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Monitoring of the aging of magnetic nanoparticles using Mössbauer spectroscopy



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ABSTRACT

Magnetic nanoparticles made of magnetite have the advantage to be biocompatible and to have a good saturation magnetisation. In this work we show that magnetite nanoparticles change their magnetic and chemical characteristics over time, depending on their storage conditions. To determine the oxidation state of the iron in the core of the nanoparticles Mössbauer spectroscopy was used at 4.2 K. This method is very accurate, especially in distinguishing maghemite and magnetite. The nanoparticles prepared by a co-precipitation method and peptized using acidic media had a core diameter of 5–7 nm. The aging process was monitored until the core was completely oxidised to maghemite and no further change occurred. The greatest change in the magnetic content of the particles was seen during the first 12 h after preparation. To preserve the good magnetic characteristics of magnetite nanoparticles a coating that prevents oxidation is therefore essential. Our results show that the point in time of the characterisation of small magnetic nanoparticles is crucial for the results. Even though magnetite nanoparticles have been formed nearly stoichiometrically, their chemical properties change over time. © 2014 Elsevier B.V. All rights reserved.

1. Introduction

Magnetic nanoparticles (MNPs) made of magnetite have good magnetic characteristics due to their high saturation magnetisation and can be prepared by the co-precipitation of iron salts. Coprecipitation of Fe³⁺ and Fe²⁺ salts in aqueous solutions has the advantage of producing large amounts of iron oxide particles, but it is difficult to control of the particle size distribution [1–4]. For the optimisation of the particle size and its distribution various parameters have to be properly adjusted. First, the appropriate concentration and nature of the precursors have to be found. Then one has to optimise the pH and the ionic strength of reaction solution, as well as the stirring speed, the amount of nitrogen gas to bubbling through the solution. The temperature and the base for precipitation as well as the reaction time must also be chosen [2,4,5]. Other methods for the synthesis of monodisperse magnetic nanoparticles with a high level of size and shape control are based on thermal decomposition. Here, organic iron precursors are decomposed using organic solvents and surfactants. However, severe drawbacks are the small amounts of particles that can be produced and difficulties with the transfer of the particles from the organic into an aqueous phase [2,3,6–8]. Polyol methods can

* Corresponding author. E-mail address: ruemenapp@tum.de (C. Rümenapp). be considered as sol-gel reactions in which the solvents are polyols like diethylene glycol (DEG). These processes harvest a large amount of iron oxide particles with defined shapes, a good control of the size distribution and have the advantage that the polyol solvents also act as stabilisers for the produced particles. The elevated temperature leads to higher crystallinity of the formed particles. They therefore represent a good compromise between methods based on co-precipitation and thermal decomposition. However, comparable to the co-precipitation method, parameters like the solvent, temperature, pH, concentration and nature of the precursors and the agitation level have to be carefully adjusted for optimal results [2].

There are two iron oxides, besides pure metals and other metal oxides, which can be used for the preparation of magnetic nanoparticles [9]. One is Fe₃O₄, magnetite, a mixed Fe(II)–Fe(III) oxide. The other is the Fe(III) oxide γ -Fe₂O₃, maghemite, and can be formed by the gentle oxidation of Fe₃O₄ or the heating of γ -FeO (OH), lepidocrocite. Due to the high electron mobility in the spinel structure of magnetite, magnetite nanoparticles have an interesting surface chemistry, and are subject to an interfacial transfer of ions and/or electrons. This leads to their high sensitivity to oxidation and therefore transformation into maghemite [10]. As a consequence, the synthesis requires not only control of the pH, temperature and ionic strength, but also strictly anaerobic conditions.

In Mössbauer spectra, Fe(II) and Fe(III) can easily be distinguished by their different isomer shifts. The Mössbauer spectra of both magnetite and maghemite are magnetically split into superpositions of six line patterns. Both, magnetite and maghemite can be easily distinguished even at ambient temperature as long as the oxides are macrocrystalline [11,12]. Nanoparticles of magnetite and maghemite with sizes of the order 10 nm or below, however, are superparamagnetic at ambient temperature [13]. The magnetic splitting then collapses into a broad pattern with little structure, which renders a distinction between Fe(II) and Fe(III) difficult or impossible. Magnetite particles with sizes of about 10 nm or below show such relaxation effects quite strongly [14]. At low temperatures, however, the superparamagnetic relaxation is blocked and magnetically split spectra with narrow lines are observed [15,16]. In the spinel structure of magnetite, Fe₃O₄, the tetrahedral sites are occupied by one Fe(III) per formula unit, while the octahedral sites accommodate one Fe(II) and one Fe(III). Above the Verwey transition near 120 K, the two oxidation states on the octahedral sites cannot be distinguished in the Mössbauer spectra due to charge delocalisation. Hence, two magnetic patterns are observed in the Mössbauer spectra, one for Fe(III) on the tetrahedral sites and another one for the mixed-valence iron on the octahedral sites [17,18]. Below the Verwey transition temperature the charges become localised and one can distinguish between octahedral Fe (II) and Fe(III) in the Mössbauer spectra of magnetite. However, the fitting of the spectra is quite complicated because, owing to lattice distortions, a further distinction of lattice sites arises in the Mössbauer spectra. The Fe(II) and Fe(III) contributions can, however, be distinguished quite well by their different isomer shifts [11]. In maghemite, γ -Fe₂O₃, Fe(III) occupies both the tetrahedral and, together with vacancies, the octahedral sites. At low temperatures, the magnetic hyperfine splittings of Fe(III) on both sites in magnetite and maghemite are similar. Their hyperfine patterns overlap with the consequence that one can, at best, distinguish tetrahedral and octahedral Fe(III) by their slightly different isomer shifts [19]. Fe(II), however, can be observed quite reliably even in nanoparticles, where a certain amount of line broadening due to bad crystallinity or surface effects may be present.

In this work, we show how magnetite nanoparticles change their chemical characteristics over time due to oxidation of the Fe (II) to Fe(III) depending on their storage conditions. To determine the oxidation state of the iron in the nanoparticles, Mössbauer spectroscopy at 4.2 K was used. Besides Raman spectroscopy this method has the advantage to be very accurate, especially in distinguishing maghemite and magnetite.

2. Materials and methods

2.1. Materials

Iron(II) chloride tetrahydrate, 37% hydrochloric acid, sodium hydroxide pellets and the Fe Spectroquant Kit (Merck Millipore division of Merck KGaA), 45% iron(III) chloride hexahydrate solution (Riedel-de Haën Laboratory Chemicals), 69% nitric acid (AppliChem GmbH) and diethylene glycol (DEG) (Carl Roth GmbH & Co. KG) were used without further purification. Water was supplied by an Ultra Clear TWF System (Siemens Water Technology) and will be named H_2O_{dd} for double distilled water.

2.2. Magnetic nanoparticle synthesis

For the synthesis of MNPs with a narrow size distribution the protocol of Forge et al. [20] was applied with minor modifications. 45 mmol iron(II) chloride tetrahydrate were dissolved in 37 mmol 45% iron(III) chloride hexahydrate solution. To the mixture 300 ml

of DEG were added under stirring at 150 rpm. The solution was purged with nitrogen throughout the reaction and heated to 170 °C. Subsequently, 15 g of sodium hydroxide pellets were quickly added. The suspension turned black immediately and was kept at 170 °C for 1 h. The following steps were carried out under aerobic conditions. After cooling to room temperature the magnetite particles were magnetically separated and redispersed in 1 M nitric acid using a magnetic stirrer. This washing step was repeated four times. After the last separation the particles were resuspended in H_2O_{dd} to remove most of the acidic environment and stirred at room temperature overnight. The black suspension was sonicated in a water bath at room temperature for 45 min and afterwards centrifuged at 16,700 rcf at 21 °C for 1 h. The iron content of the particle suspensions was determined using the Fe Spectroquant Kit.

2.3. Size characterisation

The size of the particles was determined by transmission electron microscopy (TEM) and dynamic light scattering (DLS). TEM was performed with a JEM-100CX (JEOL Ltd.) at 100 kV. 5 μ l of 10 mM Fe MNP suspensions were applied to a 300 mesh grid coated with carbon. Subsequently, the particles were air-dried at room temperature. The size distribution of the cores of the MNPs was determined from the TEM images with *Analyze Particles* feature of the image-processing software *ImageJ*. A Zetasizer Nanoseries NanoZS (Malvern Instruments GmbH) was used to determine the hydrodynamic diameter of the particles. The particles were diluted in deionised water to 10 mM Fe for both techniques.

2.4. Magnetisation measurements

The particles from aqueous suspensions were freeze-dried, embedded in Fixogum (Marabu GmbH & Co. KG) and the Superconducting Quantum Interference Device (SQUID) measurements were performed with a MPMS XL (Quantum Design Inc.) from -3.5 T to 3.5 T to obtain room temperature M(H) data.

2.5. Mössbauer spectroscopy

The Mössbauer measurements were performed in a liquid helium bath cryostat with the source of ⁵⁷Co in rhodium also at 4.2 K. Samples for Mössbauer spectroscopy were taken when the particles were still in DEG right after the first magnetic separation of the particles after synthesis, after every washing step with 1 M HNO₃ and after resuspension in water. The samples were immediately frozen and kept in liquid nitrogen until being transferred into the Mössbauer sample holders in a nitrogen atmosphere. They were then cooled again in liquid nitrogen and transferred into the liquid helium bath of the cryostat without intermediate warming. A reference spectrum of magnetite was obtained with natural crystalline magnetite at 4.2 K. The fittings for Fe(II) and Fe(III) were done with four octet components for Fe(II) on the octahedral sites, two sextet components for Fe(III) on the octahedral sites and one sextet for Fe(III) on the tetrahedral sites. The four components for Fe(II) were found necessary because the patterns for Fe(II) were found to be substantially broadened. The Lamb-Mössbauer factors for the divalent and trivalent iron were assumed to be equal [21].



Fig. 1. TEM image of the particles (a), size determination by TEM image analysis ($d=5.8 \pm 1.7 \text{ nm}$) (b), and size determination by DLS measurements ($d=9.7 \pm 1.1 \text{ nm}$) (c).

3. Results

3.1. Transmission electron microscopy and dynamic light scattering

Fig. 1a shows a TEM image of the nicely dispersed MNPs. The size distribution of the particle cores (Fig. 1b) was obtained from this image. The log-normal fit gave a size distribution of 5.8 ± 1.7 nm. DLS measurements gave a hydrodynamic diameter of 9.7 ± 1.1 nm (Fig. 1c), which is slightly larger than the core diameter obtained by TEM image analysis.

3.2. Magnetisation measurements

Fig. 2 shows the magnetic moment of the MNPs at different field strengths obtained by SQUID measurements four weeks after the synthesis. The saturated magnetic moment was calculated by fitting to the Langevin function after the subtracting of the diamagnetic contribution. Its value was 41 A m² kg⁻¹ (=41 emu/g).

3.3. Mössbauer spectroscopy

Mössbauer spectra of MNPs were recorded at 4.2 K after the different preparation steps and after different times of ageing. The ratios of Fe(II) to Fe(III) in the particles were determined from the intensities of the individual magnetically split components fitted to the data. Fig. 3a shows, as a reference, an example of a natural crystalline magnetite. The magnetic patterns of Fe(II) are shifted towards positive velocities with respect to those of Fe(III), which causes a typical asymmetric overall Mössbauer spectrum. The most prominent feature caused by the presence of Fe(II) is the peak at the position indicated by an asterisk. The intensity of this peak gives a rough impression of the amount of Fe(II) in a sample



Fig. 2. Magnetic moment of four-week-old particles at different field strengths.

even without a quantitative evaluation of the spectra. Fig. 3b is the spectrum obtained for MNPs still in suspension in DEG. There is a substantial amount of Fe(II) present, though visibly less than in the reference sample (Fig. 3a). After the first wash in 1 M HNO3 (Fig. 3c), the amount of Fe(II) is found slightly diminished. During the following washing steps the amount of Fe(II) decreases but very little. After the fourth wash, the amount of Fe(II) present is still nearly the same as after the first wash (Fig. 3d). Fig. 3e depicts the Mössbauer spectrum of four-day-old particles in aqueous solution. There still seems to be some iron (II) present, but the strong oxidation is evident. After the acidic solution was exposed to air for four weeks, the magnetite is found to have completely oxidised and the Mössbauer spectrum is that typical for maghemite (Fig. 3f). The Fe(II)/Fe(III) ratios derived from the fits of the spectra are summarised in Fig. 4, where the open circles represent the ratios obtained from the spectra of Fig. 3b-f.

4. Discussion

The particles were synthesised using a combination of the coprecipitation and the polyol method [20]. By the applied modifications the size of the particles was tailored to 5.8 ± 1.7 nm. The obtained particles were reasonably mono-disperse and a large amount could be produced. DEG is a non-toxic polyol and its use prevents the agglomeration of the particles during synthesis as well as their oxidation, which at ambient temperature occurs within a few days in an aqueous environment. The elevated temperature during the synthesis improved the formation of the iron oxide crystallites and therefore their magnetic properties [2].

TEM image analysis measures the diameter of each single particle and at the same time provides morphological information. The disadvantage is the clustering of the particles, which can occur during the sample preparation. Liquid samples have to be dried before TEM imaging, since it is performed in vacuum. Due to the lack of a cryo-TEM, where the imaging of native particles in DEG could be possible, images of such particles could not be obtained. An observation of a possible morphological difference between the dried particles and the particles suspended in DEG could therefore not be attempted.

From DLS measurements the hydrodynamic diameter can be obtained within a few minutes. The measurements are done in the liquid environment of the samples and represent large ensembles of the particles. However, the sizes obtained by DLS measurements are larger compared to the sizes obtained by TEM image analysis. The solvent for the measurements has to be chosen appropriately to avoid hydratation artefacts and ion shells around the particle. Due to the intrinsic properties of the DLS method, larger particles are always more prominent in their detection than smaller particles [22]. To reduce the resulting distortion of the observed size distribution, the particle diameters from the number



Fig. 3. 4.2 K Mössbauer spectra of nanoparticles after different stages of synthesis and aging and of natural crystalline magnetite: (a) natural crystalline magnetite; (b) particles in DEG, synthesised under nitrogen conditions; (c) particles after first wash with 1 M HNO₃ under air; (d) particles after the fourth and last wash with 1 M HNO₃ under air; (e) particles in aqueous solution after four days exposure of the solution to air in the Mössbauer sample holder; (f) the same particles in aqueous solution after four weeks in air.



Fig. 4. Ratio of Fe(II) to Fe(III) obtained from the Mössbauer spectra plotted against the particle age, when particles are kept in aqueous solution and exposed to air.

distributions were calculated from the intensity distributions taking this size shift into account.

Nevertheless, one has to keep in mind that the diameters obtained from the DLS measurements are hydrodynamic diameters and are most likely larger compared to the true size obtained by TEM image analysis [22]. Considering this, the agreement of the particle size distributions obtained by the two methods is satisfactory.

The size of magnetite nanoparticles of less than 10 nm makes them easy targets for oxidation [7]. Due to the high surface to volume ratio nanoparticles are chemically very reactive. The large surface leaves many atoms without binding partners compared to atoms in the crystal structure making them willing to react with other chemical partners [13,23], above all with oxygen. The oxidation of magnetite to maghemite could be followed in this work by Mössbauer spectroscopy. By this method, one can follow the oxidation of Fe(II) to Fe(III), which presumably begins at the surface and proceeds into the interior of the particles, although there is no direct evidence for this from the Mössbauer method.

The saturation magnetisation of bulk magnetite is 92–100 A m² kg⁻¹ [10] and for bulk maghemite it is 60–80 A m² kg⁻¹ [10]. Both saturation magnetisations are considerably higher than the magnetisation of the synthesised particles. However, it is known that the saturation magnetisation of nanoparticles is smaller compared to the bulk material. This is caused by the high surface to volume ratio of nanoparticles leaving the ions on the surface without binding partners. This disrupts the crystal structure, leading to a loss of overall magnetisation [24]. The saturation magnetisation obtained by SQUID measurements confirmed the presence of maghemite after four weeks as seen in the Mössbauer spectrum of similarly aged particles. Its value of 41 A $m^2 kg^{-1}$ fits well with the values given in the literature for MNPs, which are in the range of 30–50 Å m² kg⁻¹ [25]. For a better comparison and for an investigation of the development of the magnetisation values during aging, the magnetisation should be determined at different times rather than only four weeks after the synthesis, when, according to the present Mössbauer data, the magnetite would have at least largely oxidised to maghemite. Since the particles had to be dried for the measurement of their magnetisation in the SQUID magnetometer, it was not possible to obtain data for particles in DEG or partly peptized by 1 M HNO₃, where some DEG is still present in the sample. For samples in suspension different methods have to be applied. In order to keep the higher saturation magnetisation of magnetite right after the particle synthesis, a coating of the particles has to be applied as early as possible. Thereby, the influence of the acidic environment and of the ageing process, which was observed in Mössbauer spectra, might be reduced. As expected for superparamagnetic nanoparticles, no hysteresis was observed in the magnetisation measurements. The slight shift, which can be seen in the inset of Fig. 4, is caused by measurement artefacts and not due to hysteresis.

5. Conclusion

In this work we have shown by Mössbauer spectroscopy at liquid helium temperature that the magnetite content of naked magnetic nanoparticles with sizes below about 10 nm decreases rather rapidly after synthesis. Even though magnetite nanoparticles may have been formed initially under carefully maintained anoxic conditions, their characteristics are changing over time, probably within hours, when they are exposed to air. This occurs in hydrous solutions as well as for dried particles. Solvents like diethylene glycol, on the other hand, afford a rather effective protection against oxidation of magnetite to maghemite. A more detailed study of the time dependence of the magnetite to maghemite transformation is under way, but it is already clear that a coating that prevents oxidation is essential for the longterm stability of magnetite particles. In any case, the point in time of the characterisation of small magnetite nanoparticles is crucial for the results of the analysis. The size difference between the TEM image analysis and DLS measurements can be explained by the intrinsic characteristics of the methods. TEM determines the core and DLS the hydrodynamic diameter.

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