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# Preparation of nanocrystalline $Fe_3O_4$ by $\gamma$-ray radiation

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## Abstract

The $\gamma$-radiation method has been successfully used to prepare pure nanocrystalline $Fe_3O_4$ powders from ferric hydroxide sols. Electron microscopy and X-ray powder diffraction techniques show that the average particle size is 16 nm. The influences of experimental conditions on the preparation of nanocrystalline $Fe_3O_4$ are discussed. © 1997 Elsevier Science B.V.

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$Fe_3O_4$ has been widely studied because it is one of the technologically important magnetic materials and served as a precursor for $\gamma$-$Fe_2O_3$ recording materials. The methods for preparing magnetite are as follows: reduction of hematite, $Fe_2O_3$, by $CO/CO_2$ [1] or $H_2$ [2], co-precipitation of a solution of ferrous/ferric mixed salts [3] and oxidation of the ferrous hydroxide gels using oxidants such as $KNO_3$ [3]. Also, it was reported that Kandori et al. prepared fine magnetite particles from iron(III) hydroxide sol in the presence of iron powder [4]. However, the yield was only about 5%, and the remaining iron powder would contaminate the product.

The $\gamma$-radiation technique for preparing ultrafine particles has been developed within recent decades [5–9]. Compared with other methods of preparing ultrafine particles, the $\gamma$-radiation method can enable processing under ambient pressure at room temperature and no reducing agent contaminating the products. In this letter, we report on a new method of the preparation of nanocrystalline $Fe_3O_4$ magnetite particles by $\gamma$-irradiation of ferric hydroxide sols.

The procedure includes two steps: (1) preparation of ferric hydroxide sols, and (2) $\gamma$-irradiation of the sols. The sol was made by dripping an $NH_3 \cdot H_2O$ solution into the solution of ferric salt slowly, stirring the solution continuously until the brown–red sol was forming. Then isopropanol was poured into the solution to act as a scavenger for the OH radicals. The sol was then irradiated in the field of a 70000 Ci $^{60}Co$ $\gamma$-ray source with different doses. After the irradiation the precipitate was separated and washed with distilled water, then dried at 60°C for several hours.

X-ray powder diffraction (XRD) patterns were recorded at a scanning rate of $0.05° s^{-1}$ in the $2\theta$ range from 10 to 70° using a Rigaku Dmax $\gamma_{\text{A}}$ X-ray diffractometer with high-intensity Cu K$\alpha$ radiation

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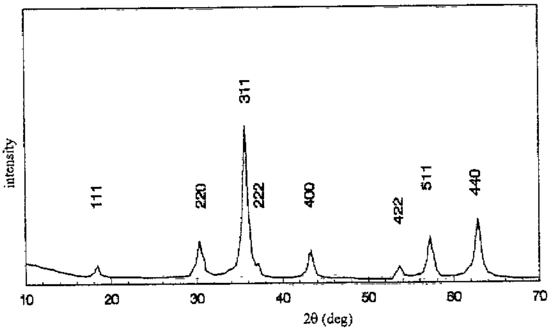

Fig. 1. X-ray diffraction pattern of sample 4 prepared by the $\gamma$-radiation method.

($\lambda = 1.54178$ Å). TEM images were taken with a Hitachi model H-800 transmission electron microscope, using an accelerating voltage of 200 kV. Particle sizes were measured from the dark field TEM micrographs and also calculated from XRD patterns. Particle size distribution was determined by photographic image microstructure densitometry analysis, which was performed with a Perkin–Elmer microdensitometer and an IBM PC-486 computer.

Fig. 1 shows the XRD patterns of sample 4. The peaks correspond to those of the standard $Fe_3O_4$. Though the XRD patterns of $Fe_3O_4$ are similar to those of $\gamma$-$Fe_2O_3$, there are still slight differences between them. From the fact that the peak (222) appeared while the peak (221) did not, and all the *d*-values calculated from XRD patterns conform more to that of standard $Fe_3O_4$ than to that of standard $\gamma$-$Fe_2O_3$, the sample prepared by the $\gamma$-ray irradiation was identified to be $Fe_3O_4$ instead of $Fe_2O_3$.

According to the Scherrer formula, the broadening of peaks of XRD patterns is inversely proportional to the average crystallite size ($L$):

$$\beta = K\lambda / L \cos\theta$$

where $\lambda$ is the wavelength, $\theta$ is the Bragg angle and $K$ is the Scherrer constant which is considered as depending on the (*hkl*) index and on the crystallite shape [10]. With experimental errors of about 11% and for relative determination of sizes in a series of samples rather than the absolute value, it may be assumed that $K = 1$ [11]. The contribution of particle size broadening is obtained from the Warren and Biscoe equation [12]:

$$\beta^2 = B^2 - b^2,$$

where $B$ and $b$ are the observed angular halfwidth for the sample under investigation and for a standard sample, respectively. The average particle size, calculated from the XRD patterns (Fig. 1), was found to be 16 nm.

Fig. 2 shows the TEM image and selected area diffraction pattern of sample 4. As shown in Fig. 2a, the particles of $Fe_3O_4$ powder are mostly equiaxied and their sizes are consistent with those obtained from the XRD patterns. Using the electron diffraction pattern (Fig. 2b), the *d*-spacings corresponding

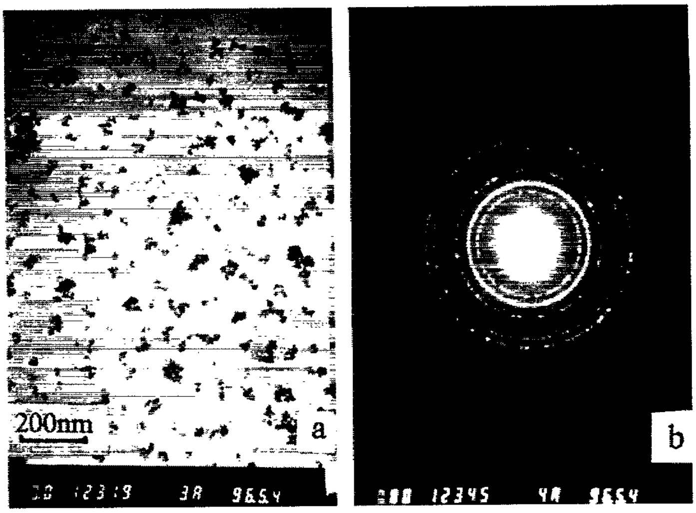

Fig. 2. TEM of sample 4: (a) dark field micrographs of $Fe_3O_4$, (b) selected area diffraction pattern.

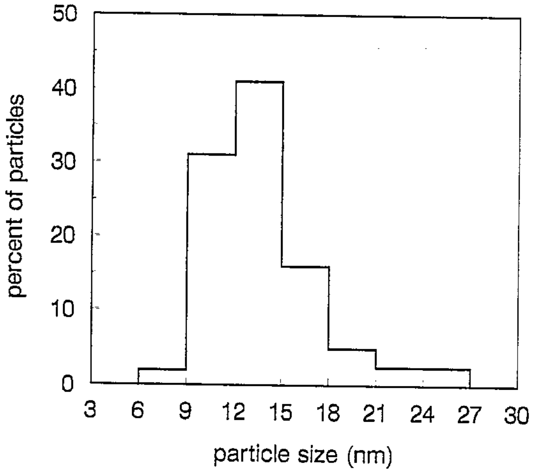

Fig. 3. Particle size distribution of sample 4.

to the rings were calculated using the formula $rd = L\lambda$, where $r$ is the radius of each ring, $d$ is the $d$-spacing to be calculated, and $L$ and $\lambda$ are the camera length and the electron wavelength, respectively. The $L\lambda$ value was calibrated using the known structure of a polycrystalline Au thin film which was deposited onto an amorphous carbon substrate. The calculated $d$-spacings correspond well to the $d$-values obtained from the XRD patterns. This indicated further that the sample prepared by the $\gamma$-ray radiation was $Fe_3O_4$ and contained no impurity.

The distribution of particle size of sample 4 is shown in Fig. 3, from which one can see that the particle size range is from 6 to 27 nm, and the largest percentage is about 41% in the size range 12 to 15 nm. The average particle size is 14 nm calculated from Fig. 3, which is in agreement with that obtained from XRD patterns (16 nm) considering experimental errors.

The results pertaining to the influence of the experimental conditions (concentration of ferric ion ($Fe^{3+}$), amount of $NH_3 \cdot H_2O$, $\gamma$-radiation dose, etc.) on particle size and yield are listed in Table 1.

The experiments reveal that the preparation of ferric hydroxide sols and the control of the amount of $NH_3 \cdot H_2O$ in the sols before irradiation is indispensable for the preparation of $Fe_3O_4$ by $\gamma$-ray radiation. When there was no $NH_3 \cdot H_2O$ addition into the ferric salt solution, after a long time irradiation the solution changed from yellow to colourless and no precipitation occurred. By irradiation of the ferric hydroxide sols containing different amounts of $NH_3 \cdot H_2O$ (the preparation method mentioned above), it was found that at the ratio $m_{NH_3 \cdot H_2O}/m_{Fe^{3+}} = 1.5$ ($m_{NH_3 \cdot H_2O}$ and $m_{Fe^{3+}}$ stand for the molar values of the $NH_3 \cdot H_2O$ and the $Fe^{3+}$) used in preparing the sols, precipitation began after irradiation with a dose of $1.5 \times 10^5$ Gy. The particle size of $Fe_3O_4$ was 8 nm, but the yield (the yield is defined as the molar ratio of the iron element in the product to that used in preparing the sols) was less than 2% and the products contained about 40% (in molar ratio, the same below) $\beta$-FeOOH. When $m_{NH_3 \cdot H_2O}/m_{Fe^{3+}} = 1.8$, the yield increased to above 50% and the maximum yield was 67% (sample 4). The irradiation dose

Table 1
The correlation between the experimental conditions and results

| Sample | $[Fe^{3+}]$ (M) | $m_{NH_3 \cdot H_2O}/m_{Fe^{3+}}$ | Radiation dose (Gy) | Average size (nm) | Yield (%) |
|---|---|---|---|---|---|
| 1 | 0.01 | 0.0 | $3.06 \times 10^5$ | — | — |
| 2 | 0.01 | 1.5 | $1.02 \times 10^5$ | 8 | < 2% [a] |
| 3 | 0.01 | 1.8 | $1.02 \times 10^5$ | 15 | 11 |
| 4 | 0.001 | 1.8 | $5.14 \times 10^4$ | 16 | 67 |
| 5 | 0.01 | 1.8 | $5.14 \times 10^4$ | 16 | 62 |
| 6 | 0.05 | 1.8 | $5.14 \times 10^4$ | 18 | 51 |
| 7 | 0.1 | 1.8 | $5.14 \times 10^4$ | 23 | 47 |
| 8 | 0.01 | 2.0 | $2.8 \times 10^4$ | 32 | 78 [a] |
| 9 | 0.01 | 2.2 | $2.8 \times 10^4$ | 41 | 82 [a] |

[a] Stand for the products containing impurities.

essential for precipitation was reduced to $5.14 \times 10^4$ Gy and the sample was single phase $Fe_3O_4$. When $m_{NH_3 \cdot H_2O}/m_{Fe^{3+}} = 2.0$ (sample 8), the yield increased further, but α-FeOOH (about 10%) appeared in the product, at the same time the particle size increased to 32 nm. When $m_{NH_3 \cdot H_2O}/m_{Fe^{3+}} = 2.2$, the amount of α-FeOOH and $Fe_3O_4$ were about half and half in the product, and the particle size of $Fe_3O_4$ increased to 41 nm. Therefore, the sol with the ratio of $m_{NH_3 \cdot H_2O}/m_{Fe^{3+}} = 1.8$ is suitable for the preparation of $Fe_3O_4$ by γ-ray radiation.

The concentration of ferric salt in the solution also affects the yield and the particle size of $Fe_3O_4$ powder. With a rise of ferric ion concentration, the average particle size of $Fe_3O_4$ increases but the yield is reduced slightly. In later work, we will investigate the magnetism of the nanocrystalline $Fe_3O_4$ prepared by γ-ray radiation.

In summary, the γ-ray radiation method is useful for preparing nanocrystalline $Fe_3O_4$ powders from ferric salt solutions. The sol with the ratio of $m_{NH_3 \cdot H_2O}/m_{Fe^{3+}} = 1.8$ is suitable for the preparation. Single phase $Fe_3O_4$ powder with an average particle size of 16 nm was successfully prepared by this method.

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