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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 $NaBH_4$ 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 $NaBH_4$. 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 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.

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 (Belloni 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 (Fe^{2+}) in atmospheric conditions, especially if magnetite particles are in the nanosize range (Gotić et al., 2007). Besides, in an aqueous solution Fe^{2+} ions quickly oxidize by taking up oxygen dissolved in water. Moreover, even with a properly deoxygenated solution, water molecules alone can oxidize Fe^{2+} 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 $\overline{M}_v = 8\cdot10^6$	1.8%	5% Fe^{3+} (acetate)	4			123	gel
PEOFe-2*	PEO $\overline{M}_v = 4\cdot10^5$	1.8%	5% Fe^{3+} (acetate)	9			123	gel
PEOFe-3*	PEO $\overline{M}_v = 2\cdot10^5$	1.8%	5% Fe^{3+} (acetate)	12			442	gel
PEOFe-4*	PEO $\overline{M}_v = 4\cdot10^5$	1.8%	5% Fe^{3+} (acetate)	12			442	gel
PEOFe-5*	PEO $\overline{M}_v = 8\cdot10^6$	1.8%	5% Fe^{3+} (acetate)	12			442	gel
PEOFe-6*	PEO $\overline{M}_v = 8\cdot10^6$	1.8%	5% Fe^{3+} (acetate)	12			123	gel
PEOFe-7	PEO $\overline{M}_v = 4\cdot10^5$	1.8%	5% Fe^{3+} (chloride)	12			113	gel
PEOFe-8	PEO $\overline{M}_v = 4\cdot10^5$	1.8%	5% Fe^{3+} (chloride)	12			441	gel
PEOFe-9	PEO $\overline{M}_v = 4\cdot10^5$	0.5%	20% Fe^{3+} (chloride)	12			441	gel
PEOFe-10	PEO $\overline{M}_v = 4\cdot10^5$	1.8%	5% Fe^{3+} (chloride)	12		2-propanol	113	laxly gel
PEOFe-11	PEO $\overline{M}_v = 4\cdot10^5$	1.8%	5% Fe^{3+} (chloride)	12	NaBH$_4$		113	suspension
PEOFe-12*	PEO $\overline{M}_v = 4\cdot10^5$	1.8%	5% Fe^{3+} (acetate)	13–14	NaBH$_4$		113	suspension
PEOFe-13	PEO $\overline{M}_v = 4\cdot10^5$	1.8%	5% Fe^{3+} (chloride)	8–9	NaBH$_4$	2-propanol	429	laxly gel
PEOFe-14	PEO $\overline{M}_v = 4\cdot10^5$	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 Sumplementary.

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 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