SYNTHESIS AND SURFACE MODIFICATION OF DEAGGLOMERATED SUPERPARAMAGNETIC NANOPARTICLES

CHRISTOPH LESNIAK; THOMAS SCHIESTEL; RÜDIGER NASS; HELMUT SCHMIDT
Institut für Neue Materialien, Im Stadtwald, Geb. 43, D-66123 Saarbrücken, Germany

ABSTRACT

A method for the preparation of aminosilane coated, chemically stable, agglomerate-free superparamagnetic iron oxide nanoparticles (ferrites, e.g. Fe_3O_4 and γ-Fe_2O_3) has been developed. These nanocomposite particles posess core-shell structure. The well crystallized core particles are prepared by precipitation from aqueous salt solutions (primary particle size 10 nm). The surface modification of the weakly agglomerated core particles with aminosilane (e.g. γ-aminopropyl-triethoxysilane) leads to deagglomerated particles, covered by a thin polymerized aminosilane shell. A strong dependency of the particle/agglomerate size on the silane/iron oxide-ratio as well as on the disintegration time was found. A ratio of aminosilane to iron oxide of 0.8 (weight ratio) and a disintegration time of 72h result in overall particle sizes in the range of 10-15 nm. After surface modification, aminogroups are present on the particle surface (IEP of 9.5). The particles show superparamagnetic behaviour (saturation magnetization 68 EMU/g) and aqueous suspensions are stable against agglomeration. A desorption of the coating in aqueous suspensions (pH 3 to 11) is not observed.

INTRODUCTION

Cristalline ferrite particles (e.g. magnetite, maghemite) consist of one magnetic domain if the particle size is below 30 nm (single domain particles) [1]. At temperatures above the so called blocking temperature, small single domain particles become superparamagnetic. Particles, aligned in a magnetic field attain the thermal equilibrium almost immediately after removing the sample from the field (relaxation times in the range of seconds); therefore the particles exhibit a high saturation magnetisation but no remanescence, a hysteresis is not observed in H/B curves. Ferrite particles above the critical size of 30 nm have a magnetic multidomain structure and exhibit typical ferrimagnetic behaviour. Iron oxide nanoparticles are generally prepared by wet chemical methods, i. e. precipitation from aqueous salt solutions [2]. It is well known, that the particles tend to form agglomerates due to attractive van-der-Waals forces, whereby the overall surface free energy is reduced. Mere electrostatic stabilization of the colloidal particles in general is not sufficient for a complete deagglomeration.

Attempts have been made, to prepare stabilized, functionalized iron oxide nanoparticles: One approach is the precipitation of particles in the presence of surface active agents (macromolecules, charged-oligomers), which are adsorbed on the particle surface, thereby providing a stabilizing layer against agglomeration. Thus ferritic iron oxide particles with a size of 5 nm can be obtained [3,4], but the disadvantage of this method is the low stability due to desorption of the coating and a subsequent agglomeration. Another approach is the surface modification of agglomerated nanoparticles with bifunctional silanes [2,5,6]. Coated iron oxide agglomerates with sizes above 100 nm were obtained. Interparticle bridging by crosslinking of silanes, and a insufficient deagglomeration of the starting material (prepared by precipitation) cause the agglomeration. To obtain smaller, functionalized particles the deagglomeration

behaviour of iron oxide has to be improved, and a interparticle crosslinking during the modification procedure has to be avoided.

Previously, it could be shown, that surface modification of nano scale powders with short chain bifunctional molecules is a promising approach to deagglomerate nanosized particles in suspension [7,8]. Agglomerates are broken by the input of energy, and the individual particles are immediately stabilized by the interaction e.g. adsorption or reaction of the modifiers with the surface. Thereby, a stabilizing energy barrier is created and the thermodynamic equilibrium is shifted to the side of deagglomerated particles. Since the interaction of surface modifiers with the particle surface is an equilibrium reaction, parameters like chemical composition of surface modifier, reaction time, energy input and concentration of surface modifier have an influence on the modification/deagglomeration procedure. This approach was tested for the preparation of surface functionalized, deagglomerated ferritic iron oxide nanoparticles with aminosilanes as surface modifiers. Aminosilanes were selected on the basis of screening experiments, where different surface modifiers were tested with respect to their potential for iron oxide modification (carboxylic acids, complexing agents, bifunctional metal-organic compounds) [9]. Due to the low hydrolytic stability of Fe-O-Si bonds, the coupled monomer silane molecules have to be polymerized on the particle surface to achieve long term stability against hydrolytic cleavage by removal of water from the system [10]. The influence of the relevant reaction parameters energy input and amount of surface modifier was investigated to evaluate the optimum reaction conditions for the functionalized particles, and particles prepared under optimum conditions were characterized.

EXPERIMENTAL

Iron oxide preparation

$89.40g$ of ferrous chloride tetrahydrate ($FeCl_2*4H_2O$) and $243.3g$ of ferric chloride hexahydrate ($FeCl_3*6H_2O$) were dissolved in oxygen-free deionized water. The mixture was precipitated with NaOH. The precipitate was washed repeatedly with deionized water. The as prepared particles were characterized by x-ray diffraction, TEM, laser light scattering, zeta potential measurements, ICP-AES and magnetic measurements.

Iron oxide modification/functionalization

To an acidic (pH 5) aqueous suspension of iron oxide (5 wt.-%), different amounts of γ-aminopropyl triethoxysilane (APS) were added (weight-ratios silane/iron oxide X= 0.4; 0.6; 0.8; 1,2). The suspension was poured into ethyleneglycol (water/ethyleneglycol; v/v=1), heated up to 80°C and disintegrated by ultrasonic treatment for Y hours (Y = 12, 22, 48, 72). Subsequently, water and ethanol were destilled off under vacuum at 50°C. The suspension was centrifuged for 60 min at 2500 g, and the supernatant colloidal suspension was dialysed against deionized water. The as prepared particles were characterized with respect to particle/agglomerate size by laser light scattering and TEM and with respect to their composition by ICP-AES. Surface chemical properties were determined by zetapotential measurements and magnetic properties were characterized in a vibrating sample magnetometer.

RESULTS AND DISCUSSION

To investigate the approach of deagglomeration/functionalization for the preparation of stable, functionalized, deagglomerated iron oxide nanoparticles, a two step synthesis method was chosen. In the first step, the iron oxide nanoparticle were precipitated from salt solutions, and in the second step, suspensions of the as prepared particles were reacted with aminosilane under ultrasonic treatment. The optimum reaction conditions were evaluated.

Iron oxide characterisation

Iron oxide particles were precipitated from aqueous salt solutions. By laser light scattering a particle size in suspension of 40 to 100 nm was found (fig. 1a). A comparison with primary particle sizes of 8 to 12 nm, determined from a TEM micrograph (fig. 1b), shows, that the particles are agglomerated in suspension.
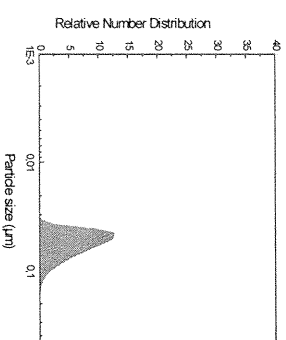
Fig. 1a: Particle size distribution of iron oxide in aqueous suspension (determined by laser light scattering)
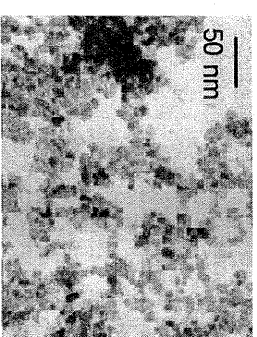
Fig 1b: TEM micrograph of unmodified iron oxide particles

According to x-ray analysis (fig. 2), the particles consist of either magnetite or maghemite. Both nanocrystalline phases cannot be distinguished due to the almost identical lattice parameters. From the peak broadening, a crystallite size of 9 nm was calculated using the Scherrer equation. Due to the small particle size, superparamagnetic behaviour is expected. Measurements in a vibrating sample magnetometer revealed a saturation magnetization of 68 EMU/g (bulk magnetite 122 EMU/g, bulk maghemite 108 EMU/g). The absence of a remanent magnetization indicates superparamagnetic properties (fig 3).
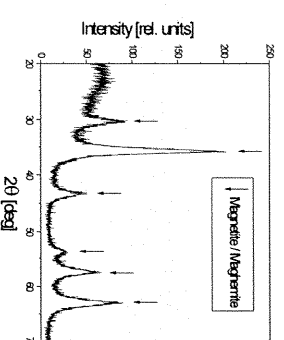
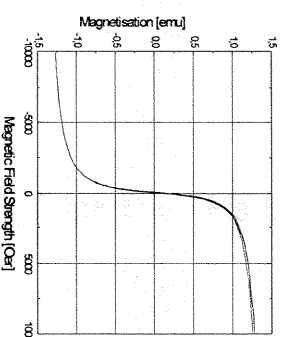Fig. 2: X-ray diffraction diagramm of iron oxide powder

Fig 3: Magnetization curve for unmodified iron oxide particles

Preparation of functionalized deagglomerated particles

Starting point for the development of a synthesis route to functionalized deagglomerated nanocomposite particles with primary particles sizes below 20 nm was the agglomerated iron oxide. According to the mechanism of deagglomeration by input of energy and of stabilization by interaction with surface modifiers, an ultrasonic treatment of an iron oxide suspension in the presence of aminosilane molecules (APS), followed by a polymerization of the silanes on the particle surface (removal of water) should result in a deagglomerated, stabilized and

functionalized individual particles. To prove this hypothesis, the reaction parameters energy input (duration of disintegration procedure) and silane concentration (weight ratio aminosilane/iron oxide) were systematically varied for the modification/polymerization procedure to define the optimum reaction conditions. The particle size in suspension, determined by laser light scattering, was the criterion for optimization. Fig 4 shows the effect of disintegration time on the average particle size (silane to iron oxide weight ratio X = 0.8) and fig. 5 the average particle size (d_{50} values) as a function of silane/iron oxide wt.-ratio (disintegration time: 72 h).
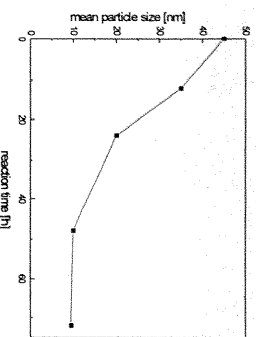
Fig. 4: Average particle/agglomerate size determined with laser light scattering as a function on disintegration time (silane content 80 wt.-% relative to iron oxide)
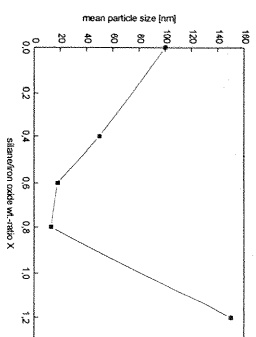
Fig 5: Average particle/agglomerate size determined with laser light scattering as a function of silane concentration (disintegration: 72 h)

The diagram in fig. 4 shows, that the ultrasonic treatment time has a strong influence on the particle/agglomerate size. After 48 h the average particle/agglomerate size is in the range of the primary particle size of iron oxide (10 nm). With shorter disintegration times, a full deagglomeration of the particles cannot be achieved.

In fig 5, the dependence of the average particle size from the silane/iron oxide wt.-ratio is shown. It is evident, that there is an optimum range of silane/iron oxide wt.-ratios between X=0.6 and X=0.8 for the preparation of small functionalized iron oxide particles. If the silane concentration is lower or higher, agglomerates are obtained after the surface modification. These observations are explained by the following model: the interaction of surface modifier molecules with the particle surface is an equilibrium reaction. If the silane concentration is too low, the equilibrium concentration of silane molecules on the particle surface is insufficient to stabilize the particles. On the other hand, if the silane concentration too high, a multilayer of coupled and adsorbed silane molecules is formed around each particle. In between, there is an optimum silane/iron oxide wt.-ratio, where a monolayer of silane molecules is formed around the particles. The structure of the silane-iron oxide particle intermediate influences directly the final particle structure and size after the polymerization of silanes on the particle surface: coated agglomerates are obtained, if the intermediates are agglomerated (silane concentration too low) or if the intermediate particles possess a multilayer structure (silane concentration too high, crosslinking of silanes). Only if the intermediate consists of a particle covered by a monolayer (optimum silane concentration), stable deglomerated, functionalized nanoparticles are obtained. Fig 6 shows the schematic model for the deagglomeration/surface functionalization reaction of iron oxide particles with aminosilanes. From these investigations, the optimum reaction parameters (energy input, aminosilane concentration) could be determined for the preparation of deagglomerated,

functionalized ironoxide particles from agglomerated iron oxide particles. Optimum conditions are a disintegration time of at least 48 hours in the presence of aminosilane with silane/iron oxide wt.- ratios between 0.6 and 0.8.
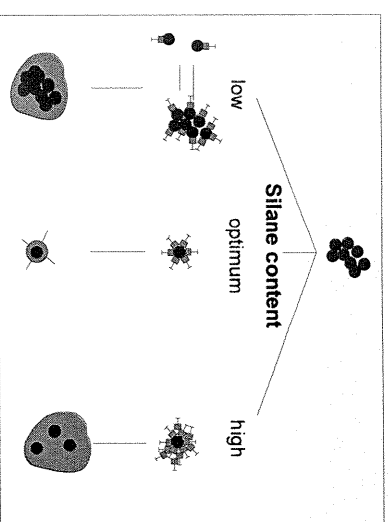
Fig. 6: Model for the deagglomeration/functionalization reaction of iron oxide nanoparticles with aminosilane

Particles prepared under optimum reaction conditions were further characterized by TEM-, zetapotential- and magnetic measurements. Fig. 7a shows a TEM micrograph and fig. 7b the particle size distribution of an aqueous suspension of a functionalized particle. The primary particle size derived from the TEM micrograph of 10 nm and the average particle size determined by laser light scattering of d_{50}=10 nm are in accordance. The particle size distribution in suspension is very narrow, indicating the absence of agglomerates above 20 nm.
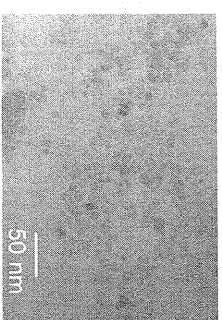
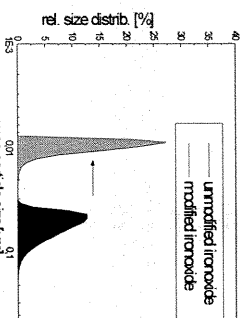Fig. 7a: TEM micrograph of a silane modified iron oxide

Fig 7b: comparison of particle size distribution for unmodified and modified iron oxide (measured by laser light scattering)

To demonstrate the effect of surface modification on the surface chemical properties, zetapotential measurements of unmodified and modified iron oxide were compared (fig. 8). After modification, the particles possess an isoelectric point of 9.5 (unmodified particles IEP of 6), indicating the presence of accessible aminogroups on the particle surface. The magnetic properties of the modified particles were determined by measurements in a vibrating sample magnetometer. A remanent magnetization could not be detected and the saturation magnetization was always in

the range of 60 to 70 emu/g. A silane content between 4 and 5 rel. wt.-% was determined by chemical analysis. From this value a monomolecular layer around the iron oxide particle can be calculated (average molecule size aminosilane appr. 60 $Å^2$), Fig. 9 shows a structure model for the prepared particles.
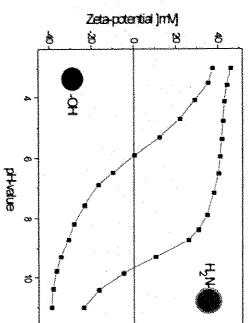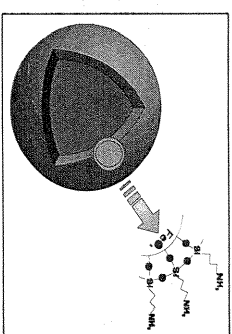
Aqueous suspensions of functionalized iron oxide are stable against agglomeration for at least 6 months and a desorption of the coating was not observed. The particles can be used as precursors for the preparation of inorganic-organic nanocomposites by dispersing them in organic monomers.

Fig. 8: Zetapotential vs. pH curves for unmodified and modified iron oxide

Fig. 9: Core-shell structure model for the functionalized particles

CONCLUSION

The preparation of deagglomerated, functionalized superparamagnetic iron oxide particles with particle sizes below 20nm was possible via a two step synthesis. After the preparation of the core particles in a first step, a surface modification with aminosilanes was carried out in a subsequent step under ultrasonic treatment. It was found, that the reaction parameters silane concentration and reaction time influence the particle/agglomerate size significantly. With a silane/iron oxide wt.-ratio between 0.6 and 0.8 and a disintegration time of at least 48 h, functionalized nanoparticles with diameters in the range of 10-15 nm can be obtained. These results support our reaction model, basing on a deagglomeration-adsorption-polymerization mechanism. Particles obtained under optimum conditions consist of single magnetic domains and exhibit superparamagnetic behaviour at room temperature ($T_{RT} > T_B$; saturation magnetization of 68 EMU/g). Aminogroups are present on the composite particle surface.

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