe ₂ O ₃ -sp@MG-3	22.0	440.0	20.0	15.0	45
α -Fe ₂ O ₃ -sp@MG-4	22.0	560.0	25.0	19.0	45

5.5.2 Loading of FePt Nanoparticles into Microgels by Solvent Exchange Method

Used PVCL-co-GMA microgels were synthesized by precipitation polymerization in aqueous solution by Garima Agrawal. Synthetic details and analysis of these colloids can be found in her dissertation.^[21] PVCL microgels were functionalized with 10 mol-% glycidyl methacrylate (GMA) during synthesis. BIS was used as a cross-linker. For the cross-linking 3 mol-% were used.

Synthetic details about FePt nanoparticles synthesis can be found in the dissertation of Katharina Wiemer (Institute of Inorganic Chemistry, RWTH Aachen).^[22]

In a first step, 60 mL microgel dispersion was centrifuged for 30 min with a centrifugation speed of 10,000 rpm. The sediment was collected and redispersed in 50 mL THF using ultrasonification and intense stirring. This procedure was repeated one more time. The solid content of the dispersion obtained in THF was 10.8 wt-%. For the loading, 5 mL of microgel dispersion and an appropriate amount of a dispersion of FePt nanoparticles were mixed for 24 h. Detailed information can be found in Table 4.9. Afterwards, the sample was transferred into dialysis membranes and dialyzed against water for four days changing dialysis water three times per day.

Table 4.9. Amounts of microgel and FePt nanoparticles for hybrid nanoparticle preparation.

Sample	MG [mg]	FePt [mg]	MG [mL]	FePt [μL] ^[a]
MG@FePt-1	54.0	0.54	5	54
MG@FePt-2	54.0	1.08	5	108
MG@FePt-3	54.0	2.70	5	270
MG@FePt-4	54.0	4.05	5	97
MG@FePt-5	54.0	5.4	5	130

^[a] The dispersions of FePt nanoparticles used were taken from the same batch, but concentration of dispersion was varied.

5.5.3 Sample Preparation and Measurement Conditions

The device designations of instruments used for the measurements can be found in the Appendix I.

For the preparation of the TEM samples a drop of the particle dispersion was trickled on a piece of formvar and carbon coated copper grid. Before being placed into the TEM specimen holder, the copper grid was air-dried under ambient conditions. For cryo-TEM the sample was quickly frozen in liquid nitrogen.

ImageJ[®] and WinTEM[™] software was employed to process the TEM digital images to analyze the particle size and morphology. At least 100 particles were measured.

For temperature dependent DLS, one drop of the dispersion is diluted with 5 mL of distilled water. For measurements 1 mL of the diluted dispersion was used. The samples were measured in a range from 15 to 45°C. Temperature was increased with 1°C per step.

For pH dependent electrophoretic mobility and DLS measurements one drop of the dispersion was diluted in 2 mL of distilled water. For further measurements one drop of this diluted dispersion is dropped into 1 mL of a solution with a pH ranging from 3 to 11. 0.8 mL of this dispersion was used for the measurements.

The sedimentation velocities of nanoparticles were measured with an analytical centrifuge. The measurements were performed with a centrifugal speed of 1,000 rpm. Throughout the measurement, 255 transmission profiles are recorded within intervals of 10 seconds.

For sample preparation of IR measurements, samples were dried and few mg of the sample was measured in KBr.

For TGA 5 to 10 mg of the dried sample was measured in a temperature range from 30 to 500°C.

5.6 References

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6 General Conclusions

In this thesis I present new approaches to obtain multi-compartment particles with a plurality of geometries and chemical compositions synthesized in aqueous media. As a template for further synthesis, mainly hematite nanoparticles were used in combination with inorganic materials or polymers. Characterization of these new structures was performed thoroughly. It was found that multi-compartment structures obtained here exhibit new and interesting chemical and physical properties.

Hematite nanoparticles were synthesized with variation of size and morphology ranging from spheres to ellipsoids. The average diameter of the spheres was found to be 73 nm; dimensions for most elongated ellipsoids were determined to be 333 nm for the longitudinal axis and 54 nm for the transversal axis. Sizes and morphologies were found to be infinitely variable between these two extremes. Even if slight differences on the surfaces of both species could be detected, most physical properties as well as chemical behavior were found to be equal for both.

The coating of hematite spheres and ellipsoids with silica was performed using two methods. Firstly, the classical method was used, where TEOS is hydrolyzed in a basic ethanolic solution. Here the influence of the molecular weight of the adhesion promoter poly(vinylpyrrolidone) was analyzed showing no significant difference for the compounds investigated. The second method was developed for the first time in this thesis. Here, water-soluble hyperbranched polyalkoxysiloxanes were used with different modifications. Vinyl-functionalized polyalkoxysiloxanes could be deposited as vinyl-functionalized silica onto the hematite surface. In further experiments it was shown that the double bonds were accessible for further chemical reactions.

Furthermore, asymmetric multi-compartment nanoparticles with extraordinary shapes were synthesized. The targeted formation of lemon-shaped as well as dumbbell-shaped was developed by the step-by-step deposition of single components. To obtain those particles, a seeded emulsion polymerization with further silica deposition method was used. Different copolymer compositions could be attached to the hematite surface with

this method. The main monomer used was styrene; glycidyl methacrylate and *N*-vinylcaprolactam were used to obtain a functional shell.

Hybrid microgel particles were synthesized with two different geometries. On the one hand, hematite core poly(*N*-vinylcaprolactam) microgel shell particles were synthesized with different hematite to polymer ratios. Core-shell particles were found to respond to temperature with a change in the polymer shell dimension. While the shell is temperature-responsive, the core is solid and therefore not influenced by external stimuli like temperature. In detailed studies the shells were found to shrink in the range of the known volume phase transition temperature of poly(*N*-vinylcaprolactam).

On the other hand, poly(*N*-vinylcaprolactam) microgels were loaded with sub-10 nm FePt nanoparticles using a solvent exchange method. What is outstanding here, is the combination of hydrophilic microgels with hydrophobic FePt nanoparticles. The distribution of the FePt nanoparticle in the microgel was found to be relatively homogeneous. Hybrid microgels were responsive to temperature and magnetic fields.

Appendix I Instruments

Transmission electron microscopy (TEM) was measured on Zeiss LibraTM 120 (Carl Zeiss, Oberkochen, Germany). The electron beam accelerating voltage was set at 120 kV. A drop of the sample was trickled on a piece of Formvar and carbon coated copper grid. Before being placed into the TEM specimen holder, the copper grid was air-dried under ambient conditions. For cryo-TEM samples were frozen quickly in liquid nitrogen.

ImageJ and WinTEMTM software was employed to process the TEM digital images to analyze the particle size and morphology. At least 100 particles were measured.

Dynamic light scattering (DLS) and zeta potential measurements were performed on highly diluted dispersion of nanoparticles using a Zetasizer Nano ZS (Malvern Instruments, Worcestershire, UK).

Colloidal stability of dispersions was analyzed by measuring the sedimentation velocity of colloids under centrifugal force using the separation analyser LUMiFuge 1112-54 (L.U.M.GmbH, Germany) with an acceleration velocity of 1,000 rpm. The slope of sedimentation curves was used to calculate the sedimentation velocity and compare the stability of the samples.

USAXS measurements were performed at beamline BW4 at HASYLAB, Hamburg with a beam size of $400 \times 400 \mu\text{m}^2$. The photon energy was set to 8.980 keV, corresponding to a wavelength of 1.381 Å. Scattering patterns were recorded by a MarCCD 165 detector at a sample-to-detector distance of 13,765 mm.

IR spectra were measured using a Nexus 470 (Thermo Nicolet). Samples were dried and measured in KBr.

UV-Vis spectra absorption spectra were measured on dispersion of nanoparticles in de-ionized water using a Cary 100 Bio (Varian).

Fluorescence emission and excitation spectra were collected with Fluoromax-4 (Horiba Scientific) measuring aqueous dispersions. For recording of the emission spectra the dye was excited at 500 nm and the excitation of the spectra was detected at 580 nm.

Field emission scanning electron microscopy (FE-SEM) images and energy dispersive X-ray spectroscopy (EDX) analysis were obtained in a Hitachi SU9000 (Tokyo, Japan) electron microscope using a beam voltage of 30 kV and AZtec control software (Version 2.2, Oxford Instruments GmbH). The EDX maps were recorded with acquisition times larger than 30 min. A BF-STEM detector and a SE detector were used parallel to detect SEM and TEM images at the same time. For sample preparation one droplet of the dispersion was applied onto a copper grid which was covered with a perforated carbon film.

Fluorescence microscopy was performed with a Zeiss Axioplan 2 microscope equipped with XBO 75 illuminating system (Xenon lamp) and by using different filters. A drop of dispersion of the samples was trickled on a 1×3 inch microscope glass slide and then carefully covered with an 18×18 mm cover slip.

X-ray Photoelectron Spectroscopy (XPS) measurements were carried out in an Ultra AxisTM spectrometer (Kratos Analytical, Manchester, UK). The samples were irradiated with monoenergetic Al $K_{\alpha 1,2}$ radiation (1486,6 eV), and the spectra were taken at a power of 144 W (12 kV × 12 mA).

TGA was performed within a range between 30 and 500°C by a NETZSCH TG 209c unit operating under nitrogen atmosphere with 10mL/min flow rate. The heat rate was set to 10 K/min.

Centrifugation was performed on Eppendorf Centrifuge 5810.

XRD measurements were carried out with a X-Ray Diffraktometer D5000HR (Siemens AG, Munich, Germany). The samples were irradiated with monochromatic $K_{\alpha}(\text{Cu})$ radiation with a wavelength of 1.54 Å. For the measurements, samples were filled in 1mm glass capillaries and 2θ scans were performed. In order to reduce Fe-fluorescence, a secondary monochromator was used.

Appendix II Chemicals

All following chemicals were used as received without further purification:

ammonia solution (25% aqueous solution, KMF)

2,2'-azobis(2-methylpropionamidine)dihydrochloride (Sigma-Aldrich)

cysteamine ($\geq 98,0\%$ Sigma-Aldrich),

2,2-dimethoxy-2-phenylacetophenone (DMPAP) (99%, Sigma-Aldrich),

divinylbenzene (98%, Sigma-Aldrich)

ethanol (absolute, AnalaR NORMAPUR)

iron (III) chloride hexahydrate (99%, Merck),

16-heptadecenoic acid (Aaron Chemistry GmbH)

N, N'- methylenebisacrylamide (Sigma-Aldrich)

poly(vinylpyrrolidone) (M_w : 10 kg/mol, M_w : 40 kg/mol, M_w : 55 kg/mol, Sigma-Aldrich)

rhodamine B isothiocyanate (RITC) (Sigma-Aldrich),

sodium dihydrogen phosphate monohydrate (99%, Merck)

tetraethyl orthosilicate (TEOS) (99%, Merck)

tetramethylammonium hydroxide (25% aqueous solution, Sigma-Aldrich)

The following substances were synthesized by

FePt nanoparticles- Katharina Wiemer

PVCL-*co*-GMA microgels, PEOS-PEG and PEOS-PEG-V- Garima Agrawal

Following chemicals were received from Sigma-Aldrich and were used after purification via distillation:

N-vinylcaprolactam

styrene

glycidyl methacrylate

Publications

- [1] Fabrication of magneto-thermo-responsive microgels. (Poster) K. Wiemer, K. Dörmbach, G. Agrwal, A. Pich, U. Simon, *European Materials Research Society 2014 Spring Meeting*, **May 2014**, Lille/ France.
- [2] A. Contin, A. Biffis, S. Sterchele, K. Dörmbach, S. Schipmann, A. Pich, Metal nanoparticles inside microgel/clay nanohybrids: Synthesis, characterization and catalytic efficiency in cross-coupling reactions, *Journal of Colloid and Interface Science*, **2014**, *414*, 41–45.
- [3] K. Dörmbach, G. Agrawal, M. Servos, S. Schipmann, S. Thies, U. Klemradt, A. Pich, Silica-Coating of Hematite Nanoparticles Using Reactive Water-Soluble Polyalkoxysiloxanes, *Part. Part. Syst. Charact.* **2014**, *31* (3), 365-373.
- [4] Loading sub-10 nm magnetic nanoparticles into thermo-responsive microgels by solvent exchange method. (Poster), K. Dörmbach, K. Wiemer, G. Agrawal, U. Simon, A. Pich, *Bayreuth Polymer Symposium*, **Sep 2013**, Bayreuth
- [5] Photochrome Systeme zur Lichtregulierung durch Textilien. (Poster) K. Schäfer, K. Dörmbach, S. Kühl, A. Pich, M. Möller, *Aachen-Dresdener Internationale Textiltagung*, **Nov 2012**, Dresden
- [6] Silica-Coated Hematite Nanoparticles using Water-Soluble Polyalkoxysiloxanes. (Poster) K. Dörmbach, G. Agrawal, X. Zhu, M. Möller, A. Pich, Conference of *European Colloid and Interface Society*, **Sep 2012**, Malmö/ Sweden.
- [7] Novel Luminecent Polymer Films and Filaments For Warning an Security Systems. (Poster) K. Schäfer, H. Wang, K. Dörmbach, A. Pich, M. Möller, C. Damm, W. Peukert, Ch. Wilms, G. Seide, T. Gries, *Aachen-Dresdener Internationale Textiltagung*, **Nov 2011**, Aachen.