

Mössbauer spectroscopy control of the preparation of citric- and mandelic acid functionalized nanomagnetites

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Abstract Iron-oxide nanoparticles were prepared by two ways of chemical methods when the coprecipitated nanomagnetites were functionalized by different (citric and mandelic) carboxylic acids. The colloid samples were characterized by ⁵⁷Fe Mössbauer spectroscopy, electron microscopy, RAMAN spectroscopy and magnetization measurements. Considerable paramagnetic contributions are present in the 80 K Mössbauer spectra in both citric acid coated and mandelic acid coated nanomagnetites. The 5 K measurement revealed that the paramagnetic component appearing at 80 K can represent a superparamagnetic fraction due to the small particle size in the case of mandelic acid functionalized sample. However, in the case of citric acid functionalized nanomagnetite sample, the paramagnetic components occurring also in the 5 K spectra can be associated with components of precursors and of by-product phases.

Keywords ⁵⁷Fe Mössbauer spectroscopy \cdot Iron-oxide nanoparticles \cdot Carboxylic acid coating \cdot Superparmagnetism \cdot Control of synthesis

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1 Introduction

In the last decade iron-oxide based nanoparticles have been used successfully in many new applications like magnetic separation, catalysis, and drug delivery. In many cases the iron-oxide nanoparticles must be coated with a functionalizing carboxylic acid layer. Precursor and by-product phases can be left in the system during the synthesis and the coating process can also result new iron microenvironments as well as and the addition of acids can partially dissolve the nanoparticles causing various processes. ⁵⁷Fe Mössbauer spectroscopy is an excellent tool to monitor these iron containing phases [1, 2]. In this study, we observed that to assign the components satisfactorily recording the Mössbauer spectra of these ferrofluids only at 80 K temperature is not always enough.

2 Experimental

In contrast to the conventional way of the preparation of carboxylic acid functionalized nano iron-oxides [3], we separated the synthetic and the functionalization steps from each other [2].

For the synthesis of nanomagnetite, $FeCl_3 \cdot 6 H_2O$ and $FeCl_2 \cdot 4 H_2O$ were dissolved in water with vigorous stirring at 20 °C under ambient atmosphere. (Excess $FeCl_2$ over the stoichiometric amount was applied to reckon upon the possible oxidation since the preparation occurred in air atmosphere). Then NH_4OH (28 m/m% in water) was quickly added to the mixture under vigorous stirring. The particles were washed with deionized water several times. The functionalization with carboxylic acid were performed in two ways:

METHOD 1. Freshly synthesized nanomagnetites was put in a reactor, then they were coated by adding carboxylic acid dissolved in NH₄OH. Then the reaction mixture was heated up to 60 $^{\circ}$ C during vigorous stirring for 60 min. After magnetic separation the samples were washed with deionized water for neutral.

METHOD 2. Nanomagnetites of different size as used for method 1 were coated by adding mandelic acid and washed with distilled water. A small amount of dispersant (MADEOL-OR95) was added to enhance the stability of the colloid system. Then the system was subjected to ultrasound for 10 min.

The ⁵⁷Fe Mössbauer measurements of nanoparticles were carried out with a conventional constant acceleration (WISSEL) Mössbauer spectrometer using integrated multichannel analyzer and scintillation detection in transmission geometry. The colloid samples were measured in a frozen state at 78 K and 5 K temperatures by the means of a JANIS liquid helium cryostat at 78 K and at 5 K by applying liquid He as coolant. In addition, Mössbauer spectra of dried samples were also recorded at 295 K. ⁵⁷Co source of 0.8 GBq activity in Rh matrix supplied the gamma rays. The isomer shift values are given relatively to α -iron at room temperature. The analysis of the Mössbauer spectra was carried out with the MOSSWINN 4.0 code [4].

Samples were also characterized by TEM (with JEOL 100CXII microscope), RAMANand IR spectroscopy (with Jobin–Yvon triple spectrometer (T64000)) as well as magnetic measurements (with (PPMS-6000 from Quantum Design), too. The details of these results will be published elsewhere.



Fig. 1 FTIR spectrum of citric acid coated iron oxide nanoparticles



Fig. 2 RAMAN spectrum of citric acid coated iron oxide nanoparticles



Fig. 3 FC and ZFC curves (on the left) and magnetization versus magnetic field curve (on the right) of citric acid coated iron oxide nanoparticles

3 Results and discussion

Transmission electron microscopy indicated an average particle size of about 10 nm with a distribution between 6 nm and 15 nm for carboxyl acid (citric acid) coated iron-oxide nanoparticles particles which were prepared by method 1. For the samples (including mandelic acid coated nanoparticles) prepared by method 2, an average size of about 13 nm was observed with a much broader size distribution than that of samples synthesized by method



Fig. 4 ⁵⁷Fe Mössbauer spectra of citric acid coated nanomagnetites, recorded at 80 K (a) and at 5 K (b)

1. These average nanoparticle sizes are consistent with those reported earlier [5] and confirm the successful preparation of nanoparticles.

Figures 1, 2 and 3 show FTIR and RAMAN spectra, as well as magnetization curves, respectively, recorded with citric acid coated iron oxide nanoparticles. All these results reveal that superparamagnetic, nanocrystalline, coated maghemite/magnetite were prepared, well corresponding to the results obtained with nano iron oxides coated different other carboxylic acids [2]. The FTIR spectrum (Fig. 1) is typical of the coated namomagnetite/nanomaghemite particles.

The RAMAN spectrum (Fig. 2) indicate the presence of both nanomagnetite and nanomagnetite since characteristic A_{1g} mode appears around 685 cm⁻¹ for magnetite and around 725 cm⁻¹ for magnetite. By taking into account the ratio between integrated areas associated to these modes the magnetite/magnetite ratio in the sample can be estimated [2].

The typical temperature dependence of FC and ZFC curves (Fig. 3) show the nanostructured nature. The saturation magnetization value around 60 emu/g is well fit to the data obtained for another carboxylic acid coated iron oxide nanoparticles [2].

The obtained particle size values are in the range where iron-oxides are superparamagnetic even at much lower temperatures than room temperature. 80 K Mössbauer spectra of such iron-oxide nanoparticles, prepared by method 1, coated with different carboxylic acids, exhibited only magnetically split subspectra and contained no paramagnetic component at all [2]. Therefore, it was unexpected that we have observed considerable paramagnetic contribution in the 80 K Mössbauer spectrum of the citric acid coated nanoparticles (Fig. 4a) prepared by the same way as those coated with other carboxylic acids.

As the spectra in the Figs. 4a and 5a illustrate, considerable paramagnetic contributions are present in the 80 K spectra not only with the citric acid coated but also with the mandelic acid coated nanomagnetites. Both spectra show envelopes composed of a dominant magnetically split component and paramagnetic contributions. The 5 K Mössbauer spectrum of citric acid coated nanomagnetite (Fig. 4b) is significantly different from the 5 K spectrum of mandelic acid coated sample (Fig. 5b). It can be well seen in Figs. 4 and 5 that while the paramagnetic component disappears from the spectrum (Fig. 5b) of mandelic acid functionalized sample, the 5 K spectrum (Fig. 4b) of citric acid coated sample reflect a significant paramagnetic contribution similar as occurs in its 80 K spectrum (Fig. 4a). For evaluation of paramagnetic components two doublets were supposed for the case of citric acid coated sample while a relaxation component was used for the 80 K spectrum of mandelic acid functionalized sample. To decompose the magnetically split component of



Fig. 5 ⁵⁷Fe Mössbauer spectra of mandelic acid coated nanomagnetites, recorded at 80 K (a) and at 5 K (b)

the 80 K spectrum of a functionalized nanomagnetite is not a simple task, since it has to take into consideration that these nanoparticles are composed from a magnetite core and a maghemite shell, the magnetite can have a non-stoichiometric composition, the relaxation effect of superparamagnetism may influence the spectrum, furthermore the Verwey temperature is shifted compared with the bulk case. At least 3 sextets, one of these representing Fe^{II}, are need for the fits [6-8]. To use hyperfine field distribution, as model independent method, may help to avoid some mentioned problems (e.g. change in Verwey temperature) and this has already been successfully applied for the evaluation of different carboxylic acid coated nanomagnetite prepared with method 1 [2]. In the present case, the hyperfine field distribution method was chosen to evaluate the magnetically split components, since it gave a possibility for comparison with the earlier results [2], too. Note, that practically the same parameters can be derived for the paramagnetic components, determination of which is the main goal, at any models applied for the evaluation of magnetically split parts. The simplest model for the decomposition of 80 K spectrum of citric acid coated sample consists of a sextet and two doublets. Using this model we could get a fit with a relative χ^2 near to 1 (1.05), resulting in parameters shown in Table 1. In the case of the evaluation of 5 K spectrum of citric acid coated sample, we used the same model by applying simultaneous fits for the 80 K and the 5 K spectra. Optimal chi-square value was achieved for the data presented in Table 1. The errors of parameters (in brackets) given Table 1 indicate the standard deviation of parameters calculated by the Mosswinn code. The isomer shifts and quadrupole splittings of components may vary in relatively wide interval taking into consideration a confidence interval of ± 3 times of the standard deviations, but the identification of occurrence of Fe(II) and Fe(III) components is possible.

The Mössbauer parameters (Table 1) of paramagnetic subspectra of citric acid coated nanomagnetite sample reveal the occurrence of Fe^{III} and Fe^{II} iron components. All these Mössbauer parameters show a regular temperature dependence when the temperature changes from 80 K to 5 K. The relative occurrences of the doublets increased at 5 K compared to those of 80 K values. This excludes the association of the paramagnetic component with superparamagnetic relaxation, since this is expected to decrease with lowering the temperature. Consequently, the paramagnetic components occurring in the case of citric acid functionalized nanomagnetite sample can be associated with components of precursors and of by-product phases. The isomer shift and quadrupole splitting data of doublets (Table 1) are close to those characteristic of Fe^{III} and Fe^{II} chlorides in aqueous solutions [9], which

Sample coating acid	Т (К)	Magnetic component hyperfine field distribution			Paramagnetic component (Fe ^{III})				Paramagnetic component (Fe ^{II})			
		A (%)	δ ^c (mm/s)	<i>В</i> ^b (Т)	A (%)	δ (mm/s)	Δ (mm/s)	Г (mm/s)	A (%)	δ (mm/s)	Δ (mm/s)	Г (mm/s)
Citric	80	67.0	0.48	48.8	21.0	0.51	0.57	0.46	11.0	1.42	3.07	0.76
Citric	5	54.8	0.51	50.6	26.8	(0.05) 0.55 (0.05)	(0.01) 0.66 (0.07)	(0.21) 0.45 (0.23)	18.4	(0.01) 1.46 (0.06)	(0.00) 3.34 (0.09)	(0.17) 0.81 (0.24)
Mandelic	80	66.9	0.47	48.95	33.1 ^a	0.50 ^a (0.02)	a	0.43 ^a (0.20)	-	-	-	-
Mandelic	5	100	0.50	50.1	_	_	_	_	_	_	_	_

Table 1 $\,$ 80 K and 5 K ^{57}Fe Mössbauer parameters of nanomagnetites coated with citric acid and with mandelic acid

^aEvaluated as superparamagnetic relaxation component

^bIntegral average hyperfine field

^cObtained by hyperfine field distribution method

might remain in the sample during the preparation since $FeCl_3 \cdot 6 H_2O$ and $FeCl_2 \cdot 4 H_2O$ were used for the synthesis of nanomagnetites. On the other hand, the occurrence of paramagnetic by-products with the citric acid coated nanoparticles might be also possible if excess iron ions in the solution could be bound with citric acid. Since citric acid acts as a tetradentate ligand, considering the stereochemistry, free groups can remain on the surface of citric acid coated nano iron oxide particles to which groups iron ions (e.g. Fe^{II}) can be bound. In the case of mandelic acid, however, no such a bond formation can occur since both free binding groups of mandelic acid are used at the coating of iron oxide nanoparticle.

In the case of mandelic acid coated nanomagnetites the paramagnetic component in the 80 K Mössbauer spectrum can be well evaluated as a relaxation component corresponding to a superpamagnetic state. This agrees that no superpamagnetic component was found in the 5 K spectrum of the sample. Thus, the paramagnetic component appearing at 80 K can represent a superparamagnetic fraction due to the small particle size in the case of mandelic acid functionalized sample. These small particles may be originated from the reprecipitation processes caused by the addition of mandelic acid to nano iron oxide particles.

Figure 6 shows the hyperfine field distributions derived from the magnetically split components of spectra depicted on Fig. 1. The hyperfine field distributions of spectra were derived by the MOSSWINN program using the Hesse-Rübartsch method in the hyperfine field interval indicated in Fig. 6. The decomposition of the distributions were made by Voigt lines in similar way as in [2].

According to our previous work [2] the magnetic field components in the hyperfine field distribution being associated with the most probable iron microenvironments (characteristic of magnetite and maghemite) can be used to derive quantitative analytical information about the maghemite/magnetite ratio. The highest field peak (blue component in Fig. 6) is associated with maghemite, while the lower field peaks reflect magnetite. By this way it was found in [2] that Mössbauer and Raman spectroscopy results both show the same tendency in relations between the nature of carboxylic acids and maghemite/magnetite ratios.



In the present work, in citric acid coated nanoparticles, the maghemite/magnetite ratio relative to that in the pristine sample, derived from the hyperfine field distributions, are in fairly good correspondence with the Raman spectroscopy results. Furthermore, we observed that the maghemite/magnetite area ratio is practically the same in the distributions of citric acid coated sample both at 80 K and 5 K (Fig. 6a and b), which supports the previous conclusions that the precursor or by-product phases represented by the paramagnetic subspectra remained separated from the nanocomposites, and citric acid coated nanomagnetite could be successfully synthesized. This is confirmed by the results of photoacoustic and magnetic measurements, too, similarly as in [2].

The relative occurrences of the components in the hyperfine field distributions of mandelic acid coated sample are very different at 80 K and at 5 K (Fig. 6c and d). Much smaller amount of maghemite is associated with the magnetic component at 80K, without having the superparamagnetic part of the sample, than that reflected at 5 K, when the distribution represents the total material. This suggests that the superparamagnetic part of the sample can be dominantly maghemite. In this case the superparamagnetic maghemite would have particle size smaller than that of magnetite. On the other hand, there is a fairly good correspondence of the hyperfine field distribution between the present mandelic acid coated sample prepared by method 2 (Fig. 6d) and the mandelic acid coated sample prepared by method 1 reported earlier in [2 (Fig. 4i)]. This allow to conclude that characteristic maghemite/magnetite ratio is determined by the applied carboxylic acid even in the case of different preparation ways for the carboxylic acid coated nanomagnetites.

4 Conclusion

Iron-oxide nanoparticles coated with different carboxylic acids were prepared by different ways with two step coprecipitation methods and were characterized by ⁵⁷Fe Mössbauer spectroscopy, TEM, RAMAN and IR spectroscopy and magnetization measurements. Paramagnetic components were observed in the 80 K Mössbauer spectra of both citric and mandelic acid coated nanoparticles. Based on the evaluation of 5 K spectra, the paramagnetic components occurring in the 80 K spectra were identified as a superparamagnetic contribution in the case of mandelic acid coated NPs, while were attributed to precursors or by-product phases in the case of citric acid coated iron-oxide nanocomposite.

Temperature dependent ⁵⁷Fe Mössbauer spectroscopy can be used as a diagnostic method to distinguish superparamagnetic state from by-product phases in the case of carboxylic acid coated iron-oxide nanoparticles.

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