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# Gamma irradiation inducing the synthesis of magnetic $Fe_3O_4$ nanorod particles in alkaline medium

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**Abstract:** Gamma irradiation has been employed to produce magnetic nanorod particles of magnetite ($Fe_3O_4$) in alkaline medium at pH 13.2, in the presence of polyvinyl alcohol solution used as an organic surfactant molecule in order to stabilize the growth of particles during synthesis. Pure sub micron sized particles with bullet-shaped morphology were prepared at pH 11.3 and well dispersed nanorod particles of $Fe_3O_4$ were synthesized at pH 13.2. It has been proven that the morphology of the as prepared oxides is strongly dependent on the pH value of the starting solution before irradiation. It has also been shown that the gamma irradiation can efficiently induce changes in structure and in morphology of the sols prepared before gamma irradiation. The XRD analysis revealed that the sol product prepared before irradiation corresponded to the standard ferric oxyhydroxide, FeO(OH) which was transformed under gamma irradiation to ferriferrous oxide ($Fe_3O_4$). The transmission electron microscopy observations indicated that the as-synthesized nanoparticles were single crystals.

**Keywords:** Iron Oxides, Nanorod Particles, Sub Micron Particles, γ-Irradiation, pH

## 1. Introduction

Nanorod materials or fibers are currently the focus of considerable research. 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 [1]. Their thermodynamically stable crystallographic phase is hematite, α–$Fe_2O_3$, which represents the most important ore of iron because of its high content and its natural abundance [2, 3]. Magnetite is a common ferrite that has a cubic structure. The compound has exhibited unique electric and magnetic properties based on the transfer of electrons between $Fe^{2+}$ and $Fe^{3+}$ in the octahedral sites. Besides practical applications in industry such as in catalysis and pigment, ceramics, energy storage, magnetic data storage, ferrofluids, and when properly coated or surface-modified magnetite, nanoparticles can be applied as leading candidate for drug delivery, diagnostic, medical imaging applications and for diagnosis or treatment of liver cancers [4-7].

$Fe_3O_4$ nanoparticles are commonly produced via aqueous or organic solution synthesis. Several methods for the synthesis of iron oxides have been reported in the literature. These include: combustion process [8], microwave plasma [9], flame pyrolysis [10], sprays pyrolysis [11], hydrothermal [12], pulsed laser ablation technique [13], and ultrasound irradiation method [14]. An organic solution phase decomposition route has been widely used in iron oxide nanoparticle synthesis, and decomposition of $Fe(CO)_5$ followed by oxidation can lead to high-quality monodispersed $\alpha$-$Fe_2O_3$ nanoparticles, which usually require relatively higher temperatures and a complicated operation. Other aqueous solution syntheses, such as coprecipitation of ferrous ($Fe^{2+}$) and ferric ($Fe^{3+}$) ions, thermal decomposition of alkaline solution of $Fe^{3+}$ chelate in the presence of hydrazine, or sonochemical decomposition of hydrolyzed Fe-(II) salt, have also been developed in recent years, but none of them could prepare nanoparticles smaller than 20 nm with a satisfactory size distribution [15-18].

In a previous work, gamma irradiation has been employed to synthesize nanocrystalline $Fe_3O_4$ with spherical morphology, but the absorbed doses of irradiation used in the preparation of this material were higher, in the range of 102 kGy and 360 kGy [19].

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

In the present work, we report on gamma irradiation as a facile technique to produce monodispersed magnetite nanoparticles in alkaline medium. We have investigated the effect of the starting solutions pH on the morphology of the prepared iron oxides under gamma irradiation. Nanorod particles consisting of pure $Fe_3O_4$ have been prepared at pH 13.2, and sub microns sized particles with bullet-shaped morphology consisting of pure magnetite were prepared by fixing the pH value of the starting solution before γ-irradiation at 11.3.

## 2. Experimental

All chemicals used in the present investigation were of the purest grade commercially available and they were used as received: ferric sulfate, $Fe_2(SO_4)$, anhydrous sodium carbonate ($Na_2CO_3$), anhydrous sodium hydroxide (NaOH), isopropyl alcohol, $(CH_3)_2CHOH$ (i-Pr-OH) and polyvinyl alcohol (PVA).

Sols constituted of ferric hydroxide were prepared by dissolving in distilled water appropriate amounts of analytically pure ferric sulfate as $Fe^{3+}$ source. In order to improve the yield production of nanoparticles, isopropyl alcohol was poured into the solutions to act as scavenger for oxidative radicals $HO^{\bullet}$, produced during the radiolysis of water under gamma irradiation. To prevent the small particles from coming into close contact, and undergoing further aggregation, polyvinyl alcohol (PVA), was used as an organic surfactant in order to stabilize the growth of particles during synthesis. By dripping slowly a concentrated solution of anhydrous sodium hydroxide into the solutions and stirring the solutions continuously, two kinds of black sols were prepared at pH 11.3 and pH 13.2, depending on the amount of sodium hydroxide added.

An experiment was setup before prepared sols were γ-irradiated. On one hand, the sols were separated from the solution by centrifugation and then filtered, washed with distilled water and absolute alcohol, and finally dried in vacuum at 60 $^{o}$C for 3 hrs. The black dried products obtained were analyzed by XRD and their morphology was observed by TEM. On the other hand, when the sols were formed at pH 11.3 and pH 13.2, they were mixed with sodium carbonate in an appropriate amount to keep the pH values constant at about 11 and 13. The prepared sols were irradiated in the field of a $^{60}$Co γ-ray source of 1.2025 x $10^{16}$ Bq (325000 Ci). The absorbed dose of irradiation was in the range of 30 kGy and 43 kGy with a dose rate of about 0.25 kGy/h.

After irradiation, two main kinds of black precipitates were obtained depending on the pH, and 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 $^{o}$C for 3 hrs. The experimental conditions of the preparation of iron oxides are detailed in Table 1.

***Table 1.*** *Preparation of iron oxides under gamma irradiation*

| Sample solution number | pH | [$Fe^{3+}$] mol/L | [i-Pr-OH] mol/L | [PVA] mol/L | [NaOH] mol/L | [$Na_2CO_3$] mol/L | Irradiation dose kGy |
|---|---|---|---|---|---|---|---|
| 1 | 11.3 | 0.08 | 3.0 | 0.2 | 1.9 | 0.30 | 30 |
| 2 | 11.3 | 0.08 | 3.0 | 0.2 | 1.9 | 0.30 | 43 |
| 3 | 13.2 | 0.08 | 3.0 | 0.2 | 2.3 | 0.35 | 30 |
| 4 | 13.2 | 0.08 | 3.0 | 0.2 | 2.3 | 0.35 | 43 |

The structure and the phase identification of the samples were characterized by X-ray powder diffraction (XRD) using a D-MAX-R3 type of X-ray diffractometer equipped with a graphite monochromatized Cu Kα radiation (λ = 1.54178 Å). The morphology and the particles size were determined by transmission electron microscopy (TEM; Hitachi H-800), and selected area electron diffraction (SAED). The TEM micrographs were taken with an accelerating voltage of 200 kV with samples deposited on a carbon coated copper grid.

## 3. Results and Discussion

The composition of the as-prepared samples was examined by XRD. The XRD patterns of the black products prepared in alkaline medium (at pH 11.3, and pH 13.2) before irradiation were similar and are shown in Figure 1a. The analysis reveals that all the peaks correspond to the standard ferric oxyhydroxide, FeO(OH), alkaganeite phase, some goethite could also be found as trace. The XRD patterns of the black precipitate produced in alkaline medium at the same pH values after irradiation are shown in Figure 1b. The analysis reveals that these powders are constituted of pure magnetite phase, ferri ferrous oxide, $Fe_3O_4$, which is cubic. Taking into account the peak (311) of the interplanar 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 (8.09 Å), ASTM powder diffraction card (No 26-1136). No characteristic peaks from impurities, such as $Fe(OH)_3$ or $Fe_2O_3$ were detected.

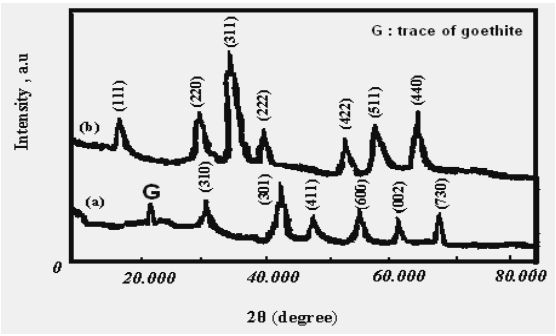


***Fig 1.*** *(a) XRD pattern of ferric oxy hydroxide, FeO(OH) prepared at pH=11.3 (and 13.2) before gamma irradiation. (b) XRD pattern of ferri ferrous oxide, $Fe_3O_4$ prepared at pH=11.3 (and 13.2) under gamma irradiation at 30 kGy.*

Moreover, from the fact that the peak (222) appears while the peak (221) does not, the black sample produced by γ-irradiation at pH 11.3 (or at pH 13.2) can be assumed to be pure $Fe_3O_4$ instead of γ-$Fe_2O_3$ [20].

The morphology of the as-prepared samples was examined by TEM. The powders were dispersed in absolute ethanol, sonicated for 5 min and dropped onto carbon-coated copper grids, then examined under a Hitachi TEM model H-800 electron microscope with accelerating voltage of 200 kV.

The TEM micrographs of the FeO(OH) products obtained before gamma irradiation are shown in Figure 2. It can be clearly seen that smaller-sized nanocrystals display roughly spherical shapes, whereas most of the larger nanocrystals exhibit cubic shape.

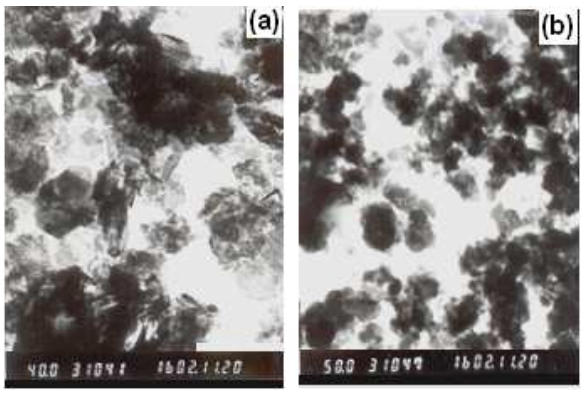


***Fig 2.*** *TEM micrographs of FeO(OH) products obtained before gamma irradiation (a) at pH=11.3; (b) at pH = 13.2.*

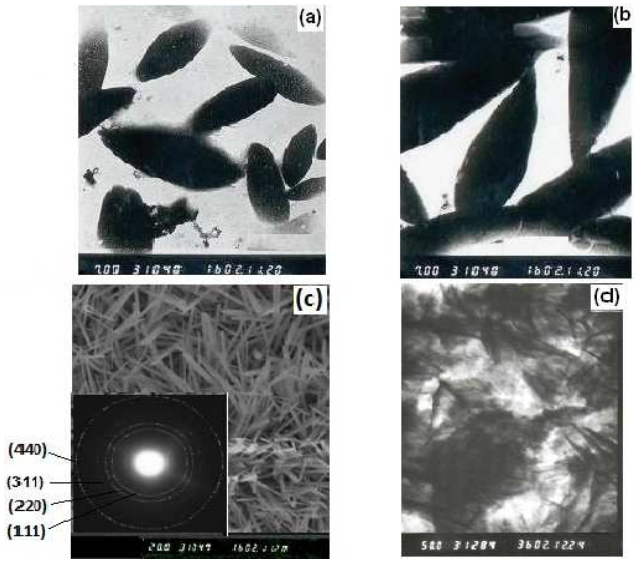


***Fig 3.*** *TEM micrographs of $Fe_3O_4$ powders prepared upon gamma irradiation. (a) pH=11.3 at 30kGy; (b) pH=11.3 at 43kGy, (c) pH=13.2 at 30kGy, and (d) pH=13.2 at 43 kGy.*

The TEM micrographs of the generated $Fe_3O_4$ oxide powders prepared under gamma irradiation at various values of pH are shown in Figure 3. The morphology of these oxides changes, and is strongly dependent on the pH value of the starting solution. There is no evidence for the formation of amorphous iron oxides and the particles are well dispersed. Figure 3c shows that the sample consists of rodlike morphology in high quantity and quasi-aligned particles constituted of pure $Fe_3O_4$ were obtained at pH 13.2. The Elliptical or bullet shaped morphology as displayed in Figure 3a and Figure 3b were observed in alkaline medium at pH 11.3 for pure $Fe_3O_4$. These oxide particles have an average size in the range of sub micrometer rather than nanometer, and it can be observed that the absorbed dose increases as the particles size grows bigger. The experimental results reveal that pH control is an important factor in preparing these materials.

From the experimental results, in order to prepare ferrous ferri oxide with small particle sizes, it is suggested to γ-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 as scavenger for both $HO^{\bullet}$ and $H^{\bullet}$ radicals during gamma irradiation [21]. TEM images provided further insight into the structure of these materials. The TEM image shows that the nanoparticles were structurally uniform with an interplanar spacing of about 2.33 Å, corresponding to the (311) lattice plane of the cubic $Fe_3O_4$ (8.07 Å) as indicated by atomic lattice fringes in Figure 3c, inset. Other peaks relative to (220), (222), and (440) did appear, which is conform to the XRD pattern. These electron diffraction (ED) micrographs were taken by using a transmission electron microscope model, JEM-200CX.

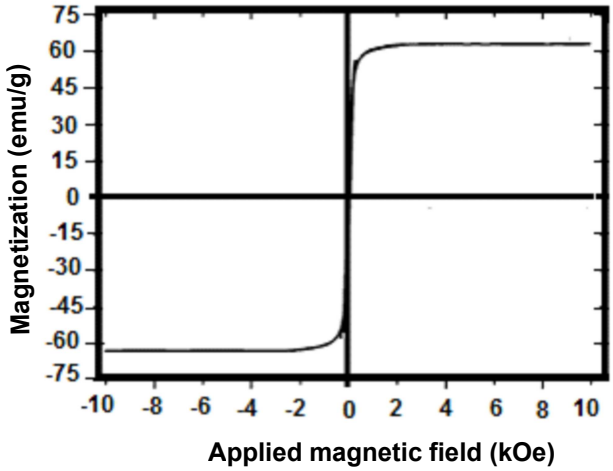


***Fig 4.*** *Magnetization as a function of the applied magnetic field of magnetite $Fe_3O_4$ prepared at pH 13.2 by gamma irradiation (30kGy)*

The magnetization (M) as a function of the applied magnetic field of the magnetite $Fe_3O_4$ prepared at pH 13.2 by gamma irradiation (30 kGy) at room temperature are shown in Figure 4. A representative hysteresis loop shows that at 300 K, the saturation magnetization (remanence) of the assembled $Fe_3O_4$ particles is extrapolated to 62 emu $g^{-1}$ at 8 kOe, while that of commercial magnetic liquid is 123 emu $g^{-1}$ [22]. The decrease of the saturation magnetization is most likely attributed to the existence of surfactants on the surface of $Fe_3O_4$ nanoparticles. The coercivity and remanence at room temperature are almost negligible. The measured lower

coercivity and remanence are due to the contribution of supermagnetic particles in the powders. These oxides could be used mostly in videotape application and also play a major role in digital data applications [23]. The adopted synthetic route is expected to be applied in the synthesis of other metal oxide semiconductor nanoparticles as building blocks for various nanodevices.

Finally, from the experiments, the mechanisms to illustrate the formation of ferri ferrous oxide $Fe_3O_4$ upon gamma irradiation process could be suggested as follows: it is well known that the radiolysis of water produces not only free radicals such as: $e_{aq}^-$, $H^\bullet$, $OH^\bullet$, and $HO_2$ or $O_2^-$, but also molecular products such as $H_2$ and $H_2O_2$.

$$\gamma - ray + H_2O \rightarrow H_2, H_2O_2, H^\bullet, OH^\bullet, e_{aq}^-, H_2O+, H_2O^*, HO_2 \quad (1)$$

Moreover, it is reported that hydrated electron, $e_{aq}^-$, and hydrogen radical $H^\bullet$ are reducing species, the standard electrode potentials of $e_{aq}^-$ and $H^\bullet$ radical at 25 °C being –2.77 V and –2.31 V, respectively, and $OH^\bullet$, $HO_2$, $O_2^-$, $H_2O_2$ are oxidizing species [24, 25].

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 the reaction. In this condition, the isopropyl alcohol (2-propanol) scavenges both $H^\bullet$ and $OH^\bullet$, but does not have any effect on the hydrated electron $e_{aq}^-$ [26]. Furthermore, in strongly alkaline solution, the hydrated electron $e_{aq}^-$ reacts rapidly with $OH^\bullet$ radicals, but deprotonation of $OH^\bullet$ may occur, leading to its conversion into $O^-$ according to the following Equations [27, 28]:

$$H^\bullet + HO^- \rightarrow e_{aq}^- + H_2O \quad (2)$$

$$H^\bullet + (CH_3)_2CHOH \rightarrow H_2 + (CH_3)_2C^\bullet OH \quad (3)$$

$$OH^\bullet + (CH_3)_2CHOH \rightarrow H_2O + (CH_3)_2C^\bullet OH \quad (4)$$

$$e_{aq}^- + HO^\bullet \rightarrow HO^- \qquad (E = 2.8V) \quad (5)$$

$$HO^\bullet + HO^- \rightarrow O^- + \mathrm{H_2O} \qquad (pK = 11.9V) \quad (6)$$

The species present in irradiated water is $O^-$. Its reaction with the reducing species such as $H^\bullet$ and $e_{aq}^-$ leads to the formation of $HO^-$ according to the reactions:

$$O^- + e_{aq}^- \rightarrow 2\,HO^- \quad (7)$$

$$O^- + H^\bullet \rightarrow 2\,HO^- \quad (8)$$

The formation of the magnetite, $Fe_3O_4$, in alkaline medium could be explained by the reduction of the starting dark sol consisting of ferric oxyhydroxide, FeO(OH), by hydrated electron under gamma irradiation [23, 24].

$$3FeO(OH) + e_{aq}^- + HO^\bullet \rightarrow Fe_3O_4 + H_2O + 2HO^- \quad (9)$$

# 4. Conclusion

Nanorod particles made of supermagnetic $Fe_3O_4$ with different morphologies were prepared successfully by employing γ-radiation at room temperature, ambient pressure and without any kind of catalysts, in water system. The results show that the morphology of the prepared oxides is strongly dependant on the pH value of the solution before irradiation. The present investigation has proven the efficiency of the gamma irradiation in inducing changes in structure and in morphology of the sols prepared before gamma irradiation. The adopted synthetic route is expected to be applied in the synthesis of other metal oxide semiconductor nanoparticles as building blocks for various nanodevices.

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