Correlation between particle size/domain structure and magnetic properties of highly crystalline Fe₃O₄ nanoparticles

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Highly crystalline single-domain magnetite Fe₃O₄ nanoparticles (NPs) are important, not only for fundamental understanding of magnetic behaviour, but also for their considerable potential applications in biomedicine and industry. Fe₃O₄ NPs with sizes of 10–300 nm were systematically investigated to reveal the fundamental relationship between the crystal domain structure and the magnetic properties. The examined Fe₃O₄ NPs were prepared under well-controlled crystal growth conditions using a large-scale liquid precipitation method. The crystallite size of cube-like NPs estimated from X-ray diffraction pattern increased linearly as the particle size (estimated by transmission electron microscopy) increased from 10 to 64.7 nm, which indicates that the NPs have a single-domain structure. This was further confirmed by the uniform lattice fringes. The critical size of approximately 76 nm was obtained by correlating particle size with both crystallite size and magnetic coercivity; this was reported for the first time in this study. The coercivity of cube-like Fe₃O₄ NPs increased to a maximum of 190 Oe at the critical size, which suggests strong exchange interactions during spin alignment. Compared with cube-like NPs, sphere-like NPs have lower magnetic coercivity and remanence values, which is caused by the different orientations of their polycrystalline structure.

Magnetite (Fe₃O₄) nanoparticles (NPs) have attracted considerable interest as a result of their attractive properties, such as their strong magnetic moment, biocompatibility, chemical stability, and magnetoelectric properties. Numerous reports have described their advances in nanotechnology and their development of a wide range of applications, such as medical application, catalysis, Li batteries, printer toners, and wastewater treatment. For the broad application of these NPs, control of the crystal size, shape, and domain structure is important for defining their chemical and physical properties. This was demonstrated in our previous study of photoluminescent NPs, for which the performance was attributable to the domain size rather than the particle size. The particle size, which originates from the magnetic domain structure, has also been recognised as a key factor in the application of magnetic NPs.

The relationship between particle size and the magnetic properties, such as the coercivity (Hc), of Fe₃O₄ NPs has been widely reported. The critical size of magnetic NPs, which indicates the transition from a single- to multi-domain structure, was evaluated by the change in Hc with respect to the particle size. However, the critical size for Fe₃O₄ NPs has not yet been systematically demonstrated because this value depends on the crystal structure, which can have spherical, cubic, or multiple phases. Therefore, investigation of the critical size on the basis of the crystal structure is necessary.

The particle size required to achieve superparamagnetism in Fe₃O₄ NPs is widely estimated to be below 20 nm, whereas the critical size for forming a multi-domain structure has been theoretically estimated to be 76 nm for cubic and 128 nm for spherical Fe₃O₄ NPs. However, the critical size for cubic Fe₃O₄ NPs has been experimentally determined to be higher than 160 nm. Much smaller critical sizes of 30–46 nm have also been reported for cubic Fe₃O₄ NPs. Multi-granule Fe₃O₄ NPs with sizes of 16–312 nm showed a transitional size...
of approximately 120 nm\(^{19}\). Although the effects of size and shape on the behaviour of magnetic particles have been known for more than half a century\(^{19}\), the quantitative effects on Zn\(_{0.4}\)Fe\(_{2.6}\)O\(_4\) NPs remained undiscovered in the size range of 20–140 nm until 2012\(^{20}\), when the critical size was found to be approximately 60 nm, and the saturation magnetisation (\(M_s\)) was found to be lower for spherical particles than for cubic ones.

Owing to the experimental difficulty in controlling particle sizes over a wide size range\(^{21}\), a systematic investigation of the magnetic domain structures of the most commonly used Fe\(_3\)O\(_4\) NPs is still lacking, although such an investigation is needed to meet the currently increasing requirements for various applications. The current study therefore investigates the size dependence of the magnetic properties of Fe\(_3\)O\(_4\) NPs with sizes of 10–300 nm. The study includes cube- and sphere-like NPs that were produced under well-controlled crystal growth conditions on a large scale. The critical size of highly crystalline cube-like Fe\(_3\)O\(_4\) NPs was examined through the correlation between the particle size measured by transmission electron microscopy (TEM) and the crystallite size estimated by X-ray diffraction (XRD). The value was further confirmed by observing the lattice fringes and examining the dependence of \(H_c\) on the particle size. The high \(H_c\) value obtained in this study is discussed in detail in terms of the spin interactions in a single-domain structure.

**Methods**

Two types of highly crystalline Fe\(_3\)O\(_4\) NPs, i.e., cube-like and sphere-like ones, were synthesised on a large scale under precise control of the Fe\(^{3+}\) concentration, pH, temperature, and aeration rate. The cube-like Fe\(_3\)O\(_4\) NPs were prepared by a two-stage oxidation reaction, which is described in patent No. US 5843610A (Toda Kogyo Co., Ltd., Japan)\(^{22}\). In contrast, the sphere-like Fe\(_3\)O\(_4\) NPs were prepared by a one-stage oxidation reaction, which is described in patent No. US 4992191A (Toda Kogyo Co., Ltd., Japan)\(^{23}\). All data generated or analyzed during this study are included in this article and its Supplementary Information files.

The morphologies of the prepared NPs were analysed using field-emission scanning electron microscopy (FE-SEM; Hitachi S-5000, Tokyo, Japan) and TEM (JEM-2010, 200 kV, JEOL Ltd., Tokyo, Japan). The crystallite size and chemical composition of the prepared NPs were examined by XRD and Raman spectroscopy (RINT2000, Rigaku Denki Co., Ltd., Tokyo, Japan), using Cu K\(\alpha\) radiation with a scanning range of 20°–80°. Their magnetic performance was assessed using a superconducting quantum interference device (SQUID, Quantum Design, Tokyo, Japan), operated at 300 K. The prepared cube-like NPs with particle sizes \(d_p\) of 9.6, 19.6, 24.4, 31.9, 45.3, 64.7, 130, 243, and 287 nm were named as C1, C2, C3, C4, C5, C6, C7, C8, and C9, respectively. The sphere-like NPs with \(d_p\) of 93.3 and 121 nm were named as S1 and S2, respectively.

**Results and Discussion**

SEM images of the cube-like Fe\(_3\)O\(_4\) NPs are shown in Fig. 1. The \(d_p\) of these particles are 9.6, 19.6, 24.4, 31.9, 45.3, 64.7, 130, 243, and 287 nm for C1–C9, respectively, and their size distributions are given in Supplementary Fig. S1. The high-resolution TEM (HRTEM) images of the cube-like Fe\(_3\)O\(_4\) NPs in Supplementary Fig. S2 show the lattice fringes of the NPs, and indicate that the NPs have a single crystalline structure up to a \(d_p\) of 64.7 nm. In contrast, the C7–C9 NPs, with diameters larger than 100 nm, show a polycrystalline structure. SEM images and size distributions of the sphere-like Fe\(_3\)O\(_4\) NPs are shown in Supplementary Fig. S3(a–d). The values of \(d_p\) were 93.3 and 121 nm for S1 and S2, respectively. All of the Fe\(_3\)O\(_4\) NPs exhibit quasi-narrow size distributions compared with previously reported particles\(^{7,14}\).

The HRTEM images shown in Supplementary Fig. S2 confirm that NPs with a diameter \(d_p\) of 64.7 nm have a single crystalline structure, which is shown by the single direction of the lattice fringes. This result is consistent with those obtained for particles produced by a colloidal chemical synthetic route\(^{3,14}\). The sphere-like NPs show different crystal properties. For these NPs, the \(d_p\) is much smaller than the \(d_p\), and also much smaller than those of the cube-like NPs with a similar \(d_p\), as shown in Supplementary Table S1 and Fig. 3. Supplementary Fig. S4 shows a detailed comparison of the cube-like C7 and sphere-like S2 NPs, which have a similar average \(d_p\). The dark-field TEM image and electron diffraction pattern show that the C7 NP is polycrystalline with a single orientation. However, a polycrystalline structure containing different orientations was observed in the S2 NPs. This was further confirmed from the HRTEM images by the existence of different directions of the lattice fringe in a single S2 NP (Supplementary Fig. S4(g–i)). Sphere-like NPs commonly consist of agglomerates of variously sized cubic NPs\(^{5,14,25}\). The different morphological structure arises from the different preparation processes\(^{21}\), as described in the patent\(^{22,23}\).
**Figure 1.** Scanning electron microscopy images of cube-like Fe₃O₄ nanoparticles with various particle sizes. (a) 9.6, (b) 19.6, (c) 24.4, (d) 31.9, (e) 45.3, (f) 64.7, (g) 130, (h) 243, and (i) 287 nm, which are named as C1–C9, respectively.

**Figure 2.** X-ray diffraction patterns of cube-like Fe₃O₄ nanoparticles with various particle sizes.
The hysteresis loops for these particles, shown in Fig. 4(a), show the ferrimagnetic nature of the Fe₃O₄ NPs. The cube-like Fe₃O₄ NPs possess high $M_s$ values, which are affected by the $d_p$ as shown in Fig. 4(b). The $M_s$ value, obtained by applying the law of approach to saturation²⁶, increases with increasing $d_p$ for all samples, including the sphere-like NPs. This trend is consistent with those found in other reports on Fe₃O₄ NPs with diameters lower than 100 nm⁵, 16, 27, 28. The $M_s$ value increased from 54.7 emu/g (9.6-nm NPs) to 84.7 emu/g (287-nm NPs), which is close to the theoretically estimated $M_s$ for bulk Fe₃O₄ (92 emu/g). The $H_c$ and remanent magnetisation ($M_r$), which are also affected by $d_p$, are shown in Figs 4(c) and 5. These values increase from around 0 for the 9.6-nm NPs, which are known to be superparamagnetic²⁶, 29, 30, to a maximum value of around 190 Oe ($H_c$) and 13 emu/g

Figure 3. Relationship between average particle size and crystallite size. The solid line shows the trend in the relationship for cube-like Fe₃O₄ nanoparticles. The black open triangles were replotted from Table 1 in ref. 19 for multi-granule Fe₃O₄ nanoparticles.

Figure 4. (a) Hysteresis loops of cube-like Fe₃O₄ nanoparticles, and particle size dependence of (b) saturation magnetization and (c) remanent magnetization for all Fe₃O₄ nanoparticles.
(Mr) at a dp of around 80 nm, and then decrease continuously with further increases in dp. The trends in these two parameters are consistent with previous theoretical estimations18,19,31, and they have similar characteristics to those obtained for Zn0.4Fe2.6O4 NPs20. The initial increase in Hc with domain size corresponds to the sixth power of the domain size. The high Hc value may be caused by the strong spin interactions in highly crystalline Fe3O4 NPs during spin alignment, which has previously been observed in soft magnetic NPs32.

By fitting the measured Mr and Hc values using a log-normal distribution function, shown by the dark blue solid line, the critical sizes for the maximum Mr and Hc values were determined to be 77 ± 2 nm and 75 ± 3 nm, respectively. On average, therefore, the critical value for the transition is about 76 ± 4 nm. This value is consistent with the critical size of 76 nm estimated theoretically for the transition from single- to multi-domain behavior12. Furthermore, the critical size of about 76 nm is almost the same as the transition size obtained from the relationship of dc and dp, as shown in Fig. 3. Single-domain cube-like Fe3O4 NPs, such as those with a size of 64.7 nm, can be applied effectively as starting materials for many real products, especially for new rare-earth-free magnets with high magnetic moments, by transformation into α″-Fe16N2 NPs and subsequent dispersion and assembly under a magnetic field33–38.

The crystalline properties of the NPs affect their magnetic properties, especially Hc. The different crystalline properties of the cube- and sphere-like NPs result in their different magnetic performances, as shown in Figs 4(c) and 5. The measured Mr and Hc values for the sphere-like NPs (S1 and S2) are both lower than the corresponding fitted values for the cube-like NPs. This may be caused by their composite small crystallite size. A comparison of the hysteresis loops of the two NPs with similar dp (C7 and S2) in Supplementary Fig. S5 shows the difference between the two samples, although their Ms values are similar (79.4 and 79.7 emu/g as listed in Supplementary Table S1). The multiple orientations of the polycrystalline in the sphere-like NPs, which lead to the multiple orientations of their easy axes, is considered to be the reason for their lower Mr and Hc values compared with those of the cube-like NPs. This is consistent with a previous study on the particle-size and shape dependence of Fe3O4 NPs5. However, further theoretical explanation and experimental investigation are still required.

Conclusions
The magnetic properties, including the Ms, Mr, and Hc, of Fe3O4 NPs are highly influenced by the particle size and domain structure. The Ms increases with increasing particle size, regardless of the crystal structure and particle shape. After exceeding the superparamagnetic limit, the Hc and Mr values increase with increasing particle size up to a maximum value of about 190 Oe and 13 emu/g, respectively, at the critical size of 76 nm. Above this critical size, the Hc and Mr values decrease with further increases in the particle size, and the cube-like Fe3O4 NPs change from a single- to multi-domain structure. The multiple orientations of the crystallites within the multi-domain-structured NPs lead to the decrease in the Hc value. These findings suggest that considerable attention should be given to the particle size and crystalline properties of Fe3O4 NPs, which have potential biomedical and industrial applications. These applications require that magnetic particles are sized appropriately to achieve a good balance between effective surface area and satisfactory magnetic performance.

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Contributions of each Author is as follows: Qing Li: Writer of the manuscript and conducted the analyses. Christina W. Kartikowati: Writer of the manuscript and conducted the analyses. Shinji Horie: Synthesis of nanoparticles. Takashi Ogi: Supervision on manuscript writing and analyses. Toru Iwaki: Supervision on manuscript writing and analyses. Kikuo Okuyama: Supervision on manuscript writing and analyses.
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