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Gamma-irradiation synthesis of iron oxide nanoparticles in the presence of PEO, PVP or CTAB



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HIGHLIGHTS

- γ -irradiation synthesis produced a small amount of δ -FeOOH in samples.
- The use of 2-propanol increased the yield of rod-like goethite particles.
- Experimental conditions for the synthesis of pure magnetite particles were found.
- γ -irradiation of an Fe(III)/PEO aqueous precursor produced rigid black hydrogels.

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ABSTRACT

Black hydrogels were synthesized using γ -irradiation of poly(ethylene oxide) (PEO)/iron(III) chloride precursor solutions. The magnetic properties of such hydrogels were improved by adding 2-propanol as a hydroxyl scavenger and/or NaBH₄ as a strong chemical reducing agent; however, the rigidity and compactness of thus synthesized PEO hydrogels deteriorated. The magnetic suspension containing pure magnetite nanoparticles was obtained using γ -irradiation of an Fe(III)/PEO deoxygenated aqueous solution in the presence of 2-propanol and NaBH₄. The γ -irradiation of an iron(III) chloride aqueous precursor solution in the presence of PVP produced a magnetic suspension due to the formation of a small amount of δ -FeOOH (feroxyhyte). The γ -irradiation of Fe(III)/CTAB (cetyltrimethylammonium bromide) aqueous solutions favored the formation of goethite. γ -irradiation in the presence of 2-propanol increased the yield of rod-like goethite nanoparticles. A small amount of δ -FeOOH found in the Fe(III)/PVP and Fe(III)/CTAB suspensions suggests the formation of Fe(OH)₂ upon γ -irradiation, which then under atmospheric conditions rapidly oxidized into δ -FeOOH.

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1. Introduction

γ -irradiation is a powerful technique to synthesize nanoparticles (NPs) of controlled size and shape in a solution as well as in heterogeneous media such as hydrogels. γ -irradiation takes the advantage of inducing solvated electrons and other reducing species to reduce metal ions homogeneously in the whole volume of the sample. γ -irradiation synthesis takes place at room temperature and under ambient pressure, whereas the control of physico-chemical properties of synthesized samples can be achieved by adjusting the dose rate and the absorbed dose. In addition to that γ -irradiation synthesis can yield products that could not be obtained by conventional synthesis routes. γ -irradiation synthesis has been frequently used in the reduction of

noble metal ions, followed by the formation of metal clusters and the growth of nuclei into metal nanoparticles. Usually various polymers, surfactants or small organic molecules (Hanžić et al., 2015) have been used in order to inhibit coalescence and aggregation of noble metal particles through steric hindrances or electrostatic repulsion. It is also noted that some of these polymers, like poly(vinyl alcohol) (PVA) and polyvinylpyrrolidone (PVP), act simultaneously as stabilizers and reducing agents (Beloni et al., 1998; Hoppe et al., 2006; Krklješ et al., 2007). However, the γ -irradiation synthesis and stabilization of transition metals or metal oxides such as magnetite that are highly susceptible to the presence of oxygen is very difficult due to easy (re-)oxidation of ferrous ions (Fe²⁺) in atmospheric conditions, especially if magnetite particles are in the nanosize range (Gotić et al., 2007). Besides, in an aqueous solution Fe²⁺ ions quickly oxidize by taking up oxygen dissolved in water. Moreover, even with a properly deoxygenated solution, water molecules alone can oxidize Fe²⁺ ions. A conventional method for the synthesis of magnetite

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Table 1

Experimental conditions for the synthesis of samples PEOFe-1 to CTABFe-3. The dose rate of γ -radiation was ~ 7 kGy h^{-1} , whereas the absorbed doses (D) are given in the second last column. All the samples were γ -irradiated in the deoxygenated (nitrogen) atmosphere at room temperature.

Sample	Polymer / surfactant	wt% of polymer aqueous solution	wt% of Fe^{3+} (in relation to polymer mass)	pH	NaBH_4	2-propanol (0.2 M)	D / kGy	Obtained gel or suspension
PEOFe-1*	PEO $\bar{M}_v = 8 \cdot 10^6$	1.8%	5% Fe^{3+} (acetate)	4			123	gel
PEOFe-2*	PEO $\bar{M}_v = 4 \cdot 10^5$	1.8%	5% Fe^{3+} (acetate)	9			123	gel
PEOFe-3*	PEO $\bar{M}_v = 2 \cdot 10^5$	1.8%	5% Fe^{3+} (acetate)	12			442	gel
PEOFe-4*	PEO $\bar{M}_v = 4 \cdot 10^5$	1.8%	5% Fe^{3+} (acetate)	12			442	gel
PEOFe-5*	PEO $\bar{M}_v = 8 \cdot 10^6$	1.8%	5% Fe^{3+} (acetate)	12			442	gel
PEOFe-6*	PEO $\bar{M}_v = 8 \cdot 10^6$	1.8%	5% Fe^{3+} (acetate)	12			123	gel
PEOFe-7	PEO $\bar{M}_v = 4 \cdot 10^5$	1.8%	5% Fe^{3+} (chloride)	12			113	gel
PEOFe-8	PEO $\bar{M}_v = 4 \cdot 10^5$	1.8%	5% Fe^{3+} (chloride)	12			441	gel
PEOFe-9	PEO $\bar{M}_v = 4 \cdot 10^5$	0.5%	20% Fe^{3+} (chloride)	12			441	gel
PEOFe-10	PEO $\bar{M}_v = 4 \cdot 10^5$	1.8%	5% Fe^{3+} (chloride)	12		2-propanol	113	laxly gel
PEOFe-11	PEO $\bar{M}_v = 4 \cdot 10^5$	1.8%	5% Fe^{3+} (chloride)	12	NaBH_4		113	suspension
PEOFe-12*	PEO $\bar{M}_v = 4 \cdot 10^5$	1.8%	5% Fe^{3+} (acetate)	13–14	NaBH_4		113	suspension
PEOFe-13	PEO $\bar{M}_v = 4 \cdot 10^5$	1.8%	5% Fe^{3+} (chloride)	8–9	NaBH_4	2-propanol	429	laxly gel
PEOFe-14	PEO $\bar{M}_v = 4 \cdot 10^5$	0.5%	5% Fe^{3+} (chloride)	8–9	NaBH_4	2-propanol	113	suspension
PVPFe-1	PVP M.W. 10 000	3.6%	2.5% Fe^{3+} (chloride)	12			113	suspension
PVPFe-2	PVP M.W. 10 000	3.6%	2.5% Fe^{3+} (chloride)	12		2-propanol	113	suspension
CTABFe-1	CTAB	1.8%	5% Fe^{3+} (chloride)	9			113	suspension
CTABFe-2	CTAB	1.8%	5% Fe^{3+} (chloride)	9–10		2-propanol	113	suspension
CTABFe-3	CTAB	1.8%	5% Fe^{3+} (chloride)	12		2-propanol	113	suspension

* Results of the analysis for these samples are given in Supplementary.

particles is based on alkaline precipitation from the properly deoxygenated aqueous solution of mixed Fe(II)/Fe(III) salts. The syntheses of magnetite starting from pure Fe(III) salts include the use of reducing agents, which can be avoided by γ -irradiation synthesis. For instance, Gotić et al. (2009a) avoided the use of an Fe(II) precursor and opted for the γ -irradiation of an Fe(III) precursor in a microemulsion, which in turn promoted the reductive dissolution and recrystallization of ferrihydrite nanoparticles into magnetite. Moreover, it was shown that the ferrihydrite nanoparticles formed in a microemulsion transform easily and quantitatively to magnetite nanoparticles upon γ -irradiation. Based on these results one can conclude that there are no difficulties in the transformation of ferrihydrite to magnetite nanoparticles with the aid of γ -irradiation. Quite to the contrary, however, Jurkin et al. (2011) have shown that ferrihydrite nanoparticles settled (precipitated) at the bottom of a flask did not transform to magnetite (Fe_3O_4) or to any other iron oxide phase upon γ -irradiation. These results are not in contradiction with the results of Wang et al. (1997,1999) who have reported the transformation of akaganeite (β - FeOOH) to magnetite in a γ -irradiated aqueous suspension containing 20 vol% of isopropanol as a hydroxyl scavenger. Wang et al. (1997) performed the γ -irradiation experiments under constant stirring. In this way akaganeite particles were mechanically dispersed in an aqueous suspension by stirring, thus enabling a good contact between the solid and liquid phases. Accordingly, to ensure and to maintain the well dispersed system is as important as achieving the reducing conditions upon γ -irradiation.

In this work iron(III) precursors were γ -irradiated in the presence of poly(ethylene oxide) (PEO), polyvinylpyrrolidone (PVP) or cetyltrimethylammonium bromide (CTAB). The aim of this work was to study the influence of these selected polymers/surfactants on the radiolytical synthesis of iron oxides. Generally, the type of polymers or surfactants can influence the particle size distribution, morphology, stability and dispersivity of iron oxide nanoparticles in aqueous solutions. Specifically, the PEO, PVP and CTAB have been selected due to the following reasons: PEO is a

semicrystalline polymer that easily crosslinks and forms hydrogels upon γ -irradiation in aqueous solutions (Jurkin and Pucić, 2012, 2013; Savaş and Güven, 2002; Ulański et al., 1995a,1995b). PEO is a biocompatible and hydrophilic polymer with numerous applications such as hydrogels for active substance release and polyelectrolytes. PVP is a water soluble and biocompatible polymer with important applications in the pharmaceutical field. PVP can modify iron oxide surface properties and stabilize NPs in aqueous solutions (Wang et al., 2007). PVP is also a polymer that predominantly crosslinks under irradiation, and can form hydrogels on irradiation of aqueous solutions (Kaplan and Guner, 2000; Jovanović et al., 2011). CTAB, cationic surfactant, is a face selective adsorption additive that favors the formation of 1D nanostructures, for instance CTAB is crucial in the formation of 1D nanorod gold nanoparticles (Jana et al., 2001).

2. Materials and methods

2.1. Synthesis of samples

Iron(III) chloride and iron(III) acetate salts were used as precursors for the synthesis of iron oxide nanoparticles in different polymeric systems. To prepare nanocomposites polymer/surfactant aqueous solutions with added Fe(III)-salts were irradiated. Polymer/surfactant aqueous solutions were 1.8 wt% and 0.5 wt% in systems with PEO, 1.8 wt% in systems with PVP and 3.6 wt% in systems with PVP. The mass of Fe(III) ions was 5 wt% (2.5 wt% and 20 wt% in systems with PEO) in relation to polymer mass. The pH of solutions was adjusted to a 2 M NaOH aqueous solution. To some solutions a strong reducing agent NaBH_4 was added as a 2 M $\text{NaBH}_4/2$ M NaOH aqueous solution. The final concentration of 2-propanol in a solution was 0.2 M.

All the prepared precursor solutions were bubbled with nitrogen for at least 20 min in order to remove dissolved oxygen before γ -irradiation. The detailed experimental conditions and exact

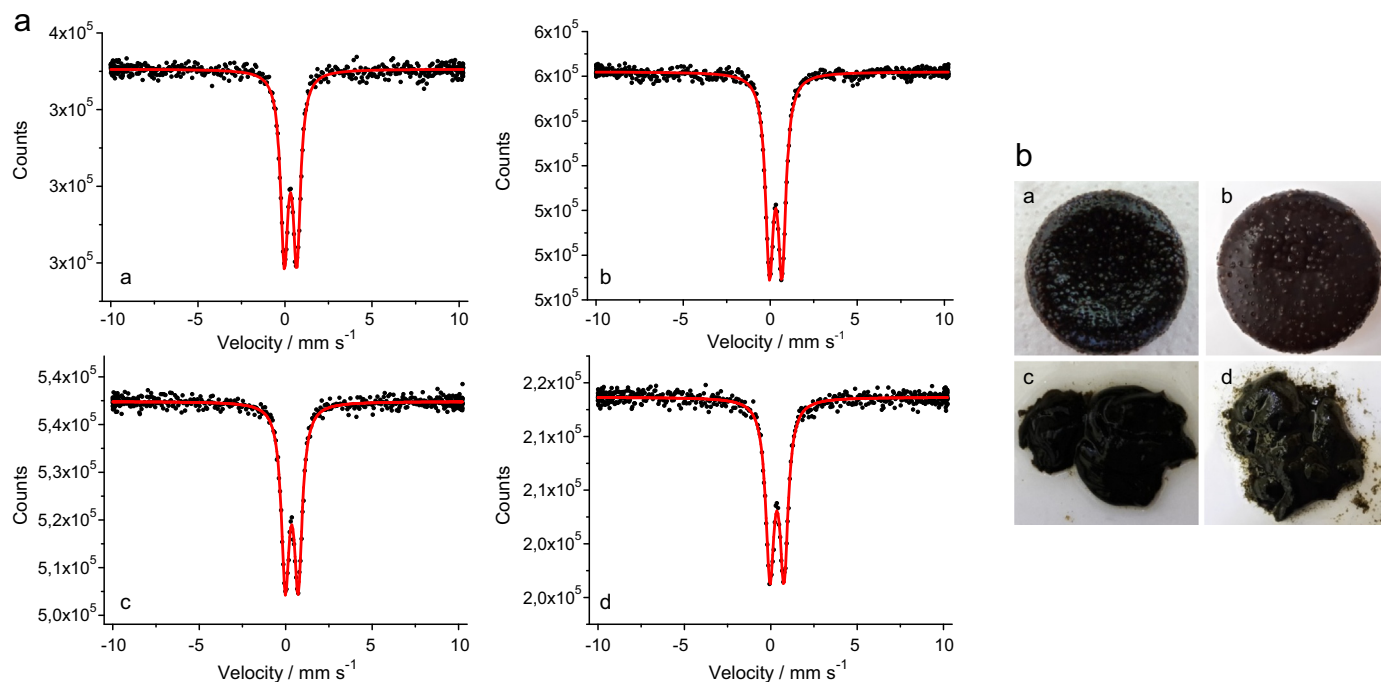


Fig. 1. The Mössbauer spectra recorded at 20 °C (panel A) and photographs (panel B) of samples PEOFe-7 (a), PEOFe-8 (b), PEOFe-10 (c), and PEOFe-13 (d). Mössbauer parameters are given in Table 2.

absorbed doses are given in Table 1. γ -irradiation was performed at room temperature in a ⁶⁰Co γ -irradiation facility located in the Laboratory for Radiation Chemistry and Dosimetry, Division of Materials Chemistry at the Ruđer Bošković Institute. The dose rate of γ -irradiation was ~ 7 kGy h⁻¹.

2.2. Characterization of samples

Synthesized samples were characterized as dried gels or as isolated suspensions/precipitates. Precipitates were isolated from suspensions by centrifugation, followed by washing with ethanol. Scanspeed 2236R high-speed centrifuge was used. In the case of magnetic suspensions samples were isolated by repeated decantations with the help of a permanent magnet. Obtained gels and isolated precipitates were dried under vacuum at room temperature, then characterized using FE SEM, XRD and ⁵⁷Fe Mössbauer spectroscopy.

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

X-ray powder diffraction (XRD) patterns were recorded at room temperature using the APD 2000 X-ray powder diffractometer (CuK α radiation, graphite monochromator, NaI-Tl detector) manufactured by ItalStructures, Riva Del Garda, Italy. The XRD patterns were recorded over the 15–75 ° 2 θ range with a 2 θ step of 0.03 ° and a counting time per step of 15–30 s.

⁵⁷Fe Mössbauer spectra were recorded at 20 °C in the transmission mode using a standard instrumental configuration by WissEl GmbH (Starnberg, Germany). The ⁵⁷Co in the rhodium matrix was used as a Mössbauer source. The spectrometer was calibrated at 20 °C using the standard α -Fe foil spectrum. The velocity scale and all the data refer to the metallic α -Fe absorber at 20 °C. The experimentally observed Mössbauer spectra were fitted using the MossWinn program.

3. Results and discussion

3.1. γ -irradiation synthesis of iron oxide nanoparticles in the presence of PEO

Irradiation of PEO/iron oxide aqueous solutions resulted in the formation of gels or suspensions depending on the starting composition of the systems (Figs. S1 and S2 in the Supplementary Information).

Fig. 1 shows the photos and Mössbauer spectra of samples PEOFe-7, PEOFe-8, PEOFe-10 and PEOFe-13. These black PEO/Fe-oxide gels were formed upon γ -irradiation of Fe(III) chloride/PEO aqueous solutions at high pH ~ 12 (the detailed experimental conditions are given in Table 1). Sample PEOFe-10 was γ -irradiated in the presence of 2-propanol, while sample PEOFe-13 contained NaBH₄ beside 2-propanol. Samples synthesized without 2-propanol were rigid and compact (Fig. 1a and b). In contrast to that, the γ -irradiation of an Fe(III)/PEO precursor in the presence of 2-propanol deteriorated the rigidity and compactness of gels (Fig. 1c). With the addition of NaBH₄ (Fig. 1d) the deterioration of gels continued to increase. All samples in Fig. 1 were characterized with a Mössbauer doublet having an isomer shift of about 0.32 mm s⁻¹ and a quadrupole splitting of about 0.7–0.8 mm s⁻¹ (the Mössbauer parameters are given in Table 2). The dark color of the samples suggests the formation of magnetite or maghemite; however an accurate phase analysis in the present case is not possible because the Mössbauer doublet can arise from any paramagnetic and/or superparamagnetic iron oxide phase. It should be pointed out here that the XRD powder diffraction patterns of such type of samples (iron oxide gels) do not allow the phase identification of samples due to extremely broad XRD maxima (Fig. S3). Nevertheless, sample PEOFe-10 is slightly magnetic, whereas sample PEOFe-13 is highly magnetic (checked by a permanent magnet), which suggests the formation of magnetite or maghemite.

The FE SEM images and Mössbauer spectra of samples PEOFe-9

Table 2
 ^{57}Fe Mössbauer parameters at 20 °C calculated for samples PEOFe-6 to CTABFe-3.

Sample	Fitting curve	δ (mm s $^{-1}$)	Δ or E_Q (mm s $^{-1}$)	B_{hf} (T)	Γ (mm s $^{-1}$)	Relative area (%)	Phase composition	Phase fraction
PEOFe-6*	D1	0.32	0.72		0.52	100	PD and/or SP	1.00
PEOFe-7	D1	0.32	0.71		0.52	100	PD and/or SP	1.00
PEOFe-8	D1	0.31	0.71		0.55	100	PD and/or SP	1.00
PEOFe-9	D1	0.31	0.67	31.1	0.51	55.4	PD and/or SP	0.55
	G1	0.35	-0.27		0.30	44.6	Goethite	0.45
PEOFe-10	D1	0.35	0.74		0.57	100	PD and/or SP	1.00
PEOFe-11	D1	0.33	0.77	24.5	0.49	58.3	PD and/or SP	0.58
	M1	0.22	-0.09		0.19	41.7	Maghemite	0.42
PEOFe-12*	D1	0.33	0.83		0.61	100	PD and/or SP	1.00
PEOFe-13	D1	0.36	0.81	47.9	0.58	100	PD and/or SP	1.00
	M1	0.32	-0.00		0.46	32.8	Substoichiometric magnetite (Fe $_{2.81}$ O $_4$)**	1.00
	M2	0.55	-0.03		0.59	14.9		
PEOFe-14	M3	0.51	-0.04	40.1	0.62	52.3		
	D1	0.33	0.67		0.79	9.6	PD and/or SP	0.10
	G1	0.40	-0.26	37.8	0.31	15.6	Goethite	0.75
CTABFe-2	G2	0.39	-0.27	32.4	0.47	60.2		
	H1	0.39	-0.09	49.7	0.75	14.6	Hematite	0.15
	G1	0.39	-0.27	35.4	0.25	86.9	Goethite	0.87
CTABFe-3	D1	0.37	0.65		0.69	13.1	PD and/or SP	0.13

Key: δ =isomer shift given relative to α -Fe at RT; Δ or E_Q =quadrupole splitting or quadrupole shift; B_{hf} =hyperfine magnetic field; Γ =line width. Error: $\delta = \pm 0.01$ mm s $^{-1}$; Δ or $E_Q = \pm 0.01$ mm s $^{-1}$; $B_{\text{hf}} = \pm 0.2$ T.

Remarks: PD=paramagnetic doublet; SP=superparamagnetic doublet; G1=sextet of goethite; G2=goethite sextet fitted to the distribution of hyperfine magnetic fields; M1=outer subsextet of magnetite or maghemite sextet fitted to the distribution of hyperfine magnetic fields; M2=inner subsextet of magnetite; M3=introduced imaginary subsextet ("smear" subsextet) fitted to the distribution of hyperfine magnetic fields; H1=sextet of hematite.

* Mössbauer spectra of samples are given in Supplementary material (Fig. S2).

** In the substoichiometric magnetite Fe $_{3-x}$ O $_4$, x represents the vacancy concentrations. x is calculated by formula $x = [2 - S_{M2}/S_{M1}] / [6 + 5(S_{M2}/S_{M1})]$, where S_{M2} is relative surface area of inner (octahedral) M2 subsextet (14.9%) and S_{M1} is relative surface area of outer (tetrahedral) M1 subsextet (32.8%) in the Mössbauer spectrum.

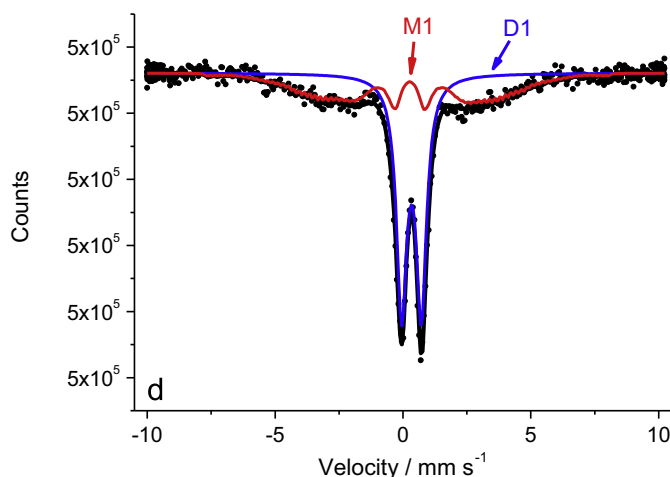
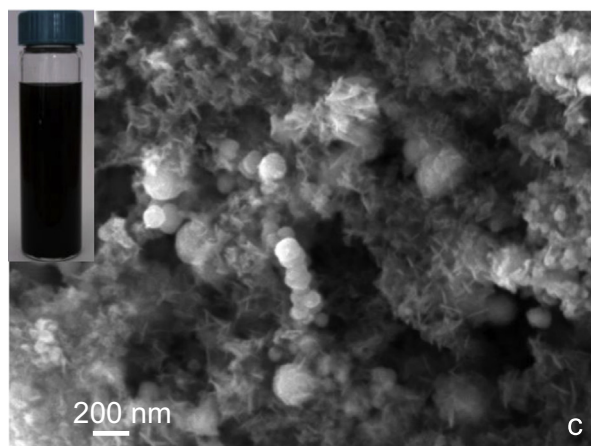
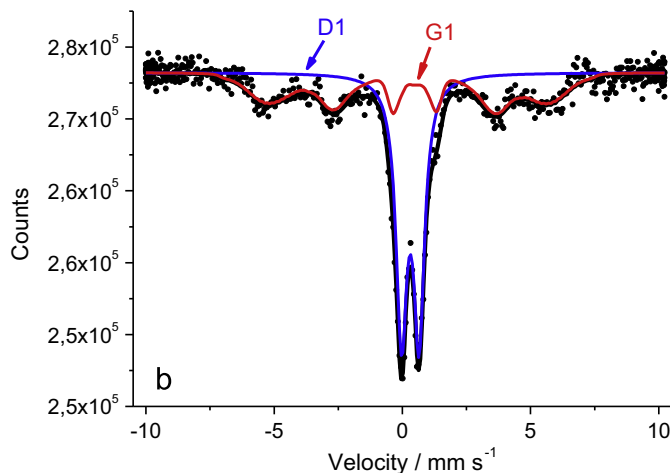
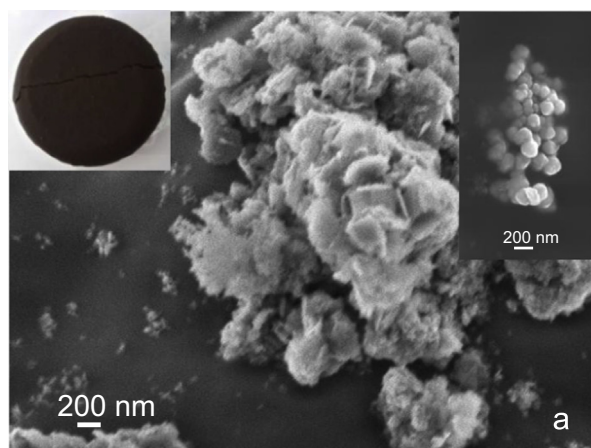


Fig. 2. The FE SEM images and Mössbauer spectra recorded at 20 °C of samples PEOFe-9 (a) and (b) and PEOFe-11 (c) and (d). Mössbauer parameters are given in Table 2. The inset shows the corresponding photographs of the obtained gel (a) and suspension (c). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

and PEOFe-11 are given in Fig. 2. Fig. 2a shows the FE SEM images of sample PEOFe-9. This sample was formed by γ -irradiation of a solution without 2-propanol or NaBH_4 and it contained a lower amount of PEO and a higher amount of Fe(III) chloride than other samples. The sample consists of two types of iron oxide particles dispersed through the whole polymer matrix with a tendency to aggregate. The inset shows pseudospherical smooth particles about 150 nm in size. The big image shows highly aggregated plate-like nanoparticles. The Mössbauer spectrum of sample PEOFe-9 (Fig. 2b) is a superposition of G1 sextet (44.6%) and D1 doublet (55.4%). Based on fitted parameters ($\delta=0.35 \text{ mm s}^{-1}$, $B_{\text{hf}}=31.09 \text{ T}$ and $\Delta=-0.27 \text{ mm s}^{-1}$) (Table 2) the G1 sextet can be assigned to goethite. The G1 sextet shows a broadening of spectral lines. 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. Besides, the room temperature Mössbauer spectrum of goethite may vary from a well-shaped sextet down to a paramagnetic doublet, which depends on the size and crystallinity of goethite particles (Gotić and Musić, 2007; Gotić et al., 2009a, 2007). Hence the Mössbauer doublet (Fig. 2b) is due to the presence of a paramagnetic and/or superparamagnetic iron oxide phase. Sample PEOFe-9 is brown (inset of Fig. 2b), which suggests the presence of a very small proportion of some other iron oxide phase (magnetite, maghemite or ferrihydrite), because the color of goethite is yellow to dark yellow.

Fig. 2c shows the FE SEM image of sample PEOFe-11: a magnetic suspension formed upon irradiation with the addition of NaBH_4 at a high pH. This sample consists of irregular spherical particles about 100–200 nm in size and of plate-like particles. The Mössbauer spectrum of sample PEOFe-11 (Fig. 2d) is a superposition of a M1 collapsing sextet fitted to the distribution of hyperfine magnetic fields (41.7%) and a D1 doublet (58.3%). Based on fitted parameters ($\delta=0.22 \text{ mm s}^{-1}$, $B_{\text{hf}}=24.5 \text{ T}$ and $\Delta=-0.09 \text{ mm s}^{-1}$) the sextet can be assigned to maghemite. The reduced hyperfine field of 24.5 T compared with the well-crystallized maghemite (50.0 T) can be generally assigned to aggregation and/or small particle size as well as to a low crystallinity of maghemite. The assignment to maghemite is in accordance with the EDS analysis (Fig. S4) which revealed the Fe:O ratio of 2:3 at the position of the spherical particle and about 1:2 at the position of plate-like particles. In addition to that, sample PEOFe-11 is magnetic as checked by a permanent magnet.

Fig. 3 shows the FE SEM, Mössbauer and XRD characterizations of sample PEOFe-14: a black highly magnetic suspension formed upon γ -irradiation of a PEO solution of lower concentration (0.5%) containing both 2-propanol and NaBH_4 . Softly agglomerated discrete spherical particles about 20 nm in size are visible in Fig. 3a. The Mössbauer spectrum (Fig. 3b) is fitted with three subsixtets. The outer M1 subsixtet (32.8%) with a hyperfine magnetic field $B_{\text{hf}}=47.9 \text{ T}$ and the isomer shift $\delta=0.32 \text{ mm s}^{-1}$ corresponds to the Fe_A^{3+} ions at the tetrahedral A site. The inner M2 subsixtet (14.9%) with $B_{\text{hf}}=44.8 \text{ T}$ and $\delta=0.55 \text{ mm s}^{-1}$ is due to Fe^{2+} and Fe^{3+} ions at the octahedral B site. The M3 subsixtet corresponds to the imaginary subsixtet introduced to improve the fit (“smear” subspectrum). A possible physical implication of thus introduced imaginary sextet is to compensate for the structural disorder and broad distribution of magnetic fields at the octahedral positions of substoichiometric magnetite. The ratio of relative surface areas of the inner M2 and outer M1 sextets is a good measure of magnetite (non)stoichiometry (Topsøe et al., 1974; Gotić and Musić, 2008; Gotić et al., 2009b). The stoichiometric magnetite has a relative surface area ratio $S(\text{M2}):S(\text{M1})=1.88$. In the present case the relative areas of sextets M2 and M1 imply the substoichiometric ($\text{Fe}_{3-x}\text{O}_4$) nature of magnetite particles. Moreover, the approximate stoichiometry of $\text{Fe}_{2.81}\text{O}_4$ has been calculated on the basis of relative surface areas under the formula $x=[2-S(\text{M2})/S(\text{M1})]/[6+5$

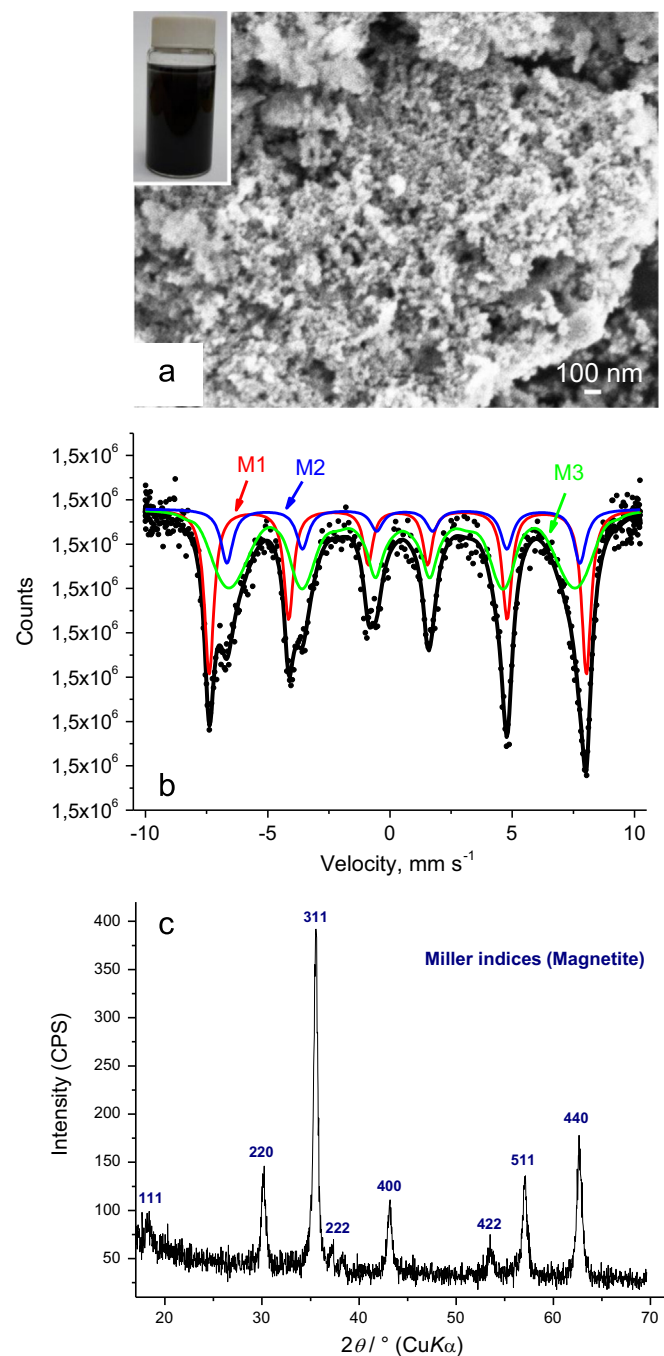


Fig. 3. The FE SEM image (a), the Mössbauer spectrum recorded at 20 °C (b) and the XRD pattern (c) of sample PEOFe-14. The inset shows the corresponding photograph of suspension. The hkl indices of magnetite (ICDD card no. 19-0629) are given. Mössbauer parameters are given in Table 2.

$(S_{\text{M2}}/S_{\text{M1}})]$, where x is the vacancy concentration in substoichiometric magnetite $\text{Fe}_{3-x}\text{O}_4$, S_{M2} is a relative surface area of the inner (octahedral) M2 subsixtet and S_{M1} is a relative surface area of the outer (tetrahedral) M1 subsixtet in the Mössbauer spectrum (Fig. 3 and Table 2). The XRD analysis (Fig. 3c) confirmed the presence of magnetite. The Williamson–Hall analysis and size-strain plot (Fig. S5) indicated that the crystals were almost strain free ($\epsilon=2 \times 10^{-4}$), whereas the estimated volume average domain size (D_v) corresponded to the value of 18.7 nm (Fig. S5).

From the above results it can be inferred that the addition of 2-propanol to enhance reducing conditions had an effect on the

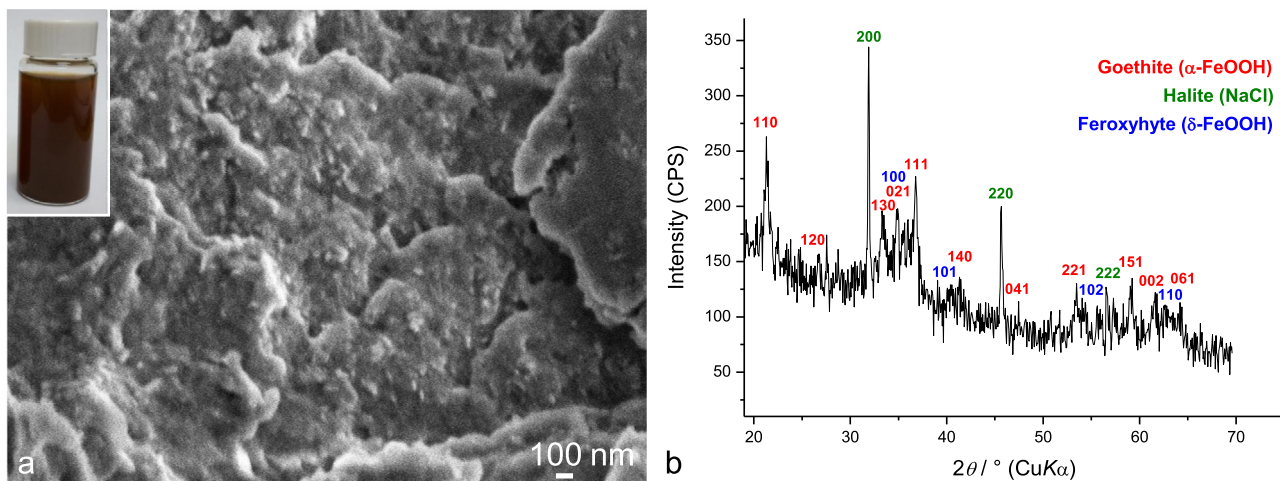
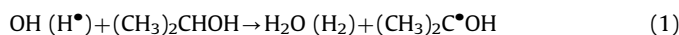
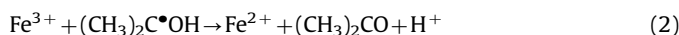


Fig. 4. The FE SEM image (a) and the XRD pattern (b) of sample PVPFe-2. The inset shows the corresponding photograph. The *hkl* indices of goethite (ICDD card no. 29–0713), δ -FeOOH (ICDD card no. 13–87) and halite (ICDD card no. 05–0628) are given. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

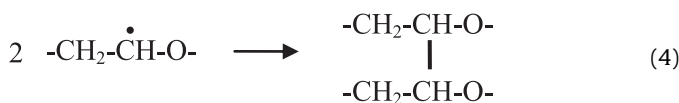
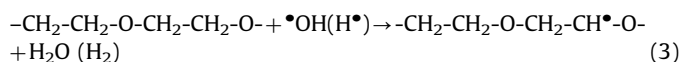
formation of PEO gels. 2-propanol is often added to the system as a scavenger for hydroxyl radicals which are oxidizing agents. It can also scavenge proton radicals:



Thus formed 2-propanol radical can additionally reduce the ferric (Fe^{3+}) ions:



On the other hand, it is known that irradiation crosslinking of PEO chains in a dilute aqueous solution is mainly induced by hydroxyl radicals formed by water radiolysis (Ulański et al., 1995a):



Under the conditions in which intermolecular crosslinking dominates (a relatively low dose rate and a diluted PEO concentration) the crosslinking of PEO results in macrogel formation (Ulański et al., 1995b). By scavenging the $\bullet\text{OH}$ radicals 2-propanol reduced the yield of PEO radicals, $-\text{CH}_2\text{C}^\bullet\text{HO}-$, responsible for PEO crosslinking, which in turn resulted in a less rigid and deteriorated gels (Fig. 1c and d).

The influence of a strong chemical reducing agent NaBH_4 on synthesized samples is basically twofold: (i) it additionally deteriorates the physical properties of the formed gel and favors the formation of suspensions (sample PEOFe-11 and 12; Fig. S2); and (ii) it enables a higher yield and better stabilization against reoxidation of magnetic nanoparticles in samples (sample PEOFe-14, Fig. 3).

3.2. γ -irradiation synthesis of iron oxide nanoparticles in the presence of PVP

The irradiation of Fe(III)/PVP aqueous solutions at a high pH with or without adding 2-propanol resulted in the formation of suspensions.

Fig. 4 shows the FE SEM image (a) and XRD patterns (b) of sample PVPFe-2, synthesized by irradiation, with adding

2-propanol. The inset shows the orange-brown color of the sample suspension. The FE SEM image shows no discrete particles. It looks as if the particles were hidden inside gel-like morphology. The XRD patterns revealed the presence of α -FeOOH (goethite) as the dominant phase, δ -FeOOH (feroxyhyte/feroxyhyte) as a minor phase and NaCl (halite) as impurity. δ -FeOOH was identified and indexed by the ICDD card no. 13–87 and according to the references Carlson and Schwertmann (1980), Madsen et al. (1985) and Gotić et al. (1994). The formation of goethite in the highly alkaline range was expected because goethite is a stable phase in the alkaline range. Unlike that, the appearance of δ -FeOOH was quite surprising because the conventional synthesis of δ -FeOOH started from the Fe(II) salt and proceeded by a rapid oxidation of iron(II) hydroxide ($\text{Fe}(\text{OH})_2$) with H_2O_2 (Gotić et al., 1994). The synthesis of δ -FeOOH using γ -irradiation in the presence of PVP could be explained with the formation of $\text{Fe}(\text{OH})_2$ in highly alkaline and reductive conditions (deoxygenated aqueous suspension, presence of 2-propanol and PVP). In such reducing conditions $\text{Fe}(\text{OH})_2$ was formed. The formed $\text{Fe}(\text{OH})_2$ was well-dispersed in the PVP/2-propanol aqueous suspension and when it came into contact with oxygen from air due to the vial cap opening $\text{Fe}(\text{OH})_2$ rapidly oxidized into δ -FeOOH. In addition to that the sample was magnetic, as checked by a permanent magnet. The suspension formed upon irradiation of the Fe(III)/PVP aqueous solution without adding 2-propanol (sample PVPFe-1; not shown) was non-magnetic.

Generally, well-crystallized δ -FeOOH is ferrimagnetic at room temperature. However, the magnetic properties of feroxyhyte depend critically on the crystallite and/or particle size (Madsen et al., 1985). Well-crystallized synthetic feroxyhyte samples having mean crystallite sizes of 24.0 or 22.9 nm were ferro- or ferrimagnetic, whereas samples of smaller crystallite/particle sizes (below 5 nm) were antiferromagnetic or the spin directions were disordered (Madsen et al., 1985).

3.3. γ -irradiation synthesis of iron oxide nanoparticles in the presence of CTAB

Suspensions were formed upon irradiation of Fe(III)/CTAB aqueous solutions with the addition of 2-propanol (CTABFe-2 and CTABFe-3) or without it (sample CTABFe-1).

Fig. 5 shows the FE SEM images of samples CTABFe-1 (a), CTABFe-2 (b) and CTABFe-3 (c). No discrete particles are visible in sample CTABFe-1. Samples CTABFe-2 (5b) and CTABFe-3 (5c)

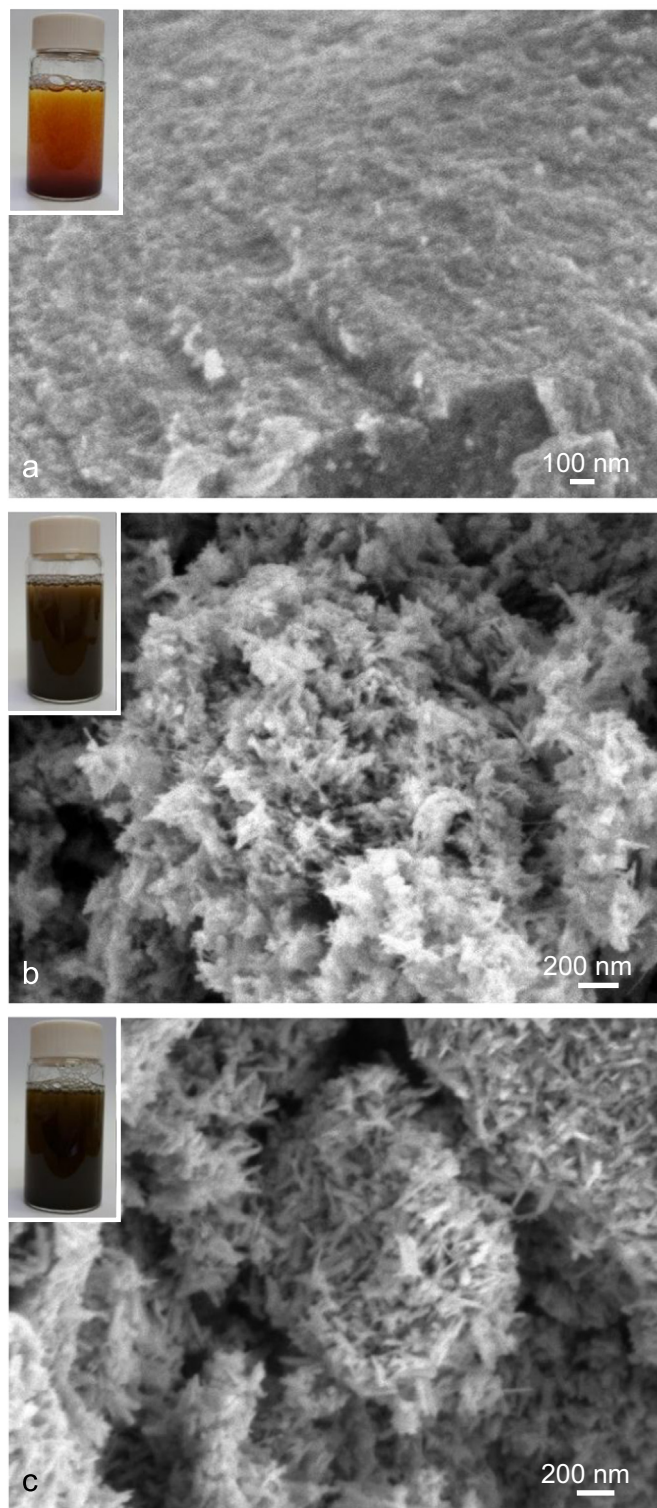


Fig. 5. The FE SEM images and corresponding photographs of samples CTABFe-1 (a), CTABFe-2 (b) and CTABFe-3 (c). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

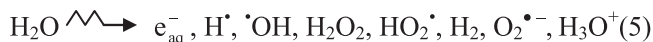
consisted of softly agglomerated discrete rod-like particles 200–300 nm long and up to 20 nm wide. The color of samples (inset) was changing from light yellow-red (5a) to brown (5b and 5c). In addition to that, the sample formed without 2-propanol (CTAB-2) lost its magnetic properties after a few days, while the ones

formed upon γ -irradiation in the presence of 2-propanol (CTABFe-2 and CTABFe-3) were still magnetic after a few months.

Fig. 6 shows the Mössbauer spectra and XRD patterns of samples CTABFe-2 (irradiated at pH=9–10) and CTABFe-3 (irradiated at pH=12). The Mössbauer spectrum of sample CTABFe-2 (Fig. 6a) is a superposition of three sextets and a doublet. Based on fitted parameters the outer sextet H1 (14.6%) can be assigned to hematite, whereas the broad sextet of goethite (Gotić and Musić, 2007) is resolved to the two subsextets G1 (15.6%) and G2 subsextets (60.2%). The doublet D1 (9.6%) is due to paramagnetic and/or superparamagnetic iron oxide particles (Table 2). The XRD analysis of sample CTABFe-2 (Fig. 6c) confirmed the presence of goethite and hematite in the sample. The small fraction of δ -FeOOH found in sample CTABFe-2 can be explained by a rapid oxidation of well-dispersed $\text{Fe}(\text{OH})_2$ in contact with oxygen from air. A very small particle size and low crystallinity of δ -FeOOH is the reason why this phase was not detected by Mössbauer spectroscopy. Actually, the doublet (9.6%) can be related to δ -FeOOH. Generally, the natural material ferrixyhte (δ -FeOOH) is a disordered form of the synthetic δ -FeOOH. Unlike all other iron oxyhydroxides δ -FeOOH is ferrimagnetic at room temperature. The Mössbauer spectrum of well-crystallized δ -FeOOH is characterized by a hyperfine magnetic field of about 35 T. The Mössbauer spectrum of sample CTABFe-3 is given in Fig. 6b. The spectrum is characterized by a sextet G1 (86.9%) belonging to goethite and a doublet D1 (13.1%). The doublet D1 can be assigned to the superparamagnetic δ -FeOOH particles or to any other paramagnetic/superparamagnetic particles including goethite. The XRD analysis (Fig. 6d) revealed the presence of goethite and ferrixyhte. Compared with sample CTABFe-2 sample CTABFe-3 does not contain hematite, which can be explained by a high pH of the suspension (pH ~12).

The obtained results revealed that 2-propanol has a strong influence on sample's phase composition. The presence of 2-propanol ensures much higher reducing conditions upon γ -irradiation, thus favouring the formation of $\text{Fe}(\text{OH})_2$ in samples PVPFE-2, CTABFe-2 and CTABFe-3. Even though $\text{Fe}(\text{OH})_2$ is not directly determined, the finding of δ -FeOOH in the sample is a strong evidence that it should be formed during the γ -irradiation synthesis in the presence of 2-propanol. The stabilization of iron(II) hydroxide nanoparticles with PVP or CTAB as well as their reducing properties *per se* contribute to the formation of $\text{Fe}(\text{OH})_2$.

Besides 2-propanol, the pH of the system highly influences the dissolution/re-crystallization properties of iron hydroxides and thus the phase composition of the obtained material. For instance, at a lower pH hematite was found in sample CTABFe-2, but not in sample CTABFe-3 at a higher pH. Furthermore, the pH of the system influences the radiolysis of water, which generates free radicals (e_{aq}^- , H^\bullet , $^\bullet\text{OH}$, HO_2^\bullet) and molecular products (H_2 , H_2O_2):



The hydrated electron e_{aq}^- and hydrogen radical H^\bullet are reducing species, whereas $^\bullet\text{OH}$, H_2O_2 , HO_2^\bullet and $\text{O}_2^{\bullet-}$ are oxidizing species. In alkaline aqueous solutions, the hydrogen atoms that are reducing species can be converted to hydrated electrons, which are stronger reducing species (Ekoko et al., 2014; Hickel et al., 1996). In the alkaline range the 2-propanol (isopropyl alcohol) scavenges both the hydrogen radicals (H^\bullet) and hydroxyl radicals ($^\bullet\text{OH}$), but has no effect on the hydrated electrons e_{aq}^- . In highly alkaline aqueous solutions the hydrated electrons e_{aq}^- rapidly react with hydroxyl radicals $^\bullet\text{OH}$, however the deprotonation of $^\bullet\text{OH}$ may occur leading to its conversion into $\text{O}^{\bullet-}$, which in turn scavenges e_{aq}^- .

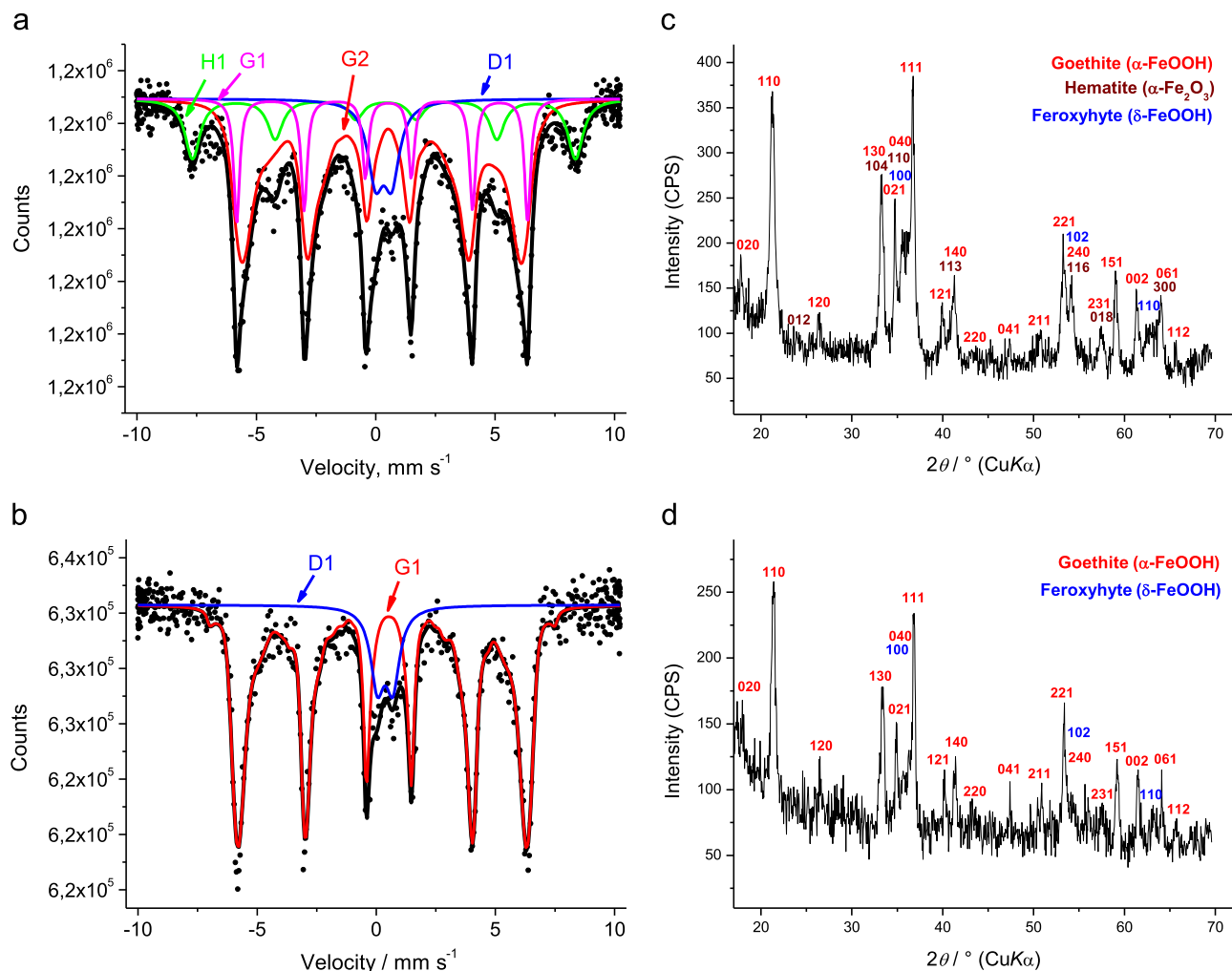


Fig. 6. The Mössbauer spectrum recorded at 20 °C (a) and the XRD pattern (b) of sample CTABFe-2; the Mössbauer spectrum (c) and the XRD pattern (d) of sample CTABFe-3. The Miller (*hkl*) indices of hematite (ICDD card no. 33–0664), δ -FeOOH (ICDD card no. 13–87) and goethite (ICDD card no. 29–0713) are given. Mössbauer parameters are given in Table 2.

4. Conclusions

The γ -irradiation of an iron(III) chloride aqueous precursor solution in the presence of PEO produced rigid hydrogels with embedded iron oxide nanoparticles. The γ -irradiation of iron(III)/PEO solutions in the presence of 2-propanol increased the reducing power of γ -irradiation, however, it reduced PEO crosslinking and thus soft hydrogels were formed. The formation of substoichiometric magnetite NPs was confirmed only in sample PEOFe-14 that was γ -irradiated in the presence of PEO, 2-propanol and NaBH_4 .

The γ -irradiation of an iron(III) chloride aqueous precursor solution in the presence of PVP produced a magnetic suspension due to the formation of a small amount of δ -FeOOH (feroxyhyte). The formation of δ -FeOOH suggests the formation of $\text{Fe}(\text{OH})_2$ upon γ -irradiation, which then under atmospheric conditions rapidly oxidized into δ -FeOOH.

The γ -irradiation of an iron(III) chloride aqueous precursor solution in the presence of CTAB favored the formation of goethite, although a small amount of feroxyhyte was also formed. The yield of goethite rod-like nanoparticles increased with adding 2-propanol.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.radphyschem.2015.11.019>.

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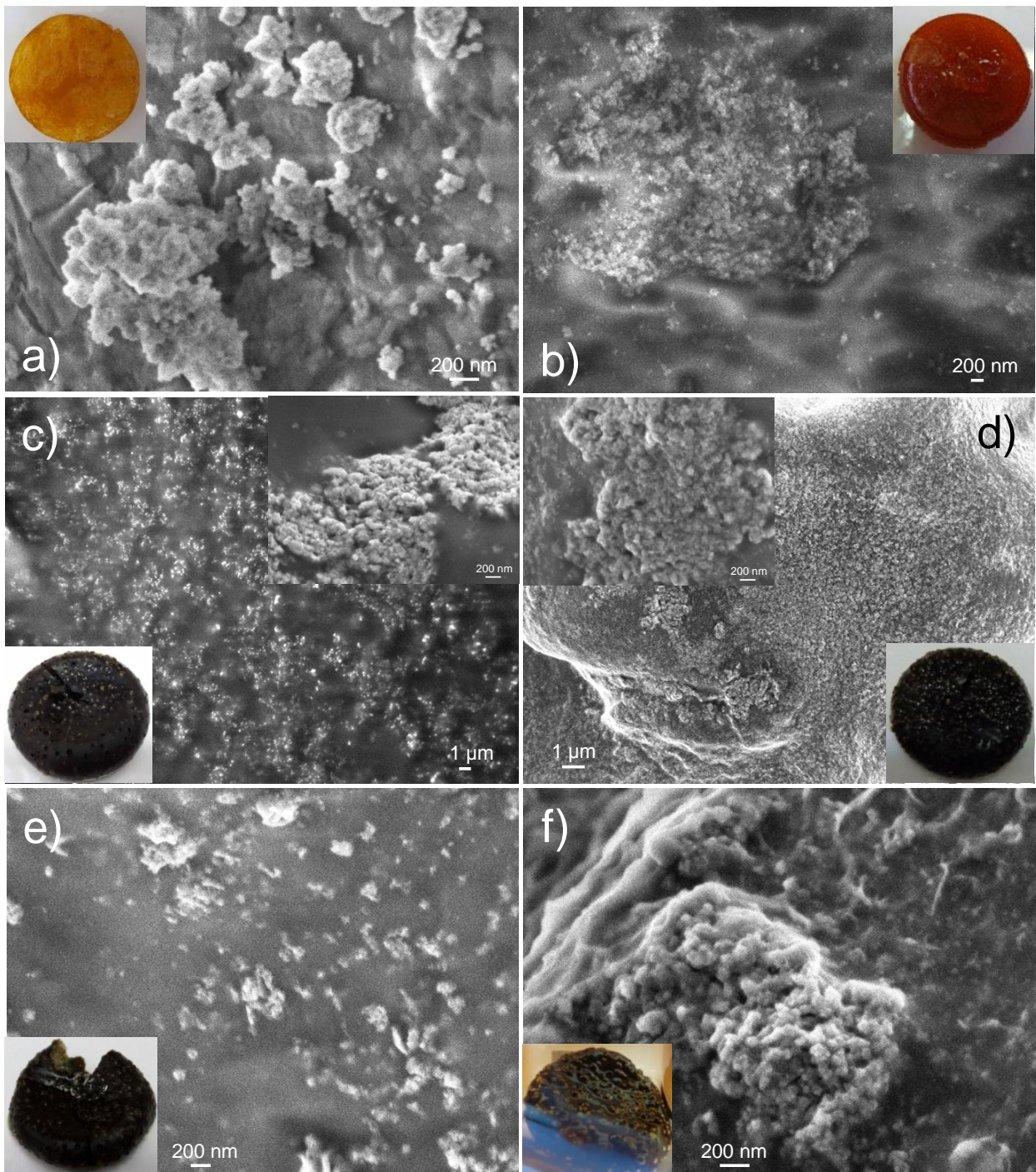


Figure S1. The FE SEM images and corresponding photographs of samples PEOFe-1, PEOFe-2, PEOFe-3, PEOFe-4, PEOFe-5 and PEOFe-6. All the samples were prepared by γ -irradiation of 1.8 wt% PEO deaerated aqueous solutions with 5 wt% Fe(III) ions (in relation to PEO mass) (Fe(III) acetate precursor) but with the difference in PEO molecular mass and pH. The detail experimental conditions are given in Table 1 of the manuscript. The quite rigid gels from orange to black in colour were formed depending on the pH of starting solutions. The black gels were formed on irradiation at high pH (~ 12), without adding 2-propanol or reducing agent such as NaBH_4 . The formed iron oxide nanoparticles are mainly of spherical

shape, to some extent agglomerated, and they are dispersed through the whole polymer matrix.

- a) PEOFe-1: PEO ($\overline{M}_v = 8 \cdot 10^6$); pH = 4; irradiated to 123 kGy
- b) PEOFe-2: PEO ($\overline{M}_v = 4 \cdot 10^5$); pH = 9; irradiated to 123 kGy
- c) PEOFe-3: PEO ($\overline{M}_v = 2 \cdot 10^5$); pH = 12; irradiated to 442 kGy
- d) PEOFe-4: PEO ($\overline{M}_v = 4 \cdot 10^5$); pH = 12; irradiated to 442 kGy
- e) PEOFe-5: PEO ($\overline{M}_v = 8 \cdot 10^6$); pH = 12; irradiated to 442 kGy
- f) PEOFe-6: PEO ($\overline{M}_v = 8 \cdot 10^6$); pH = 12; irradiated to 123 kGy

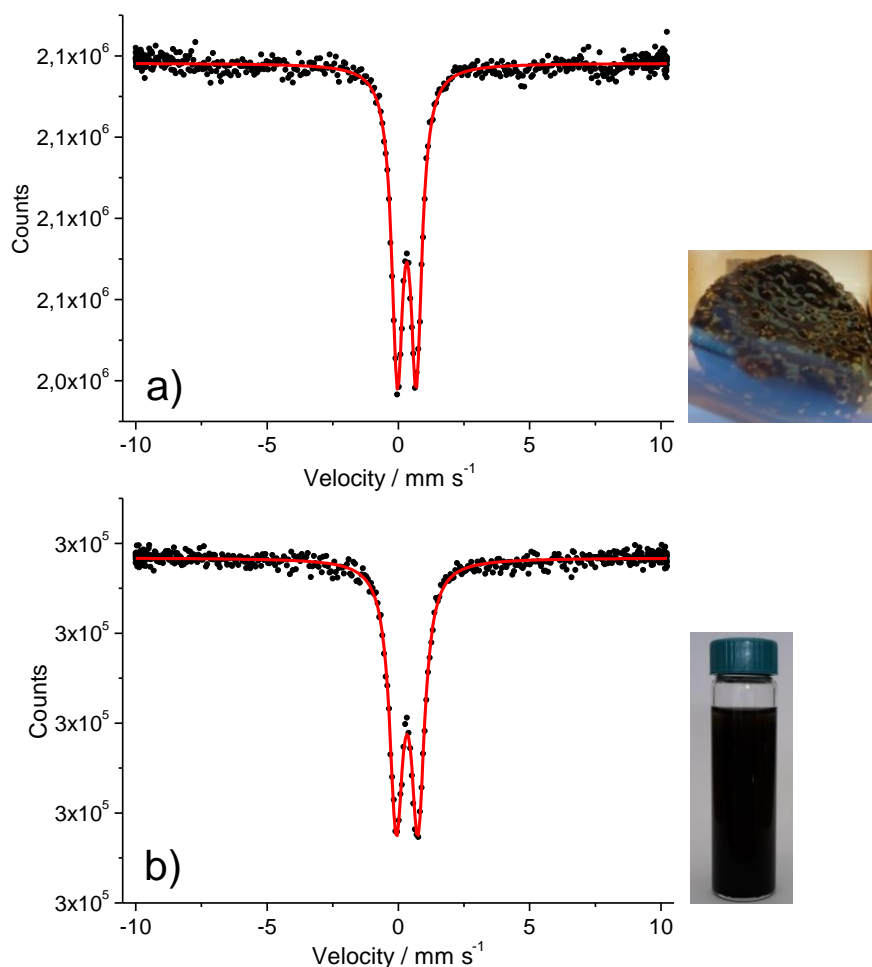


Figure S2. The Mössbauer spectra and corresponding photographs of samples PEOFe-6 and PEOFe-12. The samples were prepared by γ -irradiation of PEO/Fe(III) acetate deaerated aqueous solutions of different compositions. The detail experimental conditions are given in the Table 1 of the manuscript. On γ -irradiation of the solution without 2-propanol, the black gel was formed, while on the addition of strong reducing agent NaBH_4 black magnetic suspension was formed. The Mössbauer spectra of both samples can be fitted with a doublet. The Mössbauer parameters are given in Table 2.

- a) PEOFe-6: PEO ($\overline{M}_v = 8 \cdot 10^6$; 1.8 wt%); Fe(III) acetate (5 wt% Fe^{3+} , in relation to PEO mass); pH = 12; irradiated to 123 kGy
- b) PEOFe-12: PEO ($\overline{M}_v = 4 \cdot 10^5$; 1.8 wt%); Fe(III) acetate (5 wt% Fe^{3+}); with NaBH_4 ; pH = 13-14; irradiated to 113 kGy

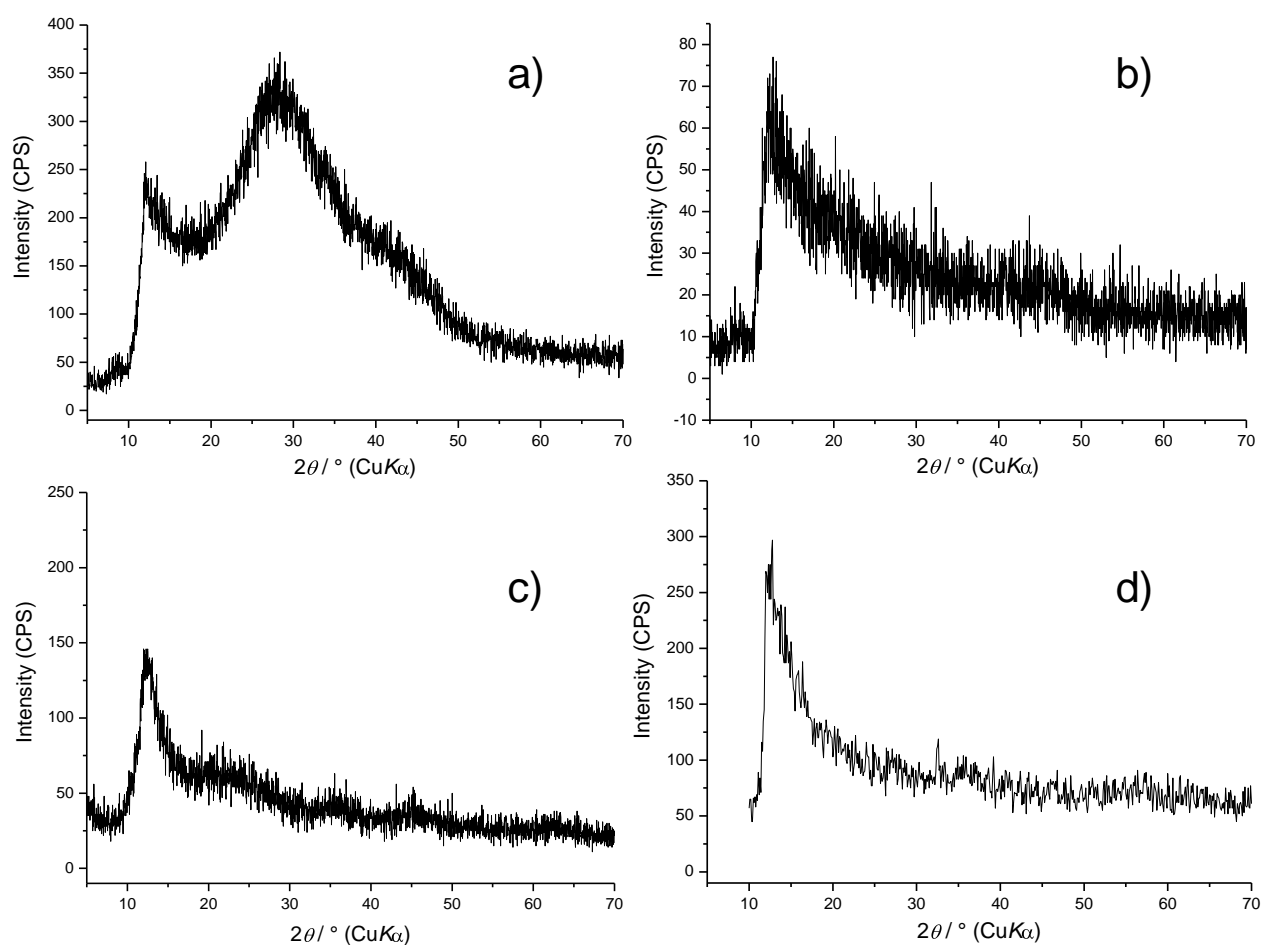


Figure S3. The XRD patterns of samples PEOFe-6, PEOFe-9, PEOFe-11 and PEOFe-13. The samples were prepared by γ -irradiation of PEO/Fe(III) aqueous solutions of different compositions. The detail experimental conditions are given in Table 1 of the manuscript. The XRD patterns show no clear maxima (the gel-like structure) and because of that the phase analysis is not possible.

- g) PEOFe-6: PEO ($\overline{M}_v = 8 \cdot 10^6$; 1.8 wt%); Fe(III) acetate (5 wt% Fe^{3+} in relation to PEO mass); pH = 12; irradiated to 123 kGy
- h) PEOFe-9: PEO ($\overline{M}_v = 4 \cdot 10^5$; 0.5 wt%); Fe(III) chloride (20 wt% Fe^{3+}); pH = 12; irradiated to 441 kGy
- i) PEOFe-11: PEO ($\overline{M}_v = 4 \cdot 10^5$; 1.8 wt%); Fe(III) chloride (5 wt% Fe^{3+}); NaBH_4 ; pH = 12; irradiated to 113 kGy
- j) PEOFe-13: PEO ($\overline{M}_v = 4 \cdot 10^5$; 1.8 wt%); Fe(III) chloride (5 wt% Fe^{3+}); 2-propanol (0.2 M); NaBH_4 ; pH = 8-9; irradiated to 429 kGy.

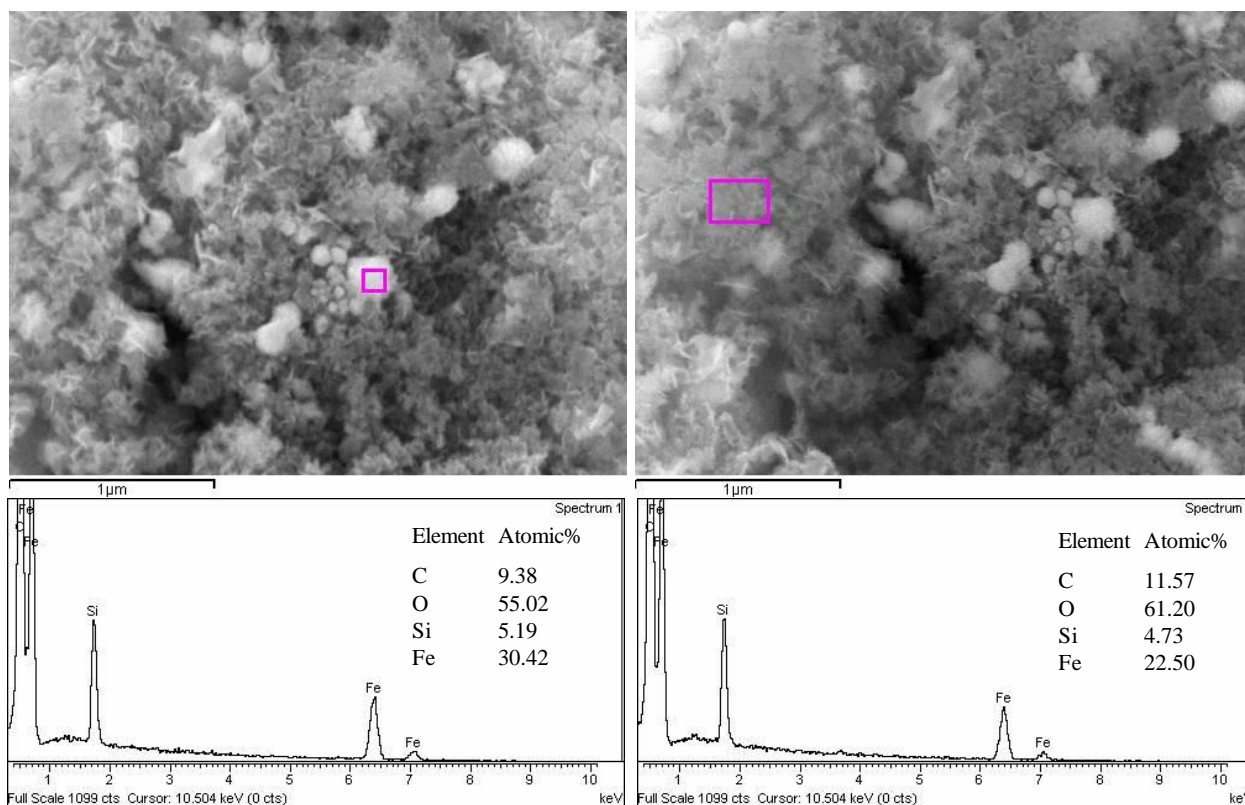


Figure S4. The EDS analysis of sample PEOFe-11 taken from different parts of the sample. The sample was prepared by γ -irradiation to 113 kGy of 1.8 wt% PEO ($\overline{M}_v = 4 \cdot 10^5$) aqueous solution with Fe(III) chloride (5 wt% Fe^{3+} in relation to PEO mass) and NaBH_4 (pH = 12). The elemental analysis of the spherical particle show the Fe : O ratio of 30.42 : 55.02. If we take in consideration that Si impurities present in the sample (leaching of Si from the borosilicate glass due to the stirring and due to the γ -irradiation) are present as SiO_2 , than the 10.38 mol % of the oxygen is bound to the Si, and the rest of the oxygen belongs to the Fe, which gives the molar ratio Fe : O = 30.42 : 44.64, and this molar ratio is very close to Fe_2O_3 . On the contrary, the elemental analysis at the position of plate-like particles gives the roughly the molar ratio Fe : O = 1 : 2, which fitted very well with FeOOH formula (*i.e.* with goethite, α - FeOOH). The sample PEOFe-11 is magnetic as checked with the permanent magnet, so the collapsing sextet in the Mössbauer spectrum (Fig. 2d in the manuscript) can arise from γ - Fe_2O_3 (maghemite), that are spherical in shape. γ - Fe_2O_3 is ferromagnetic at room temperature.

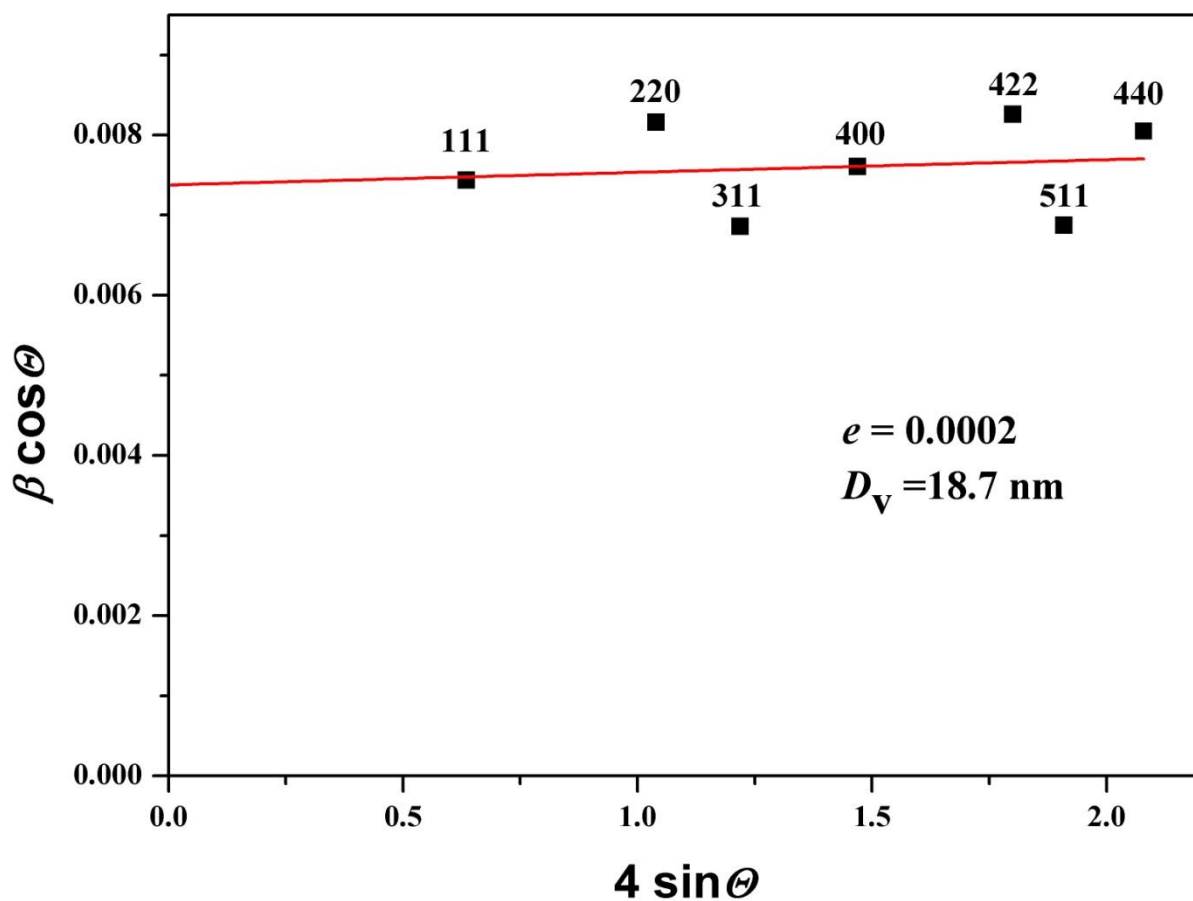


Figure S5. The results of Williamson-Hall analysis of the sample PEOFe-14 and the size-strain plot, which indicated that crystals are almost strain free ($e = 2 \times 10^{-4}$). The estimated volume average crystallite size (D_v) of the sample PEOFe-14 corresponded to the value of 18.7 nm.