

Factors that may influence the micro-emulsion synthesis of nanosize magnetite particles

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Abstract The influence of experimental conditions on the formation of nanosize magnetite by micro-emulsion method was investigated using Mössbauer and FT-IR spectroscopies, FE SEM/EDS and TEM. It was found that the concentration of starting chemicals ($\text{FeCl}_3/\text{FeSO}_4$), aeration/de-aeration, high alkalinity and γ -irradiation influenced this precipitation process. Rod-like goethite particles $\sim 200\text{--}300$ nm long and up to 10 nm wide were obtained by destabilization of the micro-emulsions aged 5 to 45 days at RT. Si-containing ferrihydrite was also formed and it retarded the formation of goethite by the dissolution/re-precipitation mechanism. A small amount of Si from a glass flask was dissolved. A very strong influence of γ -irradiation on the formation of nanosize magnetite by micro-emulsion method was observed. γ -irradiation created strong reductive conditions in the micro-emulsions. At an ~ 460 kGy dose, nanosize magnetite particles sized ~ 5 to 20 nm and very small amounts of goethite particles were obtained. The EDS measurements on the particles suggested the formation of sub-stoichiometric magnetite ($\text{Fe}_{3-x}\text{O}_4$) and not of maghemite. This finding is in line with the strong reductive conditions induced with γ -irradiation.

Keywords Micro-emulsion · γ -irradiation · Goethite · Magnetite · Si-ferrihydrite

Introduction

Synthetic *iron oxides* (a group name for iron oxyhydroxides and oxides) are important materials with numerous appli-

cations. Syntheses of these compounds are also important from the academic point of view. Researchers are trying to identify the links between the chemical syntheses of *iron oxides* and their chemical, microstructural and physical properties [1–4]. In recent years, researchers have focused on the synthesis of magnetite (Fe_3O_4) particles, which are characterized by specific chemical, electric and magnetic properties. Magnetite particles were utilized in catalysis, protection against microwave radiation, biomedical applications, etc. Many applications of magnetite depend on the size and stoichiometry of its particles. A standard method of the synthesis of magnetite particles is based on alkaline precipitation from the solution of mixed Fe(II)/Fe(III) salts. Magnetite particles can be also produced by a high-temperature decomposition of various iron-organic salts [5]. The latter method is simple and suitable for the preparation of nanosize magnetite particles. Recent research studies have focused on the synthesis of nanosize metal oxide particles using the micro-emulsion method [6–12]. The simplest way to produce these metal oxide particles is to introduce the NH_3 gas into the micro-emulsion containing dissolved metal salt(s) in an aqueous phase and thus precipitate the desired metal oxide. Better results with respect to particle size distribution can be obtained by mixing two identical micro-emulsions, one containing dissolved metal salt(s) and the other a dissolved precipitating agent.

In recent years, γ -irradiation was recognized as a new method in preparing nanocrystalline metals, alloys, composites, metal sulfides and metal oxide particles [13–17]. The main advantage of the γ -irradiation technique is its high reductive power, i.e. it yields a mass of reductive radicals, which are totally clean reductive agents from the viewpoint of green chemistry. Moreover, because γ -irradiations possess extremely high energies, there is no restriction

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regarding the volume of the reaction medium and, which is also very important, no contamination of samples occurs.

In this work, we present new results relating to the formation of nanosize magnetite particles using the two-micro-emulsion method in combination with the γ -irradiation of the resulting micro-emulsion. The objectives of the present work are: (1) to investigate the influence of γ -irradiation on the reductive transformation of ferrihydrite or goethite (α -FeOOH) into magnetite in micro-emulsions, (2) to produce nanosize magnetite particles and (3) to obtain more information about the mechanism of these colloid chemical processes.

Experimental

Chemicals

Triton X-100 (polyoxyethylene(9) 4-(1,1,3,3-tetramethylbutyl)phenyl ether) was supplied by Merck. Cyclohexane, acetone, absolute ethanol, amyl alcohol (*n*-pentanol) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ salt were of analytical purity and supplied by Kemika (Zagreb). The $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ salt was supplied by Ventron and tetramethylammonium hydroxide (TMAH, 97% solid) was supplied by Fluka. Deionized water was prepared in our own laboratory.

Preparation of samples

0.075 M FeCl_3 /0.05 M FeSO_4 aqueous solutions were obtained by mixing equal volumes (100 ml) of freshly prepared 0.15 M FeCl_3 and 0.1 M FeSO_4 stock solutions. The chemical composition of pure micro-emulsions was obtained following the procedure of Yang et al. [18]. The two-micro-emulsion method was used. As the first step, micro-emulsion A and micro-emulsion B were prepared separately under the procedure shown in Scheme 1. Then two micro-emulsions, one containing the iron precursor (micro-emulsion A) and the other containing the precipitating agent (micro-emulsion B) were mixed by rapid adding of micro-emulsion B to micro-emulsion A. The color of micro-emulsion A changed immediately from pale yellow to reddish (micro-emulsion B was colourless and completely optically transparent). Thus, obtained micro-emulsion AB was aged in a closed flask at room temperature (RT) for 5 to 45 days. In a repeated experiment, micro-emulsion AB_{irr} was prepared under the same procedure and bubbled with N_2 for 25 min to remove dissolved oxygen. The micro-emulsion AB_{irr} was then irradiated in a closed flask using ^{60}Co source located in the Division of Materials Chemistry at the Ruđer Bošković Institute. The dose rate applied was ~ 25 kGy/h. The micro-emulsions AB_{irr} were γ -irradiated for 6, 13 and 18 h (the maximal dose received was 466 kGy). Coagulation was

performed by the addition of 7–8 ml of acetone to micro-emulsion AB or AB_{irr} to destabilize reverse micelles. The precipitate was separated from the supernatant by centrifugation at 10,000 rpm for 15 min. After centrifugation, the solution above the precipitate was perfectly clear (pH \sim 11), i.e. there was no size selection of the as-synthesized particles. To properly remove the excess of organic components, the precipitate was additionally washed with absolute ethanol, three times with acetone, then again with ethanol. Each time the precipitate was separated from ethanol or acetone solvent using centrifugation.

The isolated precipitates were dried under vacuum at RT for 48 h. Dried powder samples were analyzed by ^{57}Fe Mössbauer and FT-IR spectroscopy, FE SEM and TEM.

The ^{57}Fe Mössbauer spectra were recorded in the transmission mode using standard instrumental configuration by WISSEL GmbH (Starnberg, Germany). The ^{57}Co in the rhodium matrix was used as a Mössbauer source. The spectrometer was calibrated at RT using the spectrum of standard α -Fe foil. The velocity scale and all the data refer to the metallic α -Fe absorber at RT. The experimentally observed Mössbauer spectra were fitted using the MOSSWINN program.

The FT-IR spectra were recorded at RT using a Perkin-Elmer spectrometer model 2000. The FT-IR spectrometer was coupled with a personal computer loaded with the IR data manager (IRDM) program to process the recorded spectra. The specimens were pressed into small discs using a spectroscopically pure KBr as matrix.

The XRD patterns were recorded at RT using the APD 2000 X-ray powder diffractometer (Cu $\text{K}\alpha$ radiation, graphite monochromator, NaI–Tl detector) manufactured by ITALSTRUCTURES, Riva Del Garda, Italy.

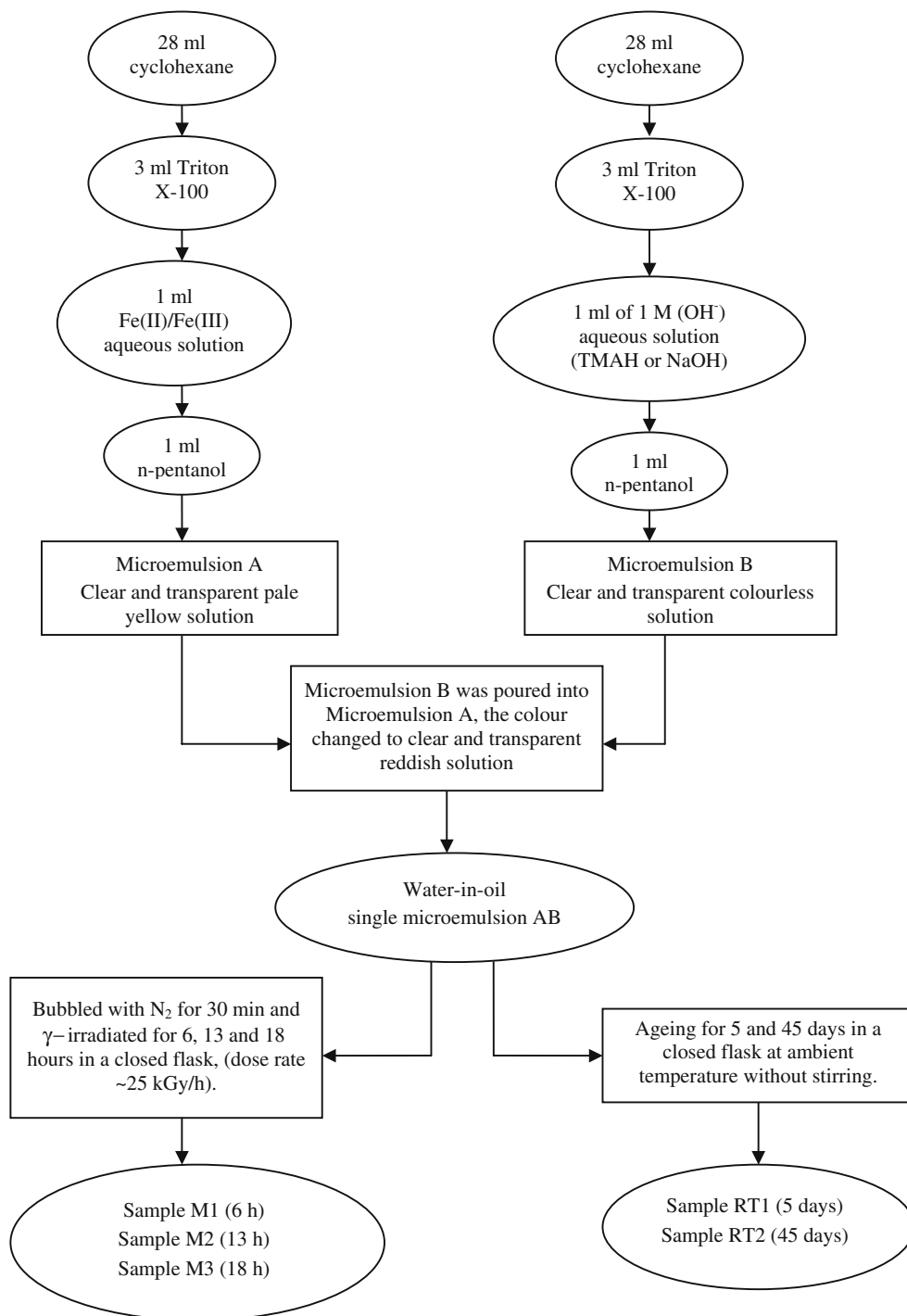
The thermal field emission scanning electron microscope (FE SEM, model JSM-7000F) was manufactured by JEOL. FE SEM was linked to the EDS/INCA 350 (energy dispersive X-ray analyzer) manufactured by Oxford Instruments.

TEM observation was made by an electron microscope manufactured by Opton (model EM-10). Before TEM observation, the powders were dispersed in acetone using an ultrasound bath, then a drop of the dispersion was put on a copper grid previously covered with a thin polymer film.

Results and discussion

Figure 1 shows the FE SEM micrographs of samples RT1 and RT2 obtained by ageing the micro-emulsion AB at RT for 5 and 45 days, respectively. Sample RT1 (Fig. 1a) consisted of the rod-like particles ~ 200 – 300 nm long and up to 10 nm wide. Similar size and geometrical shape were obtained for the RT2 particles isolated from micro-emulsion AB aged for 45 days (Fig. 1b). The FE SEM micrographs

Scheme 1 Experimental procedures for the preparation of samples M1 to M3, and RT1 and RT2.

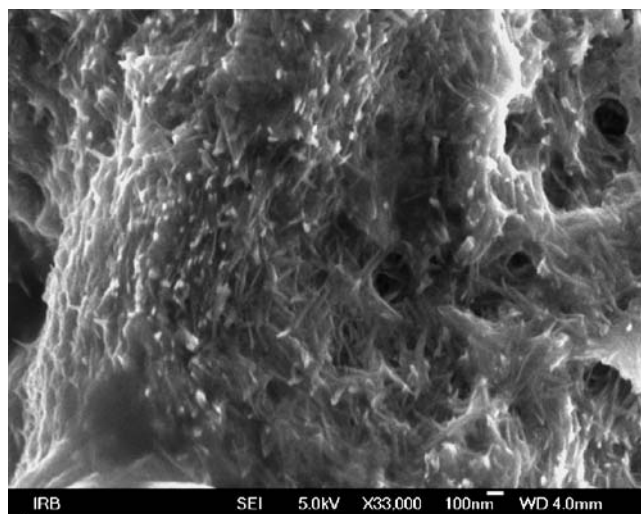


of both samples also showed the presence of an amorphous-like material.

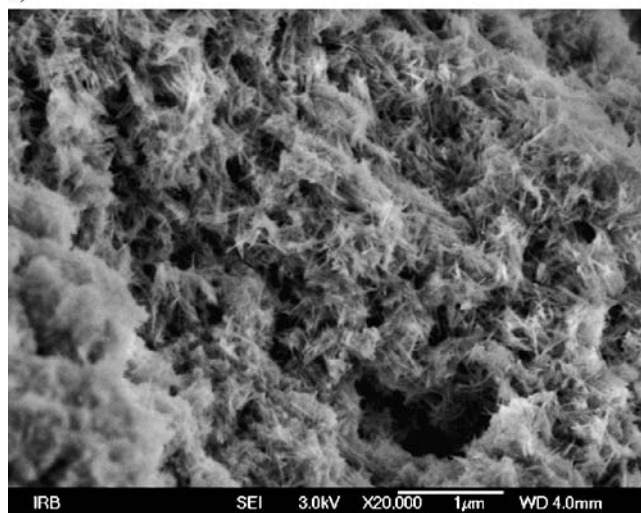
The FT-IR spectra of samples RT1 and RT2 are shown in Fig. 2. The spectrum of sample RT1 shows two very strong IR bands at 890 and 793 cm^{-1} , which can be assigned to Fe–OH bending vibrations, whereas the IR band at 626 cm^{-1} can be assigned to the Fe–O stretching vibrations. These IR bands can be assigned to goethite. A very strong and very broad IR band with two shoulders is observed at

high wave numbers, the shoulder at 3,203 cm^{-1} is due to the presence of an OH stretching vibration in the crystalline structure, whereas the IR band at 3,391 cm^{-1} can be assigned to the stretching vibration of surface H_2O molecules or the envelope of hydrogen-bonded surface OH groups. The IR band at 1,635 cm^{-1} is typical for the bending vibration of OH groups in H_2O molecules. The IR bands at 2,922 and 2,850 cm^{-1} recorded for sample RT1 can be assigned to residual organic groups. The IR

spectrum of sample RT2 showed spectral features similar to those observed for sample RT1. The FT-IR spectra of samples RT1 and RT2 showed a broad and intensive IR band centered at 989 and 1,001 cm^{-1} , respectively. In line with a review by Jambor and Dutrizac [19], this IR band can be assigned to Si-doped ferrihydrite. Carlson and Schwertmann [20] detected a shift of this IR band towards higher wave numbers with increased Si-doping. For example, the location of this IR band was at 925 cm^{-1} for 0.60% Si, whereas it shifted to 935 cm^{-1} for 4.90% Si. In an alkaline pH medium and after a longer ageing time, this IR band was located at 963 cm^{-1} . This effect was assigned to Fe–O–Si bonds in the ferrihydrite structure. Vempati et al. [21] assigned Si–O stretching and Si–O bending vibrations at 1,050 and 459 cm^{-1} , respectively to ferrihydrite having a 0.75 Si/Fe molar ratio. Very probably the location of IR bands corresponding to Fe–O–Si bonds is dependent on the method of preparation of the Si-contain-



a)



b)

Fig. 1 FE SEM micrographs of samples RT1 (a) and RT2 (b)

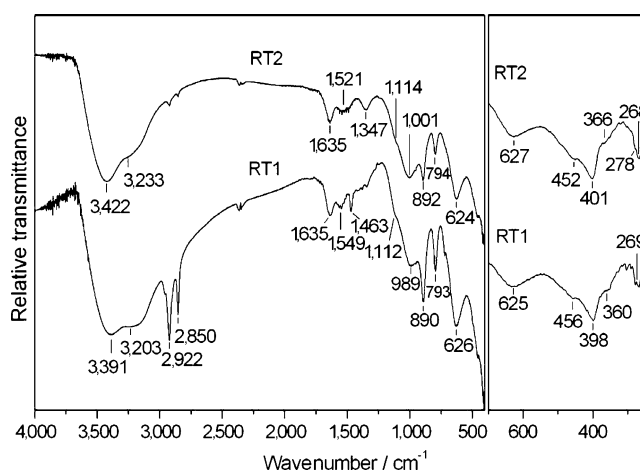


Fig. 2 FT-IR spectra of samples RT1 and RT2 collected over the wave number range of 4,000 to 400 cm^{-1} (mid-infrared region, KBr beam splitter) and 700 to 200 cm^{-1} (far-infrared region, Mylar beam splitter) in KBr pellets

ing ferrihydrite. To check the presence of Si in samples RT1 and RT2, we performed an EDS analysis. Figure 3 shows the EDS spectrum of sample RT2. It is quite clear that in this sample the appearance of Si and Na is due to the dissolving of the glass flask surface in the presence of a strong organic alkali (TMAH).

Figure 4 shows the RT Mössbauer spectrum of sample RT1. This spectrum is a superposition of one sextet ($\langle B_{\text{hf}} \rangle = 34.0$ T) and one doublet 41.2% having an isomer shift, $\delta = 0.35$ and quadrupole splitting, $\Delta = 0.64$ mm s^{-1} . The sextet showed a broadening of spectral lines. This sextet can be assigned to goethite. The Mössbauer spectrum of goethite often shows a broadening of spectral lines, while their intensities may also deviate from the theoretical ratios 3:2:1:1:2:3. Also, the RT Mössbauer spectrum of goethite may vary from a well-shaped sextet down to a paramagnetic doublet, which depends on the size and crystallinity of the goethite particles. Goethite particles smaller than ~15–20 nm show a superparamagnetic type of the Mössbauer spectrum at RT. Goethite particles smaller than 8 nm show a superparamagnetic type of the Mössbauer spectrum down to 77 K [22]. Taking into account the size of goethite particles as detected by FE SEM and the FT-IR spectra, it can be concluded that the central quadrupole doublet (Fig. 3) is due to the Si-substituted ferrihydrite. The RT Mössbauer spectrum of natural ferrihydrite showed $\delta_{\text{Fe}} = 0.35$ mm s^{-1} and $\Delta = 0.83$ mm s^{-1} , whereas a more realistic fit was performed for two doublets with parameters $\delta_1 = 0.35$ mm s^{-1} ; $\Delta_1 = 0.90$ mm s^{-1} and $\delta_2 = 0.36$ mm s^{-1} ; $\Delta_2 = 0.52$ mm s^{-1} . In the present work, the decrease in the average value of $\Delta = 0.64$ mm s^{-1} can be assigned to Si-substitution in the ferrihydrite structure.

Magnetite particles were not found in samples RT1 and RT2. It can be presumed that Fe^{2+} ions oxidized to Fe^{3+} ions because the micro-emulsion AB aged at RT was not

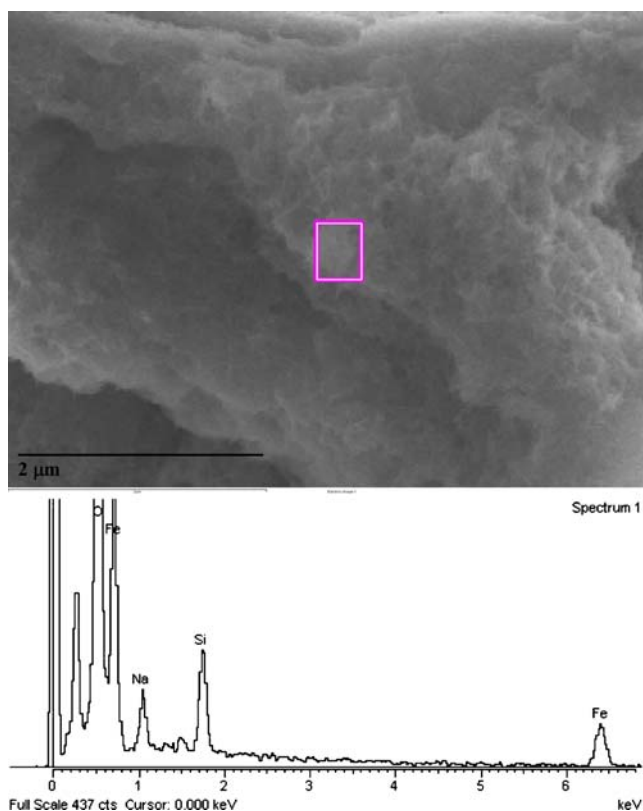


Fig. 3 EDS spectrum of sample RT2

de-aerated. In the micro-emulsion reactors, nanosize ferrihydrite precursors were formed, which upon coagulation transformed into goethite. The presence of Si-substitutions in nanosize ferrihydrite precursors suppressed the formation of nanosize goethite particles in the micro-emulsion reactors. This is also corroborated by the fact that upon 45 days of ageing (sample RT2) a significant amount of ferrihydrite is present. On the other hand, the transformation of ferrihydrite or “amorphous” iron(III)-hydroxide into goethite is a fast process in the presence of TMAH as shown by Krehula et al. [23]. In the presence of TMAH, the initially formed precipitate at RT is completely dissolved on strong shaking as visible to the naked eye. In this way, homogeneous precipitation conditions for the synthesis of α -FeOOH in a highly alkaline medium were achieved with a prolonged ageing time.

AB_{irr} micro-emulsions were exposed to γ -ray doses varying from 148 to 466 kGy. Micro-emulsion M1 received 148 kGy, M2 received 320 kGy and M3 received 466 kGy. The FT-IR spectra of the particles produced in these micro-emulsions are shown in Fig. 5. Samples M1 and M2 showed IR bands at 892 and 794/793 cm^{-1} , typical of goethite. The FT-IR spectrum of sample M3 showed a low intensity peak at 885 cm^{-1} , which can be assigned to the small amount of goethite particles. A very strong IR band was observed for sample M1 at 616 cm^{-1} , which became a shoulder at 621 cm^{-1} for sample M3. Furthermore, sample

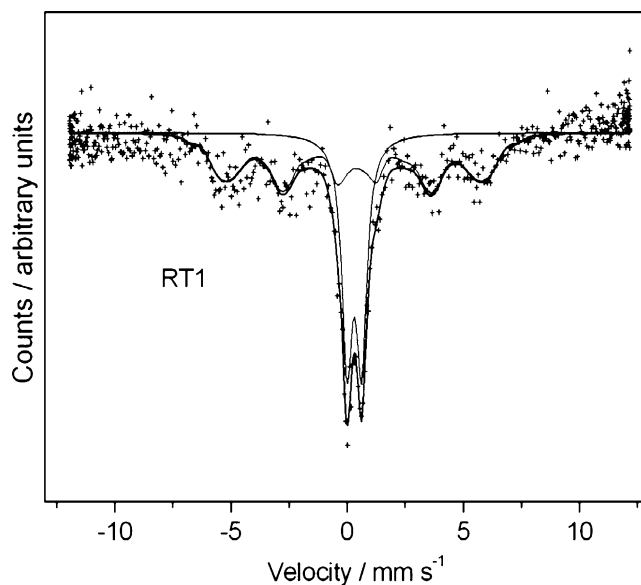


Fig. 4 Mössbauer spectrum of sample RT1

M3 showed a very intensive peak at 589 cm^{-1} . The peak at 589 cm^{-1} can be associated with the presence of magnetite particles. Ellid et al. [24] observed the IR bands at 586 and 404 cm^{-1} for commercial magnetite, whereas for magnetite obtained by the reduction of hematite with starch these IR bands were located at 583 and 393 cm^{-1} . In a work by Grzeta et al. [5], the IR bands for nanosize magnetite particles were measured at 580 and 400 cm^{-1} . Ishii et al. [25] assigned the IR bands at 565 and 360 cm^{-1} to the $\nu_1(F_{1u})$ and $\nu_2(F_{1u})$ vibration modes of Fe_3O_4 . The substoichiometry and crystallinity of magnetite influence the position of these two IR bands [26]. Nasrazadani and Raman [27] showed that upon heating of magnetite in air at 300 $^\circ\text{C}$ a new band was formed at 430 cm^{-1} along with the corresponding disappearance of the ν_2 band.

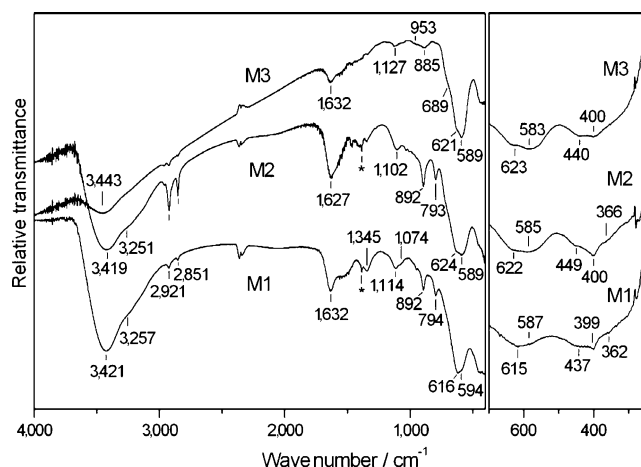


Fig. 5 FT-IR spectra of samples M1, M2 and M3 collected over the wave number range of 4,000 to 400 cm^{-1} (mid-infrared region, KBr beam splitter) and 700 to 200 cm^{-1} (far-infrared region, Mylar beam splitter) in KBr pellets

Figure 6 shows the FE SEM micrographs of samples M1 and M3 obtained by the γ -irradiation of the micro-emulsion at RT at a dose rate of ~ 25 kGy/h for 6 and 18 h, respectively. Sample M1 consists mainly of rod-like particles, whereas sample M3 consists of discrete spherical particles sized about 8–10 nm.

Sample M3 showed the highest magnetic response in the external magnetic field; this was less pronounced in sample M2, while there was no magnetic response for sample M1. Figure 7 shows the RT Mössbauer spectrum of sample M3 and stoichiometric magnetite (Fe_3O_4) for comparison. Stoichiometric magnetite was obtained on hydrogenation of commercial sub-stoichiometric magnetite ($\text{Fe}_{2.90}\text{O}_4$) for 3.5 h at 375 °C. The RT Mössbauer spectrum of these micrometer sized stoichiometric Fe_3O_4 particles can be fitted with two sextets. The outer sextet with a hyperfine magnetic field $B_{\text{hf}}=49.0$ T and the isomer shift $\text{IS}=0.26$ mm/s relative to $\alpha\text{-Fe}$ corresponds to the Fe_A^{3+} ions at the tetrahedral A sites. The inner sextet with $B_{\text{hf}}=46.0$ T

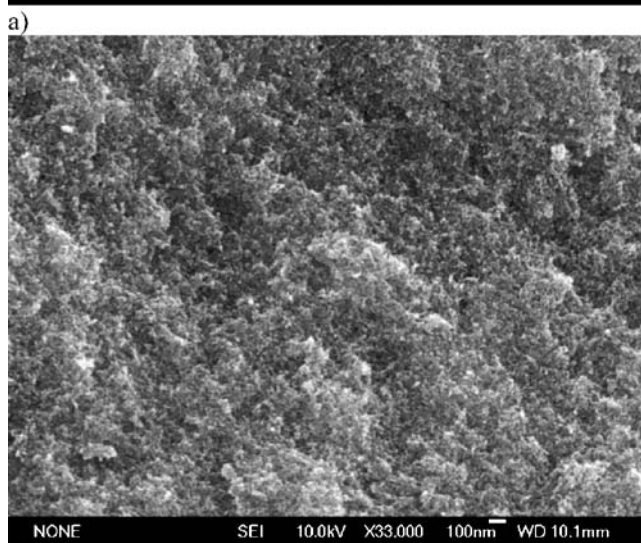
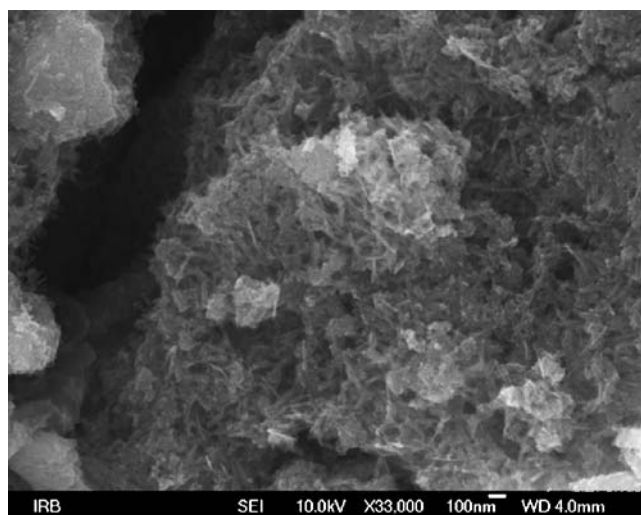


Fig. 6 FE SEM micrographs of samples M1 (a) and M3 (b)

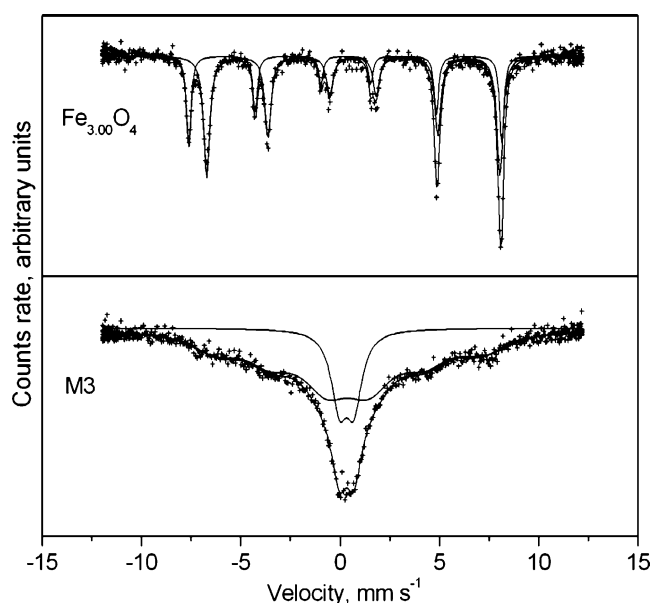


Fig. 7 Mössbauer spectra of stoichiometric magnetite ($\text{Fe}_{3.00}\text{O}_4$) and sample M3. Stoichiometric magnetite was obtained on hydrogenation of commercial sub-stoichiometric magnetite ($\text{Fe}_{2.90}\text{O}_4$) for 3.5 h at 375 °C

and $\text{IS}=0.67$ mm/s is due to the Fe^{2+} and Fe^{3+} ions at the octahedral B site. Since the Fe_B^{2+} and Fe_B^{3+} sites are indistinguishable at RT due to the rapid electron hopping process, which is faster ($\tau\sim 1$ ns) than the decay of the excited state of ^{57}Fe ($\tau\sim 98$ ns), the inner sextet is fitted to the average charged $\text{Fe}_B^{2.5+}$. The non-stoichiometry of magnetite could be precisely measured by a decrease in the relative surface area of the inner sextet in the Mössbauer spectrum. Besides stoichiometry, the particle size also has a strong influence on the Mössbauer parameters because

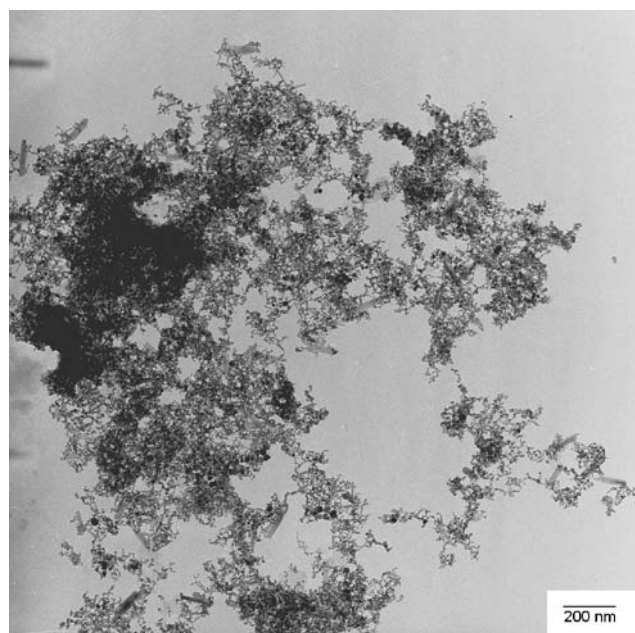


Fig. 8 TEM micrograph of sample M3

magnetically ordered materials in the form of very small particles exhibit superparamagnetic behavior. The superparamagnetic magnetite nanoparticles (smaller than 10 nm) show doublets in the Mössbauer spectrum at RT. In the intermediate range (magnetite particles size about 10–20 nm), complex Mössbauer spectra with broadened lines and unusual line shapes are formed at RT [28]. The Mössbauer spectrum of sample M3 (Fig. 7) is fitted to one average (collapsing) sextet with $\langle B_{\text{hf}} \rangle = 41.5$ T and one central quadrupole doublet (20.4%). This spectrum of sample M3 can be assigned to very fine magnetite particles. A TEM micrograph of sample M3 confirmed that the magnetite particles were in the nanosize range between 5 and 20 nm (Fig. 8). The EDS measurements of the iron to oxygen ratio in these particles were in favour of sub-stoichiometric ($\text{Fe}_{3-x}\text{O}_4$). It is evident that the γ -irradiation of micro-emulsions AB_{irr} created strong reductive conditions favoring the formation of magnetite with increased γ -doses. To be sure that strong reductive conditions in micro-emulsion were due to the γ -irradiation, we prepared the micro-emulsion under the same procedure described for sample M3 (bubbling with pure nitrogen for 30 min and aged for 18 h at RT); however, without γ -irradiation. FT-IR spectrum of the precipitate showed characteristic bands of goethite at 885, 789 and 613 cm^{-1} . Also, we recorded the corresponding XRD pattern and in line with PDF card No. 29-0713 the XRD pattern can be assigned to goethite. Thus, bubbling of the micro-emulsion with pure nitrogen was not responsible for the strong reduction conditions and for that reason we conclude that only γ -irradiation created strong reductive conditions in the micro-emulsion, which was crucial for the formation of magnetite. The effect of γ -irradiation on the phase transformation was also observed by other researchers. For example, Wang and Xin [29] detected the transformation of β - FeOOH into α - FeOOH at the initial stage of γ -irradiation. At a dose of 64.3 kGy, only the Fe_3O_4 phase was found. Ni et al. [30] prepared plate-shaped γ - Fe_2O_3 particles starting from the water/isopropyl alcoholic solution of FeSO_4 neutralized with $\text{NH}_3(\text{aq})$. The suspension was subjected to γ -irradiation, whereas the isopropyl alcohol served as a scavenger of oxidative radicals. The γ -irradiation technique was also used in the preparation of γ - Fe_2O_3 nanoparticles coated with gold [17]. These investigations and the results of the present work showed new potentials in the synthesis of magnetic *iron oxides* by using γ -irradiation of the precipitation systems.

Conclusion

The precipitation systems were obtained by mixing two micro-emulsions, one containing dissolved iron salts and

the other a strong organic alkali. These systems proved to be very sensitive to the concentration of the starting chemicals ($\text{FeCl}_3/\text{FeSO}_4$), aeration/de-aeration, high alkalinity and especially γ -irradiation.

Rod-like goethite particles ~200 to 300 nm long and up to 10 nm wide were obtained upon destabilization of the resulting micro-emulsions aged for 5 to 45 days at RT. Both precipitates showed the presence of an amorphous-like material identified as Si-containing ferrihydrite. A small amount of Si from a glass flask was dissolved in a highly alkaline medium. Si-containing ferrihydrite retarded the formation of goethite by the dissolution/re-precipitation mechanism.

γ -irradiation of the same micro-emulsion (previously de-aerated) created strong reductive conditions in the precipitation systems. At doses of up to 325 kGy, goethite and magnetite particles were formed, whereas at the dose of 466 kGy, nanosize magnetite ($\text{Fe}_{3-x}\text{O}_4$) particles ~5 to 20 nm were obtained. EDS measurements of the Fe to O ratio suggested the formation of sub-stoichiometric magnetite ($\text{Fe}_{3-x}\text{O}_4$) and not of maghemite. This finding is in line with strong reductive conditions induced with γ -irradiation.

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