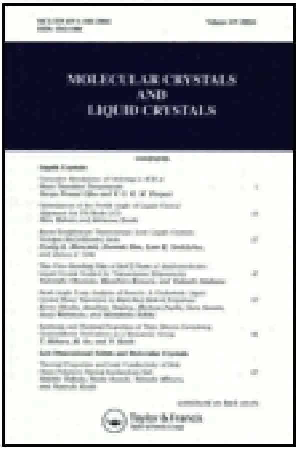

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New Synthetic Method of Magnetite Nanocrystallites Using ?-Irradiation

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NEW SYNTHETIC METHOD OF MAGNETITE NANOCRYSTALLITES USING γ-IRRADIATION

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A new method, γ-irradiation, has been developed to prepare nanocrystalline metal, alloys, metal oxide, and composites. The reactions of γ-irradiation on a rod type FeOOH in the presence of isopropanol and water have been investigated. In the initial stage of the γ-irradiation, FeOOH was turned into magnetite. With the continued γ-irradiation (over 50000 Gy), FeOOH disappeared and the product was a single phase of magnetite. XRD, SAD, LRTEM and HRTEM were used to characterize the structure and to determine their morphology, respectively. The VSM spectrum was obtained to study magnetic properties of the products.

Keywords: Fe_3O_4 nanoparticles; FeOOH nanoparticles; γ-irradiation; magnetic nanoparticles

INTRODUCTION

The majority of nanoparticle research has been focused on II-VI semiconductors and noble metals. Comparatively little work has been conducted upon the fabrication of uniform oxide nanoparticles despite their important technological applications [1,2]. The fabrication of patterned media arrays of discrete single domain magnetic nanoparticles is very important for their potential applications in multi-terabit/in^2 magnetic memory devices [3–6]. Such magnetic nanoparticles could also find applications in electromagnetic devices, pigments, ferrofluids, refrigeration systems, medical imaging, drug targeting, and catalysis. The syntheses of several uniform-sized magnetic metal nanoparticles have been reported [7–10].There have been so

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many papers in the recent years focused on the magnetic nanoparticles, such as Fe_3O_4 [11], γ-Fe_2O_3 [12], Co-Ferrite [13], Ni-Ferrite [14], Ba-Ferrite [15] and so on, because they hold many novel physical and chemical properties that are different from their bulk counterparts or atoms. The magnetic nanoparticles would find wide applications in ultra-high density magnetic storage [16], ferrofluids [7], magnetic resonance imaging (MRI) [17], and biomedical application [18].

FeOOH has been found as a major Fe-oxide component in soils and geothermal brines (Holm *et al.*, 1983) and as a corrosion product of some steels or iron meteorites (Post and Buckwald, 1991). Synthetic FeOOH finds industrial usages such as a harmless pigment for cosmetics and a precursor of hematite γ-Fe_2O_3. As a kind of rich natural resources, the FeOOH has been expected to serve as the precursor of iron oxide magnetic material. A new method, γ-irradiation, has been developed to prepare nanocrystalline metal, alloys, metal oxide, and composites [19]. In the last few years, radiation chemistry was used to initiate the growth of cadmium sulfide particles by the reaction of solvated electron with the thiol (3-mercapto-1,2-propanediol RSH) to release HS^- ions, and the resultant colloidal solutions were studied [20]. Here we report upon very easy γ-irradiation method of fabricating Fe_3O_4 nanocrystalline particles from FeOOH nanoparticles.

EXPERIMENT

$FeCl_3 \cdot 6H_2O$ (99+%) was obtained from Aldrich Chemical Co. and used without further purification. Aqueous solutions of 1.0 L dissolving 0.033 mol $FeCl_3$ was prepared. Solution was aged in a beaker at 50°C for 24 hours. Resulting suspension was filtered using microfilter. The precipitate (FeOOH) was washed with deoxygenated water (300 mL, 18 MΩ, nitrogen gas bubbling for 30 min), then dried at 40°C for 5 hours. A 0.2 g FeOOH was added into 20 mL deoxygenated water, then 4 mL isopropanol was poured into the solution as a OH-scavenger. This solution was γ-irradiated in the field of 70000 Ci ^{60}Co γ-ray source with a dose of 0 kGy, 30 kGy, 50 kGy and 90 kGy. Low-resolution transmission electron microscopy (LRTEM) and high-resolution transmission electron microscopy (HRTEM) examinations of the samples were carried out on a HITACHI H-7500 transmission electron microscope and a JEOL JEM2010 transmission electron microscope, respectively. TEM samples were prepared on the 400 mesh copper grid coated with carbon. The structural properties of synthesized nanoparticles were analyzed by X-ray powder diffraction (XRD) with a Philips X'Pert-MPD System with a Cu K_α radiation source ($\lambda = 0.154056$ nm) and selected area diffraction (SAD) pattern.

The average size of the crystals was estimated using Scherrer's formula. The magnetization curves were characterized with Lake Shore 7300 vibrating sample magnetometer (VSM).

RESULTS AND DISCUSSION

Figure 1 illustrates the XRD pattern of FeOOH nanoparticle sample. No impurity peak was observed in the X-ray diffraction pattern. The diffraction peaks were clearly broadened, which could be the result of the reduced particle size. The experimental peaks were perfectly matched with the theoretical data of the JCPDS card no. 75-1594, thus indicating the presence of pure FeOOH. Figure 2 shows LRTEM images of FeOOH nanoparticles. FeOOH nanoparticles were spindle-shaped and highly monodisperse. The range of their dimensions was 100–120 nm in length and 20–30 nm in width. Figure 3 shows X-ray diffraction pattern of the γ-irradiated FeOOH nanoparticles with different doses. Before γ-irradiation (Fig. 3A), the sample only contains FeOOH. After γ-irradiation with a dose of 30 kGy (Fig. 3B), the sample mainly contains FeOOH and partially Fe_3O_4. This indicates that the FeOOH was turned into Fe_3O_4 partially by γ-irradiation. After γ-irradiation with a dose of 50 kGy (Fig. 3C), most of FeOOH was turned into Fe_3O_4. The diffraction peaks of FeOOH almost disappeared. After γ-irradiation with a dose of 90 kGy (Fig. 3D), the experimental peaks were perfectly matched with the theoretical data of the JCPDS card no. 79-0418, thus indicating the presence of pure Fe_3O_4. No impurity peak was

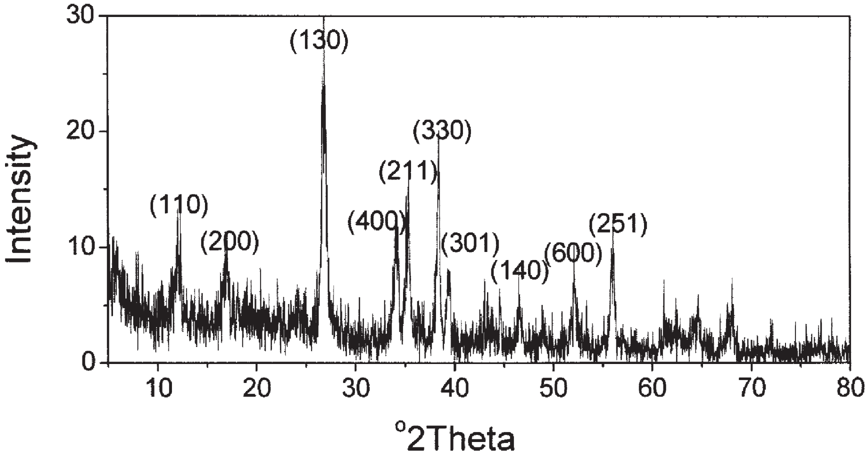

FIGURE 1 X-ray diffraction pattern (Cu K_α-radiation) of FeOOH nanoparticles.

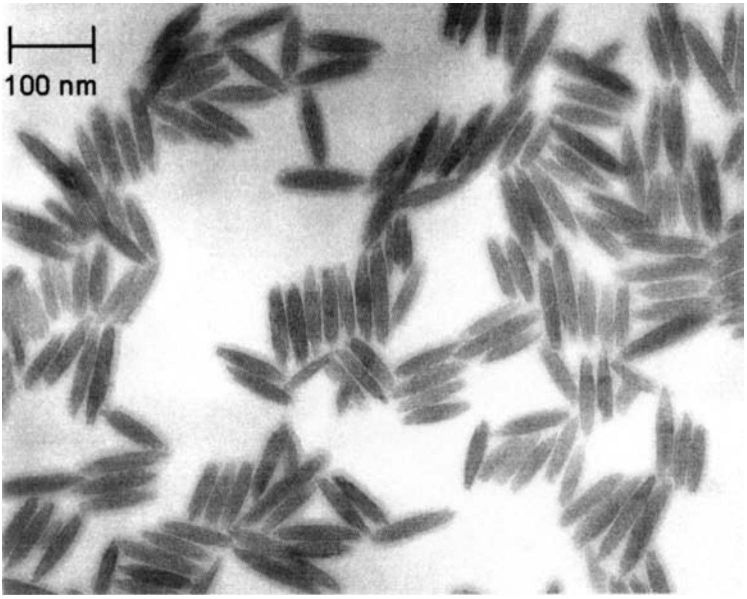

FIGURE 2 Low-resolution TEM images of FeOOH nanoparticles.

observed in the X-ray diffraction pattern. This is interpreted that FeOOH was converted to Fe_3O_4 thoroughly. Figure 4 shows LRTEM images of the γ-irradiated FeOOH nanoparticles with different doses. Before γ-irradiation (Fig. 4A), rod type FeOOH nanoparticles were highly monodispersed. After γ-irradiation with a dose of 10 kGy (Fig. 4B), rod type FeOOH nanoparticles were aggregated and some of spherical nanoparticles appeared. With the more doses of γ-irradiation, the number of rod type FeOOH nanoparticles decreased and the number of spherical nanoparticles increased (Fig. 4C–E). After γ-irradiation with a dose of 90 kGy (Fig. 4F), rod type FeOOH nanoparticles perfectly disappeared and only spherical nanoparticles existed. According to XRD spectrum, FeOOH was converted to Fe_3O_4 thoroughly after γ-irradiation with a dose of 90 kGy. This indicates that the spherical nanoparticle is Fe_3O_4 nanoparticles. Figure 5 shows particle size statistics over 100 particles in the LRTEM micrograph of Fe_3O_4 nanoparticles synthesized by γ-irradiation with a dose of 90 kGy. The mean size of spherical Fe_3O_4 nanoparticles is 37.5 nm with a standard deviation 3.1 nm. This shows that the Fe_3O_2 nanoparticles have narrow size distribution. The crystal size is determined as 35.6 nm by Debye-Scherre equation with XRD data, which is close to the particle sizes calculated from TEM images (37.5 nm for Fe_3O_4). Figure 6 indicates the selected area diffraction

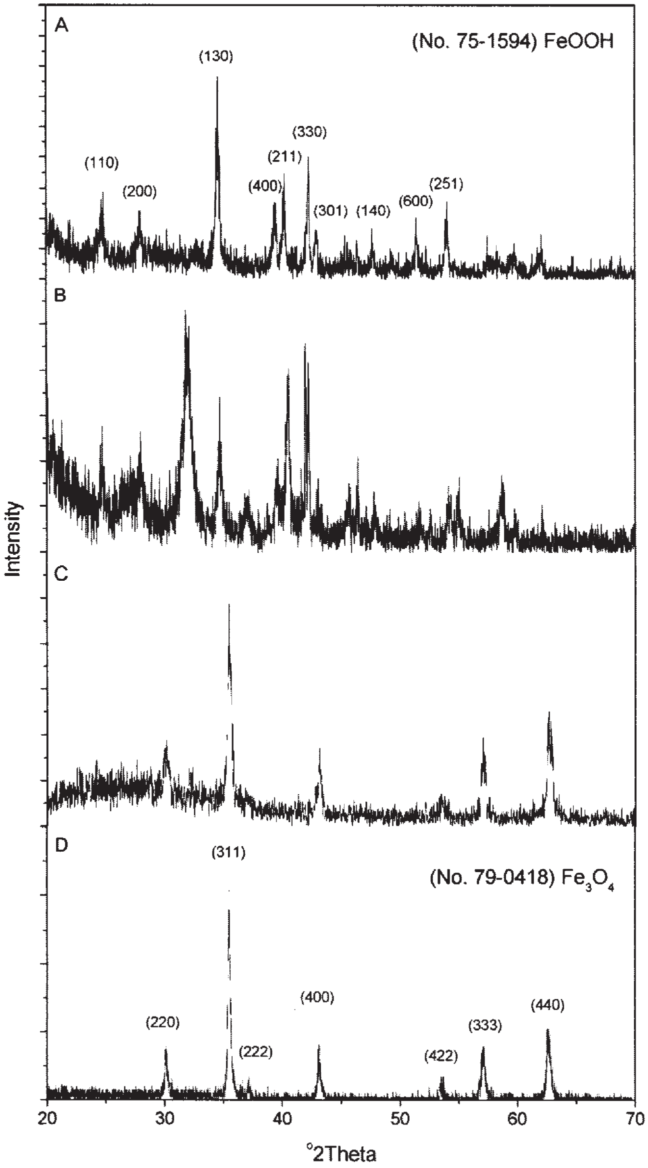

FIGURE 3 X-ray diffraction pattern (CuK$_\alpha$-radiation) of γ-irradiated FeOOH nanoparticles with a dose of 0 kGy (A), 30 kGy (B), 50 kGy (C) and 90 kGy (D).

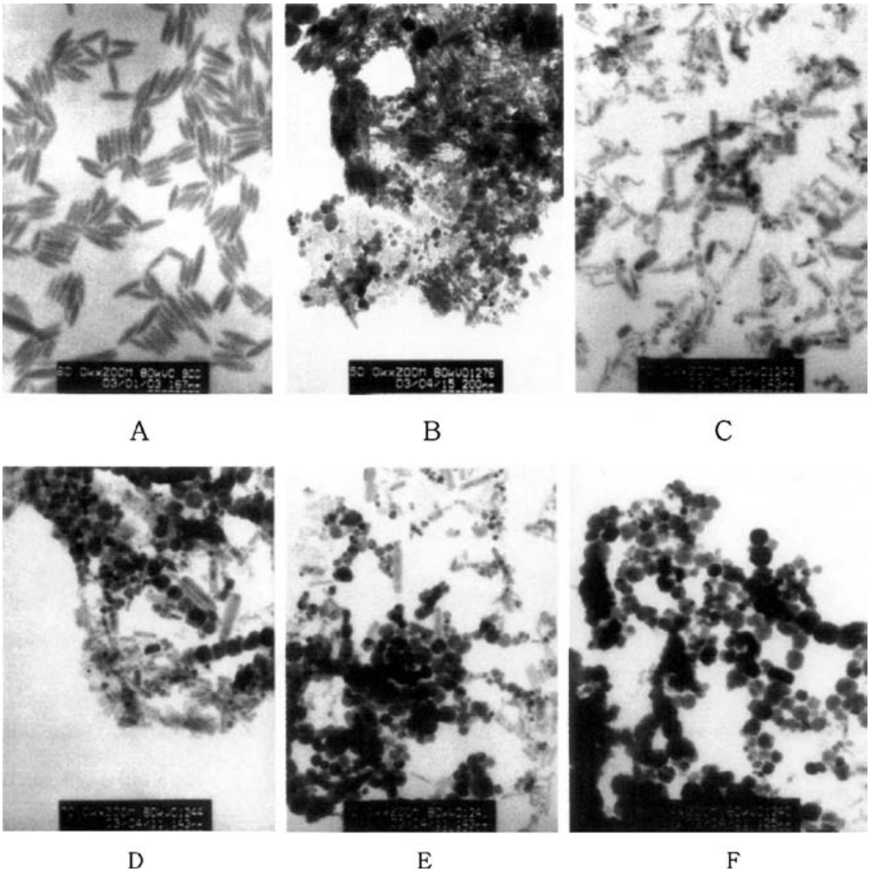

FIGURE 4 Low-resolution TEM images of γ-irradiated FeOOH nanoparticles with a dose of 0 kGy (A), 10 kGy (B), 20 kGy (C), 30 kGy (D), 50 kGy (E) and 90 kGy (F).

pattern of γ-irradiated FeOOH nanoparticles with different doses. According to the selected area diffraction pattern, the d-spaces corresponding to the ring are calculated form the formula $rd = L\lambda$, where r is the radius of each ring, d is the d-space to be calculated, and L and λ are the camera length and the electron wave length, respectively ($L = 100$ cm and $\lambda = 0.251$ Å). Before γ-irradiation (Fig. 6A), the diffraction ring patterns were perfectly matched with them of FeOOH. After γ-irradiation with a dose of 30 kGy, the d-spaces of two rings were corresponded to d-spaces of (440) and (311) planes at Fe_3O_4 crystal structure. The same result is observed for XRD spectra of Figure 3B. Figure 6C shows the selected area diffraction pattern of γ-irradiated FeOOH nanoparticles with a dose of

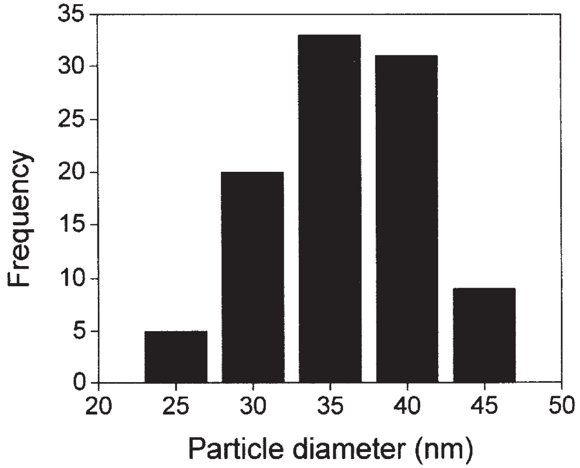

FIGURE 5 Particle size statistics over 100 particles in the TEM micrograph of Fe_3O_4 nanoparticles synthesized by γ-irradiation with a dose of 90 kGy.

90 kGy. The electron diffraction pattern exhibited a magnetite (Fe_3O_4) structure. The diffraction rings can be indexed to (220), (311), (400), (333), (422) and (440) planes at Fe_3O_4 crystal structure. The same result is observed for XRD spectra of Figure 3D. Figure 7 shows HRTEM images of Fe_3O_4 nanoparticles synthesized by γ-irradiation with a dose of 90 kGy. Figure 7A indicates that the Fe_3O_4 single domain was perfectly synthesized by γ-irradiation without any defect. A 4.83 Å of the space of two lines was corresponded to *d*-spaces of (111) planes at Fe_3O_4 crystal structure.

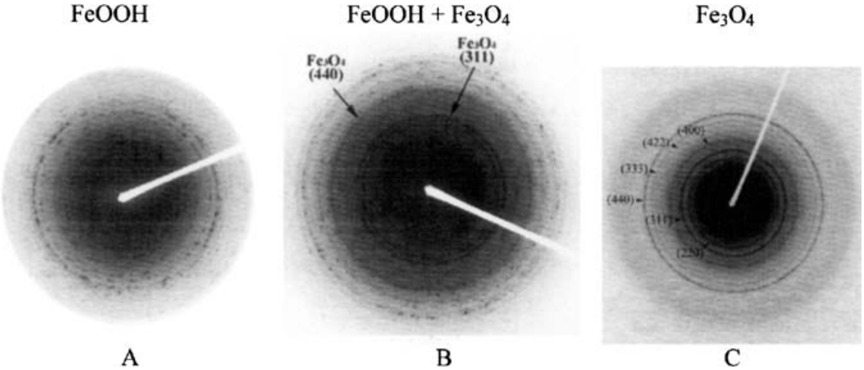

FIGURE 6 Selected area diffraction pattern of γ-irradiated FeOOH nanoparticles with a dose of 0 kGy (A), 30 kGy (B) and 90 kGy (C).

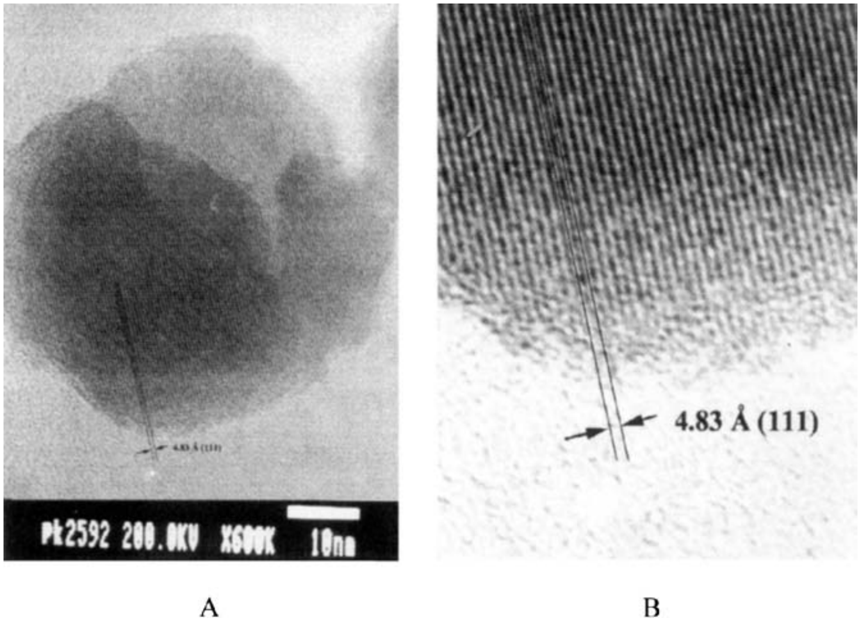

FIGURE 7 High-resolution TEM image of Fe_3O_4 single domain (B) and lattice structure (B).

Figure 8 shows magnetization versus applied field at 300 K (A) and 77 K (B) for Fe_3O_4 nanoparticles synthesized by γ-irradiation with a dose of 90 kGy. The hysteresis loop for Fe_3O_4 nanoparticle sample was not observed, but the superparamagnetic behavior for Fe_3O_4 nanoparticles were documented by the hysteresis loop measured at 300 K as shown in Figure 8A. There is almost immeasurable coercivity (0.14 Oe) at room temperature. This indicates that Fe_3O_4 particles are superparamagnetic and nanosized [21]. Below the blocking temperature, magnetic nanoclusters become magnetically frozen. Magnetic mement of the nanoclusters is fixed, and the remanence and coercivity in the hysteresis loop appears on the plot of magnetization as a function of magnetic field (Fig. 8B). The saturation magnetization, M_s, was 64.1 emu/g, which was lower than that of bulk magnetite particles ($M_{bulk} = 92$ emu/g). The decrease in M_s is due to superparamagnetism of magnetite particles, which occur when the particle size is nanometer.

The result from the present experiment indicates that FeOOH nanoparticles are also sensitive to γ-irradiation. The FeOOH nanoparticles used in this experiment have a very large surface area and high surface energy [22]. The most of the surface are very active and easily take place reactions [23].

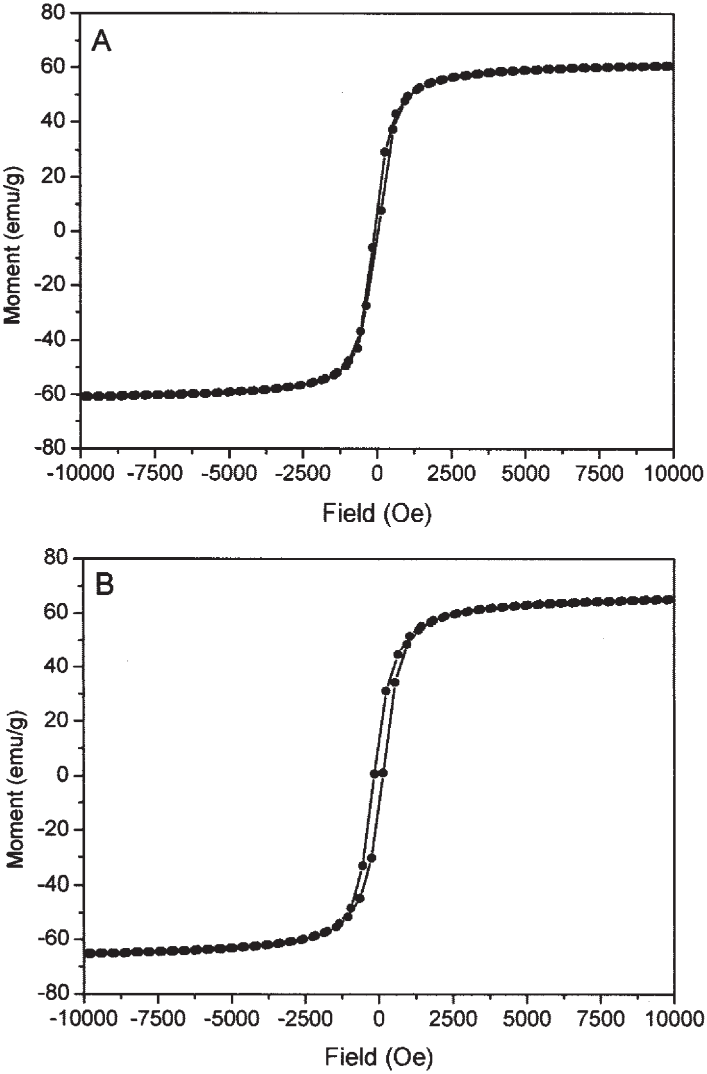

FIGURE 8 Magnetization versus applied field at 300 K (A) and 77 K (B) for γ-irradiated FeOOH nanoparticles with a dose of 90 kGy.

It is presumed that the water in this system provides the H radicals which play an important role in the course of reduction, and the isopropanol acts as a OH-scavenger which should prevent FeOOH from being reduced into Fe_3O_4. γ-ray provides the essential energy for the phase transition from FeOOH to Fe_3O_4.

CONCLUSION

The reactions of γ-irradiation on a rod type FeOOH in the presence of isopropanol and water have been investigated. With the continued γ-irradiation to a dose of 90 kGy, a rod type FeOOH nanoparticle disappeared and the product was a spherical Fe_3O_4 nanoparticle, which had an average size of 37.5 nm. FeOOH nanoparticles changed into Fe_3O_4 nanoparticles at room temperature. The result from the present experiment indicates that FeOOH is sensitive to γ-irradiation and turns into Fe_3O_4.

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