

## Effects of pH on the morphology of iron oxides synthesized under gamma-irradiation

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Gamma-irradiation has been applied to synthesize pure iron oxide nanorod particles in acid medium of pH 5.0, pure submicron sized particles of ferrous oxide with bullet-shaped morphology in alkaline medium at pH 12 and a mixture of iron oxide and ferrous oxide fanlike morphology in nearly neutral medium of pH 7.2. It has been proven that the morphology of the prepared oxides is strongly dependent on the pH value of the solution before irradiation. The mechanism of formation of these oxides is also suggested.

### Introduction

Nanorods material or fibers are currently the focus of considerable interest. A synthetic control of nanocrystalline morphology remains a daunting task and is a new challenge to scientists. In their various allotropic forms, iron oxides represent an important basic material due to their large occurrence on Earth and Mars.<sup>1</sup> Their thermodynamically stable crystallographic phase is hematite,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, which represents the most important ore of iron because of its high content and its natural abundance.<sup>2,3</sup>

Magnetic nano- and submicron particles are of interest for the development and enhancement of audio and video recording media as well as for data storage.<sup>4</sup> GRIMES et al.<sup>5</sup> have reported that iron oxide particles constitute a diverse class of materials displaying a range of optical, magnetic and catalytic properties and pigment applications and ferromagnetic iron oxides and mixed metal oxides have applications in magnetic storage, high frequency transformers and radiofrequency and microwave components. In addition to electronic applications, the stability and biocompatibility of iron oxide are making this material a leading candidate for drug delivery, diagnostic, medical imaging applications and for diagnosis and treatment of liver cancers.<sup>6,7</sup>

Several methods for the synthesis of iron oxides have been reported in the literature. These include: combustion,<sup>8</sup> microwave plasma,<sup>9</sup> flame pyrolysis,<sup>10</sup> sprays pyrolysis,<sup>11</sup> hydrothermal,<sup>12</sup> pulsed laser ablation technique<sup>13</sup> and ultrasound irradiation method.<sup>14</sup>

In a previous work, gamma-irradiation has been applied to synthesize nanocrystalline Fe<sub>3</sub>O<sub>4</sub> with spherical morphology, but the absorbed doses of irradiation used in the preparation of this material were higher, in the range of 102–360 kGy.<sup>15</sup>

Most of the previous techniques have produced nanocrystalline iron oxides with spherical morphology.

In the present work, we have investigated the effect of the pH of the starting solutions on the morphology of the prepared iron oxides under gamma-irradiation. Nanorod particles consisting of pure  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, submicrons sized particles with bullet-shaped morphology consisting of Fe<sub>3</sub>O<sub>4</sub> and fanlike morphology consisting of a mixture of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> have been prepared by controlling the pH value of the starting solution before  $\gamma$ -irradiation.

### Experimental

#### Synthesis

The following chemicals purchased from Shanghai Chemicals Factory were the purest grade commercially available and were used as received: ferric sulfate [Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>], concentrated acetic acid (CH<sub>3</sub>COOH), anhydrous sodium acetate (CH<sub>3</sub>COONa), anhydrous sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>), anhydrous sodium hydroxide (NaOH), isopropyl alcohol (i-Pr-OH) and polyvinyl alcohol (PVA).

#### Instrumentation

The structure of the particles was characterized by XRD using X-ray diffractometer equipped with a graphite monochromatized Cu K $\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ ). The morphology and the size of the particles were determined by TEM. The TEM micrographs were taken with Hitachi Model H-800 electron microscope with an accelerating voltage of 200 kV with samples deposited on a carbon coated copper grid.

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### Preparation of the particles

Sols constituted of ferric hydroxide were prepared by dissolving an appropriate amount of ferric sulfate in distilled water and isopropyl alcohol was poured into the solutions to act as scavenger for oxidative radicals,  $\text{OH}\cdot$ , produced during the radiolysis of water under gamma-irradiation. Polyvinyl alcohol was used as an organic surfactant molecule in order to stabilize the growth of particles during synthesis. By dripping slowly a concentrated solution of anhydrous sodium hydroxide into the solutions and by stirring the solutions continuously, two kinds of sols were prepared depending on the amount of sodium hydroxide added. The brown red sols were formed in acid medium of pH 5.0. In alkaline medium of pH 12.0, a darker sol was obtained.

An experiment was setup before the prepared sols to be  $\gamma$ -irradiated. On one hand the sols were separated from the solution by centrifugation and then filtered, washed with distilled water and absolute alcohol and dried in vacuum at room temperature for several hours. The dried products obtained were analyzed by XRD and their morphology was observed by TEM.

On the other hand, when the sols were formed, they were mixed with an acetic acid/sodium acetate buffer pair solutions or sodium carbonate in an appropriate amount to keep the pH values constant at about 5.0 and 12, respectively. The sols were irradiated in the field of a  $^{60}\text{Co}$   $\gamma$ -ray source of  $1.2025 \cdot 10^{16}$  Bq (325,000 curies). The absorbed dose of irradiation was 30 kGy with a dose rate of about 0.25 kGy/h.

After irradiation, two main kinds of precipitates were obtained depending on the pH. A brown precipitate was obtained at pH 5.0 and a black one at pH of about 12. Moreover, a similar sol was prepared at pH 7.2 and was irradiated in the same conditions. After irradiation, a brown dark powder was obtained. The precipitates were separated by washing with distilled water and absolute alcohol, in order to remove the by-products and finally dried in a vacuum oven at 60 °C for several hours.

The experimental conditions of the preparation of iron oxides are detailed in Table 1.

### Results and discussion

The XRD analysis revealed that the brown red product obtained before gamma-irradiation consists of ferric hydroxide as shown in Fig. 1a. From the XRD pattern of the brown precipitate prepared in acidic medium at pH 5.0, under gamma-irradiation as shown in Fig. 1b, it can be seen that all the reflection peaks were indexed as pure  $\alpha\text{-Fe}_2\text{O}_3$ , hematite phase (ASTM Powder Diffraction Card No. 33–66).

The XRD pattern of the black product prepared in alkaline medium at pH 12 before irradiation is shown in Fig. 2a. The analysis revealed that all the peaks correspond to the standard ferric oxyhydroxide,  $\text{FeO}(\text{OH})$ , almaganeite phase, some goethite could also be found as trace. The XRD pattern of the black precipitate prepared in alkaline medium at pH 12 after irradiation is shown in Fig. 2b. The analysis revealed that the powder is constituted of pure magnetite phase, ferri ferrous oxide,  $\text{Fe}_3\text{O}_4$ , which is cubic. Taking into account the peak (311) of the spacing  $d=2.3305$  Å, the calculated value of the lattice parameter is about 8.073 Å. This value agrees with the one reported in the literature,  $a=8.09$  Å (ASTM Powder Diffraction Card No. 26-1136). Moreover, from the fact that the peak (222) appeared while the peak (221) did not appear, the black sample prepared by  $\gamma$ -irradiation at pH 12 was identified to be pure  $\text{Fe}_3\text{O}_4$  instead of  $\gamma\text{-Fe}_2\text{O}_3$ .

The XRD patterns of the brown dark powder prepared in nearly neutral medium at pH 7.2, as shown in Fig. 3, indicates the presence of (012), (104), (202) peaks which characterize  $\alpha\text{-Fe}_2\text{O}_3$  and the presence of (311), (511) and (440) peaks which characterize  $\text{Fe}_3\text{O}_4$ . This observation proves that the sample synthesized at pH 7.2 is a mixture of  $\text{Fe}_3\text{O}_4$  and  $\alpha\text{-Fe}_2\text{O}_3$ .

Particle size and morphology of the prepared materials were determined by a transmission electron microscopy. The powders were dispersed in absolute ethanol, sonicated for 5 minutes and dropped onto carbon-coated copper grids, then examined under a Hitachi TEM Model H-800 electron microscope with accelerating voltage of 200 kV.

Table 1. Preparation of iron oxides under gamma-irradiation

Sample No.	$[\text{Fe}^{3+}]$ , mol/l	[i-Pr-OH], mol/l	[PVA], mol/l	[NaOH], mol/l	$[\text{CH}_3\text{CO}_2\text{H}]$ , mol/l	$[\text{CH}_3\text{CO}_2\text{Na}]$ , mol/l	$[\text{Na}_2\text{CO}_3]$ , mol/l	Irradiation dose, kGy	Solution pH
1	0.03	2.0	0.1	0.0	0.0	0.0	0.0	11	1.2
2	0.03	2.0	0.1	1.0	0.20	0.1	0.0	11	5.0
3	0.06	2.0	0.1	1.0	0.20	0.1	0.0	11	5.0
4	0.06	2.0	0.1	1.0	0.20	0.1	0.0	30	5.0
5	0.06	3.0	0.1	1.2	0.0	0.0	0.30	30	6.5
6	0.08	3.0	0.1	1.3	0.0	0.0	0.35	30	7.2
7	0.08	3.0	0.2	1.9	0.0	0.0	0.35	30	12.0
8	0.08	3.0	0.2	1.9	0.0	0.0	0.35	43	12.0

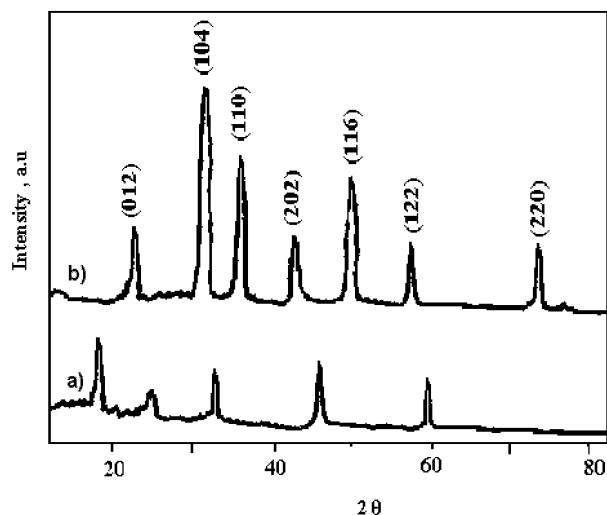


Fig. 1. XRD pattern of ferric hydroxide,  $\text{Fe}(\text{OH})_3$  prepared at pH 5.0 before gamma-irradiation (a); XRD pattern of iron oxide,  $\text{Fe}_2\text{O}_3$  prepared at pH 5.0 by gamma-irradiation (b). The various Bragg peaks are followed by the corresponding Miller indices. Results were obtained using Cu  $K\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ )

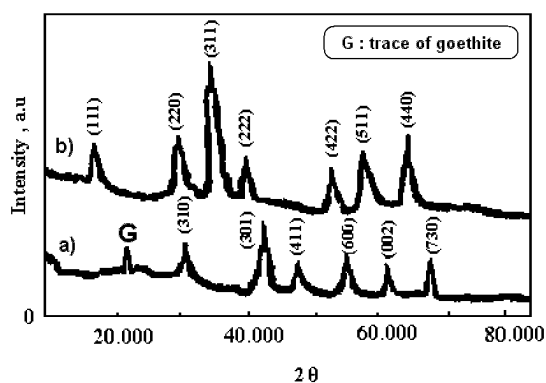


Fig. 2. XRD pattern of ferric oxy hydroxide,  $\text{FeO}(\text{OH})$  prepared at pH 12 before gamma-irradiation (a); XRD pattern of ferri ferrous oxide,  $\text{Fe}_3\text{O}_4$  prepared at pH 12 by gamma-irradiation (b). The various Bragg peaks are followed by the corresponding Miller indices. Results were obtained using Cu  $K\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ )

The TEM micrographs of the products obtained before gamma-irradiation are shown in Fig. 4. It can be seen clearly that the particles were spherically shaped. The TEM micrographs of the generated oxides powders prepared under gamma-irradiation at various values of pH are shown in Fig. 5. The morphology of these oxides is strongly dependent on the pH of the starting solution. There is no evidence for the formation of amorphous iron oxides and the particles are well dispersed.

Rod morphology particles constituted of pure  $\alpha\text{-Fe}_2\text{O}_3$  were obtained in acid medium at pH 5.0, as shown in Fig. 5a. The prepared nanorods have an

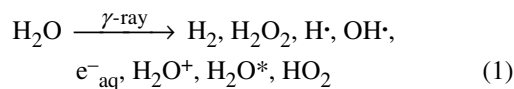
average length of about 85–100 nm and a width of about 26–32 nm in average. The size was evaluated immediately from the TEM micrographs since the calculations by SCHERER<sup>16</sup> from the XRD patterns are approximate and less accurate for the spherical like particles. Elliptical or bullet shaped morphology as displayed in Figs 5c and d were observed in alkaline medium at pH 12.0 for pure  $\text{Fe}_3\text{O}_4$ . These oxide particles have an average size in the range of sub-micrometer rather than nanometer and it can be seen clearly that the more the absorbed dose increased the larger is the particle size. Fanlike morphology displayed in Fig. 5b, was observed in nearly neutral medium at pH 7.2 for the brown dark colored powders, which was constituted of a mixture of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$ .

The experimental results revealed that the control of pH is an important factor in preparing these materials. It was found that, for pH values less than 3.0, no reaction was observed. At the range of pH 3–5, pure nanoparticles constituted of pure  $\alpha\text{-Fe}_2\text{O}_3$  was obtained. However, it was observed that, the more the pH value increases in alkaline medium, the more the formation of the black colored product constituted of  $\text{Fe}_3\text{O}_4$  is favored. In the range of pH values from 6–7.2 a mixture of  $\alpha\text{-Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  was prepared, and in the range of pH 10–12, the black precipitate consisted of pure  $\text{Fe}_3\text{O}_4$ .

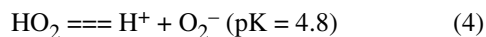
In order to prepare ferrous ferri oxide with small particle sizes, from the experimental results, the authors suggest to  $\gamma$ -irradiate the starting alkaline sols with a dose of about 30 kGy. The sol might contain a larger amount of 2-propanol with a concentration of about or more than 3.0 mol/l. In this case, 2-propanol acts effectively to scavenge both  $\text{OH}\cdot$  and  $\text{H}\cdot$  radicals during irradiation. We do suggest to synthesize ferric oxide nanorod particles by irradiating the starting acidic sol with a dose not exceeding 11 kGy with 2-propanol of about 2.0 mol/l.

Finally, from the experiment, the following mechanisms could be suggested to illustrate the formation of iron oxide,  $\text{Fe}_2\text{O}_3$  and ferri ferrous oxide  $\text{Fe}_3\text{O}_4$  upon gamma-irradiation process.

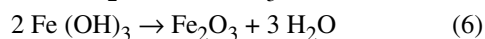
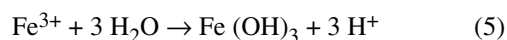
The radiolysis of water produces free radicals such as:  $e_{\text{aq}}^-$ ,  $\text{H}\cdot$ ,  $\text{OH}\cdot$  and  $\text{HO}_2$  or  $\text{O}_2^-$  and molecular products such as  $\text{H}_2$  and  $\text{H}_2\text{O}_2$ . It was reported that, hydrated electron,  $e_{\text{aq}}^-$  and hydrogen radical  $\text{H}\cdot$  are reducing species, the standard electrode potentials of  $e_{\text{aq}}^-$  and  $\text{H}\cdot$  radical at 25 °C being  $-2.77 \text{ V}$  and  $-2.31 \text{ V}$ , respectively, and  $\text{OH}\cdot$ ,  $\text{HO}_2$ ,  $\text{O}_2^-$ ,  $\text{H}_2\text{O}_2$  are oxidizing species:<sup>17,18</sup>



Since the irradiation was done in the presence of air, all reduction species such as  $e^-_{aq}$  and  $H\cdot$  radical are effectively scavenged by oxygen producing  $O_2^-$  and its protonated form  $HO_2$ , respectively.  $HO_2$  can dissociate at pH of about 5.0 to produce  $O_2^-$ , which is also an oxidizing species:

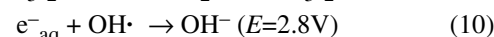
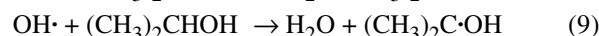
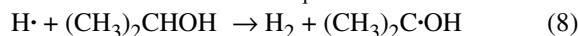
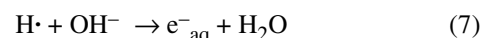


The formation of iron oxide in acid medium of pH of about 4.8 could be explained by the fact that in this condition, the ferric iron is hydrolyzed and forms ferric hydroxide, which is converted to oxide by a dehydration process with the following reactions:<sup>19</sup>



In highly alkaline solutions, the hydrogen atoms, which are reducing species, are converted to hydrated electrons, which then play an important role in the course of reaction. In this condition, 2-propanol scavenges both  $H\cdot$  and  $OH\cdot$  but does not have any effect

on the hydrated electron  $e^-_{aq}$ .<sup>20</sup> Moreover, in strongly alkaline solution the hydrated electron  $e^-_{aq}$  reacts rapidly with  $OH\cdot$  radical and there is also deprotonation of  $OH\cdot$  radical, which is converted to  $O^-$ .<sup>23,24</sup>



The species present in irradiated water is  $O^-$ . Its reaction with the reducing species such as  $H\cdot$  and  $e^-_{aq}$  are, respectively:



The formation of  $Fe_3O_4$  in alkaline medium could be explained by the reduction of the starting dark sol of ferric oxyhydroxide,  $FeO(OH)$  by hydrated electron under gamma-irradiation:<sup>21,22</sup>

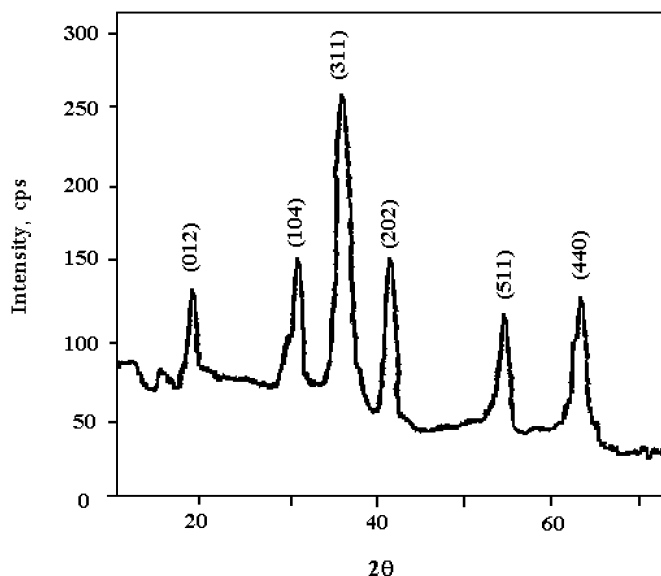
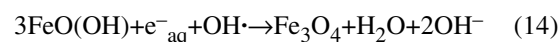


Fig. 3. XRD pattern of the mixture of iron oxide and ferri ferrous oxide obtained at pH 7.2 by gamma-irradiation. The various Bragg peaks are followed by the corresponding Miller indices. Results were obtained using Cu  $K\alpha$  radiation ( $\lambda = 1.54178 \text{ \AA}$ )

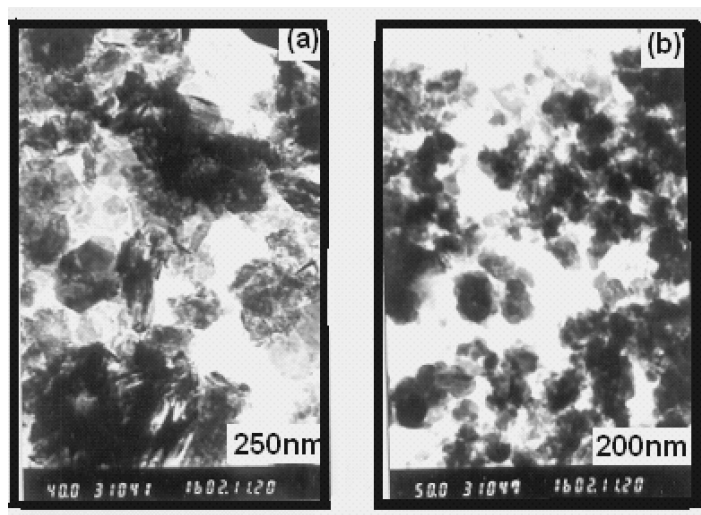


Fig. 4. TEM micrographs of products obtained before gamma-irradiation Fe(OH)<sub>3</sub> at pH 5.0 (a); FeO(OH) at pH 12 (b)

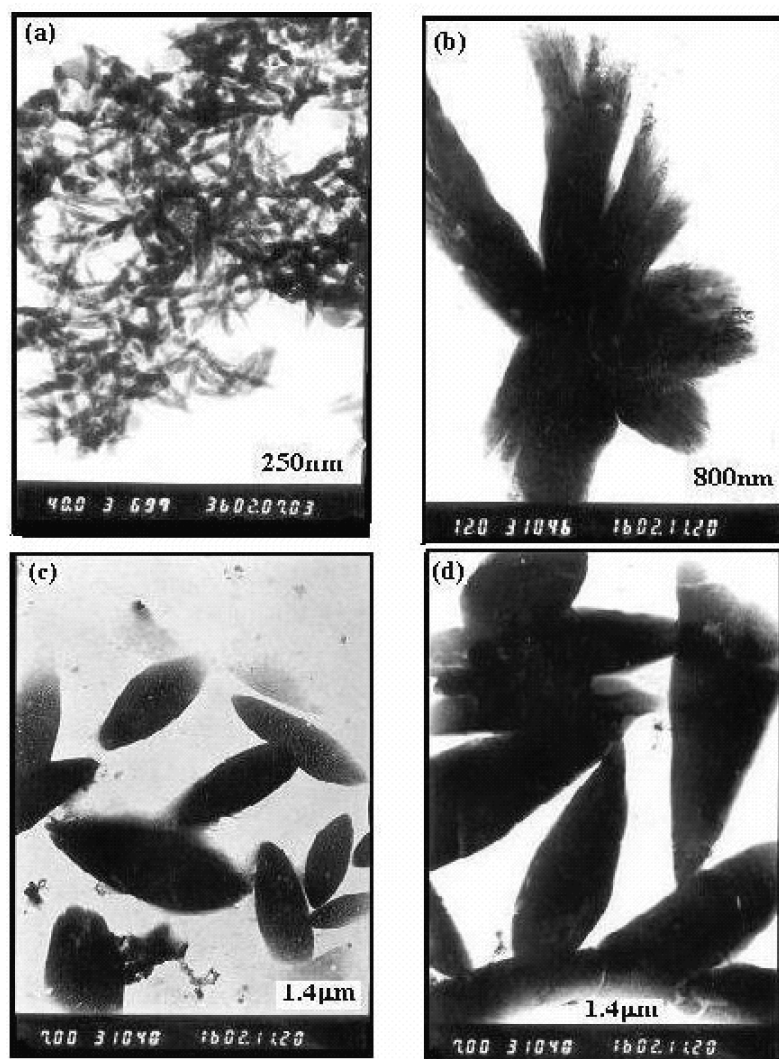


Fig. 5. TEM micrographs of powders prepared upon gamma-irradiation α-Fe<sub>2</sub>O<sub>3</sub> prepared at pH 5.0, 11 kGy (a); Mixture of α-Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> prepared at pH 7.2, 30 kGy (b); Fe<sub>3</sub>O<sub>4</sub> prepared at pH 12, 30 kGy (c) and Fe<sub>3</sub>O<sub>4</sub> prepared at pH 12, 43 kGy (d)

### Conclusions

Nanocrystalline hematite and sub micron magnetite with different morphologies were prepared successfully by  $\gamma$ -radiation at room temperature, ambient pressure and without any kind of catalysts, in a water system. The results showed that the pH value is an important factor to be controlled for the formation of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> and Fe<sub>3</sub>O<sub>4</sub> and the morphology of the prepared iron oxides is strongly dependant on the pH of the solution before irradiation.

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