Fabrication of iron oxide nanoparticles using laser ablation in liquids

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Abstract. Nanoparticles of iron oxides were synthesized through the ablation of the bulk targets of Fe, FeO, and Fe₂O₃ in water by the irradiation of a Nd:YAG laser. Our samples prepared via the laser ablation method displayed small (ca. 1 nm in diameter) and large (over 5 nm in diameter) particles. The small particles were well-dispersed, whereas large particles were agglomerated. The FeO and Fe₂O₃ phases were formed in the synthesized powders irrespective of the kind of targets. The formation of the other phases, Fe and Fe₂O₃, changed depending on the kind of targets used in the laser ablation. Poly(N-vinyl-2-pyrrolidone) (PVP) as a protective reagent was employed to disperse large particles in our samples, and accordingly, their dispersibility was improved as mole concentration of PVP increased.

1. Introduction

Iron oxide is known broadly as a magnetic material such as a permanent magnet. In iron oxide, three kinds of FeO, Fe₂O₃, and Fe₃O₄ exist and each is applied in different fields. Recently, iron oxide nanoparticles have been synthesized by various routes, and their crystal structure and magnetic property have been investigated in detail [1–7]. At present, new applications like hyperthermia and a drug delivery system using iron oxide nanoparticles are also expected, to say nothing of ordinary applications of pigment, contrast medium, and magnetic devices using iron oxide in a bulk state.

In general, chemical and physical routes have been chosen as syntheses of nanoparticles. The main advantage of chemical routes is to yield a large amount of nanoparticles, while that of physical routes is to fabricate nanoparticles with high-crystallinity. Recently, a laser ablation method in physical routes has been focused on, especially since it is easy and eco-friendly and possesses only a few experimental parameters [8–13]. Moreover, this method can provide free-standing nanoparticles, and hence their intrinsic properties can be examined because nanoparticles prepared by chemical methods are usually protected by organic molecules. However, nanoparticles synthesized by the laser ablation method are often agglomerated, and thus there is an unsolved problem with respect to nanomaterials prepared by this method [8–13].

In the present paper, iron oxide nanoparticles are fabricated via the laser ablation method, and their morphology and crystal structure are investigated. Additionally, to disperse the iron oxide nanoparticles prepared using the laser ablation method, we employ organic molecules as a protective reagent and examine their effect on dispersibility and the crystal structure of the nanoparticles.
2. Experimental procedure
To ablate three kinds of targets (Fe, Fe₂O₃, and Fe₃O₄, purity 99.99%, Kojundo Chemical Laboratory Co., Ltd., Saitama, Japan) and synthesize nanoparticles, a Nd:YAG laser (Quantel Brilliant b, Les Ulis, France) with pulse duration of 6 ns, a wavelength of 1064 nm and a repetition rate of 10 Hz was used [14,15]. Figure 1 schematically illustrates the experimental setup. The target was fixed on the bottom of a glass beaker (20 ml), and distilled water as a solvent was added at a level of 10 mm from the target-surface. The beaker was rotated at 40 rpm and target-surface was irradiated for 1 h by the Nd:YAG laser with a laser spot of approximately 250 μm. Then, colloidal nanoparticles were collected.

Crystal structure of nanoparticles was estimated by using X-ray diffraction (XRD, Rigaku SmartLab, 40 kV, 30 mA, CuKa 0.1541 nm, Tokyo, Japan). Morphology and dispersibility of nanoparticles were investigated by transmission electron microscopy (TEM, JEOL JEM-2100F, Tokyo, Japan).

3. Results and discussion
Figures 2(a) and 2(b) show TEM photographs of our sample prepared at laser power of 100 mW for 1 h by using a Fe target. Small particles and large particles co-exist. Figure 2(c) displays a size distribution histogram of small particles seen in Fig. 2(a). The particles exhibit a mean diameter of 1.0 nm and a standard deviation of 0.1 nm. The small particles are highly dispersed, but large particles over 5 nm in diameter are agglomerated. These mono- and highly-dispersed small nanoparticles in the case of the laser ablation method do not appear in the previous literatures on agglomerated iron oxide nanoparticles with 10⁻⁵⁰ nm in diameter [8,10,13]. In Fig. 1(d), an XRD pattern of the sample exhibits Fe, FeO, and Fe₃O₄ peaks. Fe₃O₄ is the main product because this pattern corresponds to bulk-Fe₃O₄ profile. Hence, this sample is a mixture of iron and iron oxide.

Figure 3 provides XRD patterns of our samples synthesized at various laser powers for 1 h by using Fe, Fe₂O₃, and Fe₃O₄ targets. In the case of a Fe target, Fe, FeO, and Fe₃O₄ peaks are detected. Fe₂O₃ peaks are also detected as laser power increases. When a Fe₂O₃ target is used, FeO, Fe₂O₃, and Fe₃O₄ peaks are seen and, FeO and Fe₂O₃ peaks increase as laser power increases. When a Fe₃O₄ target is used, FeO and Fe₃O₄ peaks are detected and FeO is decreased by increasing laser power. However, the Fe₂O₃ peak at 33° is detected as laser power increases like in the case of the Fe target. This probably suggests that FeO is oxidized to Fe₂O₃ because temperature and pressure in the plume seen in Fig. 1 increase as laser power increases. Moreover, the kind of targets may influence initial particles evaporated from these targets. In all targets, FeO and Fe₂O₃ peaks are detected in our samples. S.-Warkocka et al. claimed that Fe₃O₄ nanoparticles were reduced to form FeO phase [12].

Fe₃O₄ is the main product in our samples, and Fe₂O₃ diffractions are seen together with other iron oxide ones similar to those in the case of our samples also in Ref. [9,11,12]. Here, we consider the relationship between temperature and O₂ partial pressure in the iron oxide phase, which is determined by the H₂/H₂O equilibrium in the plume at high temperature. In the light of an Ellingham diagram [16], which represents many oxides in thermodynamic states and determines their O₂ partial pressure, our experimental environment probably keeps the most proper balance between temperature and O₂ partial pressure. When target and laser power are altered, a balance of the O₂ partial pressure in the plume is broken by ablating the target and generating new O atoms, the O₂ partial pressure in the plume changes, and then other iron oxides (FeO or Fe₂O₃) are prepared.
As shown in Figs. 2(a) and 2(b), small particles are dispersed, whereas large particles are agglomerated. Yang explained the evolution of the laser-induced plasma in liquid and reported that four kinds of chemical reactions occurred inside the plasma and liquid, and the interface between the plasma and liquid [17]. Since the first chemical reaction occurs inside the laser-induced plasma, the small initial particles are synthesized as shown in Fig. 2(a). After that, the second chemical reaction also takes place inside the plasma. However, some initial particles escape from the plume and enter the liquid area, where cooling takes place and further grain growth stops. In the second chemical reaction, the other initial particles remaining in the plasma grow into large particles at high temperature. Therefore, small and large particles exist in our samples.

Figure 2. TEM photographs of (a) small and (b) large nanoparticles in our sample prepared at laser power of 100 mW for 1 h using a Fe target. (c) A size distribution histogram of (a). A mean diameter is 1.0 nm and standard deviation is 0.1 nm. (d) An XRD pattern of the sample. The bulk-Fe$_3$O$_4$ profile is taken from ICDD, No. 01-089-2355. The values in the graph represent the index of plane for Fe$_3$O$_4$.

![Figure 2](image1.png)

Figure 3. XRD patterns of samples synthesized at various laser powers for 1 h by using (a) Fe, (b) Fe$_2$O$_3$, and (c) Fe$_3$O$_4$ targets. The bulk-Fe$_3$O$_4$ profile is taken from ICDD, No. 01-089-2355.

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To avoid the formation of large particles, organic molecules were used as a protective reagent. We tried to synthesize iron oxide nanoparticles by using various organic molecules such as several kinds of amino acids and sodium dodecyl sulfate, and consequently, it was found that poly(N-vinyl-2-pyrrolidone) (PVP, an average molecular weight of 55,000, Sigma-Aldrich), which was very useful in chemical syntheses of metallic alloy nanoparticles [18–20], was the best protective reagent in our experiments. Herein, we prepare iron oxide nanoparticles via the laser ablation in water containing PVP by using a Fe$_3$O$_4$ target. Figure 4 presents TEM photographs of samples prepared at laser power of 50 mW for 1 h under various mole concentrations of PVP. As PVP concentration increases, large particles are dispersed. Small particles around 1.0 nm in diameter show high-dispersibility as seen in Fig. 2(a) irrespective of PVP concentration (not shown).

**Figure 4.** TEM photographs of large particles in samples prepared at laser power of 50 mW for 1 h under various mole concentrations of PVP by using a Fe$_3$O$_4$ target. (a) without PVP and (b) 0.01, (c) 5, (d) 20, and (e) 50 mM of PVP.

Figure 5 exhibits XRD patterns of samples fabricated at laser power of 50 mW for 1 h and various mole concentrations of PVP by using a Fe$_3$O$_4$ target. When PVP concentration increases, these diffractions are broad, and hence, crystalline sizes of samples coated by PVP become small. This result has been reported in the previous literature with respect to PVP-coated FePt nanoparticles prepared by chemical routes [20]. By increasing the amount of PVP, the growth of nanoparticles may be retarded due to coating them with a large amount of PVP. PVP as a protective reagent affects dispersibility and crystalline size of nanoparticles irrespective of the kind of syntheses (chemical or physical methods).

**Figure 5.** XRD patterns of samples prepared at laser power of 50 mW for 1 h under various concentrations of PVP by using a Fe$_3$O$_4$ target. The bulk-Fe$_3$O$_4$ profile is taken from ICDD, No. 01-089-2355.
4. Conclusion
In conclusion, the present paper provided some new information. Our samples prepared via the laser ablation method showed small (ca. 1 nm in diameter) and large (over 5 nm in diameter) particles. Targets used in the laser ablation affected crystal structure of our samples. Irrespective of targets, FeO and Fe₃O₄ peaks were detected. When PVP was used as a protective reagent to disperse large particles, their dispersibility was improved as mole concentration of PVP increased. By adding PVP, crystalline sizes became small.

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