Iron-based Nanoparticles and Their Mössbauer Spectra

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This review describes the synthesis of iron-based nanoparticles. Iron oxyhydroxide, iron oxide, iron carbide, and iron sulfide nanoparticles have been produced using various methods. Feroxyhyte δ-FeOOH nanoparticles were produced by the oxidation of precipitates obtained by hydrazine reduction of iron chloride. Similar nanocomposites doped with foreign atoms (Ag, Cu, or Zn) have been produced as well. Iron oxide (γ-Fe₂O₃) nanoparticles have been produced by a polyol method. When a sulfide source was added into the solution during synthesis, iron sulfide nanoparticles were obtained. Using this technique, a metastable trivalent iron sulfide (Fe₂S₃) was successfully synthesized. Amorphous iron/carbon particles were obtained by the sonochemical synthesis of ferrocene in diphenylmethane. Subsequent heating of the amorphous particles produced Fe₃C, α-Fe, and γ-Fe nanoparticles. Laser ablation of iron metal in an organic solvent produced iron carbide nanoparticles. The reaction mechanism and the structures of the nanoparticles were studied using Mössbauer spectroscopy as well as X-ray diffraction and transmission electron microscopy.

Key Words: iron-based nanoparticles, Mössbauer spectroscopy, polyol methods, sonochemistry, laser ablation in liquid

1. Introduction

Various nanoparticles have been studied extensively in the last several decades. Among these, iron-based nanoparticles are very important and have attracted great attention because of their applicability to magnetic materials and catalysis. Magnetic nanoparticles have been utilized in medical and industrial applications such as drug delivery, heating through magnetism, magnetic resonance imaging, magnetic and electronic devices, magnetic shields, and sensors.1–3) Superparamagnetic behavior, which is strongly dependent on the size of the materials, is one of the most important characteristics of magnetic nanoparticles: nanoparticles behave as paramagnetic materials in the absence of an external magnetic field, but they behave as magnetic materials when an external magnetic field is applied. Their large surface-area-to-volume ratio enhances surface reactions, which is favorable for catalytic applications. The surface energy of nanoparticles plays an important role in their stability, and can help to stabilize metastable chemical compositions or metastable lattice structures unobtainable in bulk solids. The polymorphous transformation of iron oxides depending on the nanoparticle size is an interesting subject.5, 6) The iron-based nanomaterials used most widely for applications are iron oxides.7) Generally, iron nanoparticles oxidize very easily in the ambient atmosphere, and cannot be stabilized without a surface protective agent. Exploring magnetic materials other than iron oxide is an important field of study in itself. For example, iron carbide (Fe₃C) nanoparticles show a higher saturation magnetization than Fe₃O₄.8, 9) In addition, iron compound nanoparticles doped with foreign atoms are intriguing because...
they are known to exhibit unique magnetic and optical properties. A variety of methods have been employed to synthesize nanoparticles; e.g. the hydrazine reduction method, polyol method, sonochemical method, and laser ablation in a liquid. Our recent results, mainly based on Mössbauer spectroscopy, will be presented in the following sections.

2. Iron oxide nanoparticles and their composites with foreign atoms

2.1 Feroxyhyte nanoparticles

Feroxyhyte (δ-FeOOH), a very intriguing species of the iron oxide family, is the only ferric oxyhydroxide that exhibits significant magnetization at room temperature. Generally, feroxyhyte is not as abundant as other iron oxides/oxyhydroxides in nature, and hard to synthesize because of its instability. Feroxyhyte nanoparticles were found to be a promising photocatalyst for hydrogen production, and the enhancement of the Fenton-like photocatalytic response of feroxyhyte nanoflake/carbon nanodot nanohybrids was reported. Polyakov et al. synthesized anisotropic feroxyhyte nanoparticles in the presence of humic substances.

Recently, we synthesized extremely small spherical feroxyhyte nanoparticles stabilized with gela-

Fig. 1 (a) X-ray diffraction pattern, (b) TEM image, (c) histogram of diameters and (d) HR-TEM image of the feroxyhyte nanoparticles.
Iron chloride FeCl$_2$·H$_2$O, sodium tartrate, and gelatin were dissolved in water; then, the pH of this solution was adjusted by the addition of NaOH. An aqueous hydrazine solution was added, and the resulting black precipitate was collected by filtration. The precipitate surface became reddish brown upon rinsing with water and ethanol under the ambient atmosphere. This simple method successfully yielded feroxyhyte nanoparticles. The X-ray diffraction (XRD) pattern for the sample (Fig. 1a) exhibits broad characteristic feroxyhyte peaks, which indicates the presence of small particles. Transmission electron microscopy (TEM) images of feroxyhyte samples indicated the presence of spherical nanoparticles less than 10 nm in diameter (Fig. 1b, c), exhibiting lattice fringes attributed to the d-planes (Fig. 1d).

Mössbauer spectra of the feroxyhyte nanoparticles were acquired at 293 and 9 K (Fig. 2). The spectrum acquired at 293 K was fitted using a combination of a doublet, a relaxation component, and a sextet. As bulk feroxyhyte is ferromagnetic, the doublet could result from the superparamagnetic behavior of small nanoparticles. The Mössbauer spectrum of the same sample taken at 9 K shows two sets of sextets, while the doublet is absent because the specimen no longer exhibits superparamagnetism at such low temperatures. The spectral component having a smaller hyperfine magnetic field corresponds to the surface atoms of the particles, and the spectral component with the larger hyperfine magnetic field corresponds to the core Fe atoms of the particles. A superconducting quantum interference device (SQUID) was used to measure the magnetic hysteresis loops, and showed the superparamagnetic behavior of the feroxyhyte nanoparticles.

The precursor of feroxyhyte, a black precipitate before oxidation, was characterized in order to elucidate the reaction mechanism. The XRD pattern for...
the precursor exhibited characteristic peaks of ferroxyhyte and magnetite (Fe₃O₄), and the Mössbauer spectrum of a frozen sample of the precursor materials was assigned to iron(II) hydroxide (Fe(OH)₂), ferroxyhyte and magnetite. These species then rapidly oxidized into ferroxyhyte (Fig. 3). It became possible to synthesize ferroxyhyte containing foreign atoms if an adequate intermediate species containing foreign atoms could be produced. The valence of foreign metal atoms controls the oxidation reaction of iron precursors.

2.2 Silver/iron oxide composited nanoparticles

Iron oxide doped with foreign metal atoms is of interest because it is known to enhance the magnetic properties and stability. In particular, silver/iron oxide nanoparticles have been used extensively, owing to their enhanced chemical reactivity, which results from the interactions between the two components. Liu et al. reported the antibacterial properties of Ag–Fe₃O₄ nanocomposites. In comparison with individual silver nanoparticles, the aggregation of silver nanoparticles with magnetite appears unlikely to cause a significant decrease in antibacterial activity. The enhanced magnetic properties of the Ag–Fe₃O₄ nanocomposite as compared to Fe₃O₄ have been reported by Lopes et al.

Although several studies have reported silver/iron

![Figure 4](image_url)

Fig. 4 TEM images and particles size distributions of silver/iron oxide composite nanoparticles prepared with Ag/Fe molar ratios of (a, b) 1/9 and (c, d) 2/8.
oxide nanoparticles to have the magnetite structure on the basis of XRD measurements, this could not be confirmed because magnetite and other iron oxides such as maghemite have very similar diffraction patterns. Thus, it is necessary to conduct detailed Mössbauer spectroscopy measurements. A mixture of silver and iron oxide nanoparticles was synthesized by the reaction of FeSO₄, AgNO₃, and N₂H₄ in the presence of gelatin at room temperature under an ambient atmosphere. TEM observations revealed two distinct sizes of nanoparticles (Fig. 4). Small nanoparticles with diameters of less than 10 nm were assigned to maghemite, while large particles with diameters of approximately 20 nm were assigned to metallic silver. A Mössbauer spectrum of the maghemite (γ-Fe₂O₃) nanoparticles at 293 K (Fig. 5a) indicated superparamagnetic behavior due to the small particle sizes, whereas the Mössbauer spectrum measured at 3 K (Fig. 5b) indicated a magnetic sextet and a distributed hyperfine magnetic field (DHMF) component that corresponded to the surface or defects of the maghemite nanoparticles. Smaller maghemite nanoparticles with improved crystallinity were obtained by synthesis from a starting mixture with a larger Ag/Fe ratio; Ag atoms in the Ag–Fe₂O₃ precursor in solution induced mild oxidation to produce the maghemite nanoparticles. The silver and maghemite nanoparticles were obtained separately. Silver enhanced the production of maghemite nanoparticles, and the size of the maghemite particles could be controlled by varying the amount of silver salt.

2.3 Copper ferrite nanoparticles

Spinel ferrites have remarkable magnetic, catalytic, optical, and electrical properties. In particular, copper ferrite (CuFe₂O₄) nanoparticles have potential for applications in a wide variety of fields, including catalysis, cell labeling, gas sensing, and electrochemistry. Goya et al. synthesized copper ferrite nanoparticles by ball milling and measured their Mössbauer spectra. Copper ferrite nanoparticles show superparamagnetic behavior as a result of their small size. Subramanian et al. reported the high-temperature water–gas shift reaction catalyst of copper ferrite-mesoporous alumina nanocomposites. We synthesized copper ferrite nanoparticles via
the oxidation of precipitates obtained from the reaction of FeCl₂, CuSO₄, and N₂H₄ in the presence of gelatin. The average size of the copper ferrite nanoparticles was less than 5 nm, and they exhibited superparamagnetic behavior as a result of their small size. The XRD patterns for the copper ferrite samples (Fig. 6) exhibited metallic copper and copper ferrite peaks. When the proportion of copper salt in the starting materials was increased, the copper ferrite peaks broadened and the intensities of the metallic copper peaks increased. This indicated that the reduction of the copper ferrite crystallite size was dependent on the amount of copper salt. The low-temperature Mössbauer spectrum exhibited three sets of sextets, two of which corresponding to the tetrahedral and octahedral sites of the copper spinel structure and a third sextet, with a small hyperfine magnetic field, corresponding to the surface or defects of the nanoparticles (Fig. 7). When the proportion of copper salt was increased, the tetrahedral site became the preferred site for copper, and metallic copper and copper ferrite were both present in each nanoparticle.

2-4 Zinc–iron oxide nanoparticles

The magnetic structure of zinc–doped iron oxides can be controlled by varying the amount of zinc doping: the magnetization and hyperfine magnetic field intensity decrease with increasing zinc doping. However, when iron oxide is doped with a very small amount of Zn, the magnetization increases relative to that for non-doped iron oxide nanoparticles.

We synthesized zinc–iron oxide nanoparticles (ZnxFe3–xO₄ and δ-ZnxFe1–xOOH) through the chemical reaction of a solution containing ZnCl₂ and FeCl₂ in the presence of gelatin. The composition of the reaction products could be controlled by varying the Zn/Fe ratio of the starting material. The XRD patterns for these products (Fig. 8) indicated that a solution with high Zn/Fe ratio yielded zinc ferrite (ZnxFe3–xO₄) nanoparticles, whereas a solution with high Fe/Cl ratio yielded iron oxide (δ-ZnxFe1–xOOH) nanoparticles.
a low Zn/Fe ratio yielded zinc-doped feroxyhyte δ-Zn$_{x}$Fe$_{1-x}$OOH nanoparticles. The zinc ferrite nanoparticles were spherical, with diameters of approximately 10 nm, and the zinc-doped feroxyhyte particles were needle-like with lengths of approximately 100 nm. Mössbauer spectra measured at room temperature revealed the superparamagnetic behavior of the nanoparticles, while magnetic components were observed at low temperature (Fig. 9). The Zn content of the intermediate species (Zn$^{II}_{x}$Fe$^{II}_{1-x}$Fe$^{III}_{2}$O$_{4}$) before oxidation affects the final products. When the Zn concentration was high, further oxidation of
the nanoparticles was hindered, as the $\text{Fe}^{2+}$ content of the intermediate species was small. When the starting material had a low Zn concentration, the intermediate species were rapidly oxidized into $\delta$-$\text{Zn}_{x}\text{Fe}_{1-x}\text{OOH}$ during rinsing under ambient conditions, as the amount of $\text{Fe}^{2+}$ in the intermediate species became large.

3. Polyol method to produce iron oxides and iron carbides

The polyol method is applicable to producing metallic particles having a uniform size. Polyol acts as a reducing agent and simultaneously prevents particle aggregation, which controls growth. Iron oxide ($\text{Fe}_3\text{O}_4$) particles were produced by the decomposition of $\text{Fe}($acac$)_3$ in benzyl ether and oleylamine (OA), and monocrystalline $\gamma$-$\text{Fe}_2\text{O}_3$ tetrapods were synthesized from $\text{Fe}($CO$)_5$ in solution with OA. In those methods, OA was employed as a surfactant or stabilizer to protect the surfaces of the nanoparticles, but $\text{Fe}^0$ was not stabilized and iron oxides were eventually produced. Generally, it is hard to obtain metallic Fe particles by reducing Fe cations with polyol, because small Fe particles are easily oxidized to iron oxide particles. However, a few studies have successively produced $\text{Fe}^0$ compounds: FePt alloy particles, and metallic Fe particles were obtained by using NaOH.

Our group produced iron oxide ($\gamma$-$\text{Fe}_2\text{O}_3$), iron carbide ($\text{Fe}_3\text{C}$), and iron metal ($\alpha$-$\text{Fe}$) particles by using the polyol method, and the yields were controlled by varying the proportions of the compounds. Since ferrocene ($\text{Fe}($C$_5$H$_5$)$_2$) employed as an iron source does not contain any oxygen, it was expected that oxidization would be restricted. A mixture of ferrocene and 1,2-hexadecanediol was dissolved in solvents consisting of various ratios of oleylamine (OA) and 1-octadecene (OD). The solutions were stirred and refluxed at 300°C under flowing Ar, and the product particles were separated after cooling to

Fig. 10 TEM images, Mössbauer spectra, and XRD patterns of nanoparticles produced by the polyol method. Mössbauer spectra were measured at 6K. Mixture ratios of the solvents were OA/OD = (S1) 30/0 mL, (S2) 10/20 mL, and (S3) 3/27 mL. The labels M, C, and A in the XRD patterns correspond to $\gamma$-$\text{Fe}_2\text{O}_3$, $\text{Fe}_3\text{C}$, and $\alpha$-$\text{Fe}$, respectively.
Iron-based Nanoparticles and Their Mössbauer Spectra

Y. Yamada and N. Nishida

room temperature and washed with organic solvents. Then, the particles were centrifuged and dried in an Ar flow. Fig. 10 shows the TEM images, Mössbauer spectra at 6 K, and XRD patterns for three particle samples, viz., S1, S2, and S3, prepared with OA/OD volume ratios of 30/0, 10/20, and 3/27 (mL/mL). The XRD pattern and Mössbauer spectra of the samples showed that a high OA concentration (S1) yielded $\gamma$-$\text{Fe}_2\text{O}_3$ particles with 12–16 nm diameters, and a low OA concentration (S3) yielded particles consisting of Fe$_3$C and $\alpha$-Fe with various sizes. $\gamma$-$\text{Fe}_2\text{O}_3$ particles (S1) showed superparamagnetic peaks in Mössbauer spectra at room temperature, which agreed with the results shown in literatures. The decomposition of ferrocene in 1,2-hexadecanediol produced Fe$^0$ precursors. OA acted as a capping reagent, hindering nucleation and leading to form particles with uniform size. At low OA concentration, OD acted as a carbon source, Fe$_3$C nuclei formed as a precursor, and $\alpha$-Fe was obtained as well. OD is a non-coordinating solvent that acted as a carbon source for iron carbide precursors and also prevented oxidation of the $\alpha$-Fe particles.

In general, two processes, nucleation and particle growth, are important in the particle formation mechanism. The capping reagent OA hinders agglomeration, and at the same time, it coordinates with monomers and precursors, suppressing nucleation. Therefore, the presence of excess OA reduces the nucleation rate and leads to smaller nuclei and subsequently to larger particle sizes during the aggregation process. In this case, excess OA produced larger particles, but small Fe$^0$ precursors were oxidized, reacting with H$_2$O to form iron hydrates during aggregation. This resulted in the production of iron oxide particles. In contrast, OD is a non-coordinating solvent that acts as a carbon source for iron carbide precursors and prevents oxidation of the $\alpha$-Fe particles.

4. Iron sulfide produced by the polyol method

The structures and properties of commercially available iron sulfides, i.e., FeS, Fe$_3$S$_4$, and Fe$_2$S$_3$, have been investigated in detail. In contrast, there have been very few reports concerning trivalent iron sulfide (Fe$_2$S$_3$); thus, the structure of this compound remains poorly understood. Besides the interest in finding a novel species, the importance of Fe$_2$S$_3$ as a catalyst for coal liquefaction has been reported. The synthesis of Fe$_2$S$_3$ and its X-ray diffraction (XRD) pattern and Mössbauer spectrum were reported by Boehm. Yamaguchi also published an XRD pattern for Fe$_2$S$_3$ nanoparticles that was similar to that for $\gamma$-$\text{Al}_2\text{O}_3$. The sulfur K-edge X-ray absorption spectrum of Fe$_2$S$_3$ has been reported by Sugiyama, elucidating the bonding nature of the S$^{2-}$ ions. Mössbauer spectra for Fe$_2$S$_3$ were reported by Stiller, showing a paramagnetic doublet at 78 K and magnetic splitting at 4.2 K. The XRD pattern for the sample was not published because the sample was found to be amorphous. A metastable hexagonal Fe$_2$S$_3$ phase has been discovered, but only within the crystal structure of pyrrhotite. Lyubutin fabricated nanoparticles consisting of a mixture of Fe$_2$S$_4$ and Fe$_2$S$_3$. Despite these prior studies, the Mössbauer spectrum and XRD pattern of Fe$_2$S$_3$ having a well-defined lattice structure have not been reported.

Our group produced iron sulfide nanoparticles by adding the sulfur source into the solution, which enabled the production of novel iron sulfide particles using the polyol method. A mixture of ferrocene, 1,2-hexadecanediol (HD), and 1-octadecanethiol (OT) in oleylamine (OA) was refluxed, where OT acted as a sulfur source. The nanoparticles obtained were a mixture of FeS, Fe$_3$S$_4$, and Fe$_2$S$_3$, and the yields changed depending on the HD/OT ratio. The iron sulfide particles were found to contain amorphous Fe$_2$S$_3$ and FeS phases as impurities. Thus, we modified the synthesis conditions.
by adding hexadecane as a surface protective agent and succeeded in obtaining pure Fe₂S₃ particles. The surface protective agent hexadecane inhibited the transformation of metastable Fe₂S₃ into stable Fe₁₋ₓS. In this method, an Fe⁰ precursor generated in the solution subsequently yielded an iron sulfide, owing to the presence of a sulfate source. The product was a stable divalent iron sulfide species (Fe¹₋ₓS) without sufficient protective reagent. By contrast, overprotection of the surface of the Fe⁰ precursor gives only α-Fe particles. It was crucial to select the appropriate concentrations of the sulfur source and

![TEM images of an Fe₂S₃ nanoparticle.](image11)

![XRD patterns of nanoparticles: (a) the Fe₂S₃ sample, (b) calculated XRD pattern obtained using the program RIETAN.](image12)
the surface protective reagent.

Typical TEM images of Fe$_2$S$_3$ are presented in Fig. 11, demonstrating the needle-shaped particles (diameter = 10–50 nm, length = 350–1000 nm). The d-spacing was found to be 0.31 nm in the high-resolution TEM image of the needle-like Fe$_2$S$_3$ particles. EDS was employed to estimate the stoichiometry of the needle-shaped particles and the Fe/S ratio was found to be 2/2.9, as expected for Fe$_2$S$_3$. It was found that Fe$_2$S$_3$ particles were stable for about three months when kept in an Ar atmosphere below 0°C. The XRD pattern for the Fe$_2$S$_3$ particles is shown in Fig. 12. XRD patterns for Fe$_2$S$_3$ have been previously reported, but the XRD pattern obtained in the present study was different. Thus, we performed calculations to estimate the Fe$_2$S$_3$ structure needed to fit our experimental XRD pattern using the software RIETAN.$^{51}$ A structure of spinel maghemite ($\gamma$-Fe$_2$O$_3$) with a larger $a$ value of 10.6 Å was employed. The XRD pattern calculated by using RIETAN coincided fairly well with the observed pattern in Fig. 12, although the calculated (400) peak at $2\theta=33.4^\circ$ was less intense in the actual XRD pattern because of the anisotropy of the needle-like particles.
is, the (400) face disappeared as the crystal grew in the longitudinal direction. Furthermore, the peak at $2\theta = 28.8^\circ$ corresponding to the (222) surface along the side of the particles, had a $d$ value of 0.31 nm, in agreement with the high-resolution TEM image.

Mössbauer spectra of Fe$_2$S$_3$ samples were acquired at 298, 50 and 6 K (Fig. 13). The spectra obtained from this material at 298 and 50 K contained a paramagnetic doublet, while that acquired at 6 K consisted of magnetic components showing a DHMF $H$ with an average $H_{av}$ of 221 kOe, and a Curie temperature of approximately 60 K. Assuming that the structure described above was correct (Fig. 14), density functional calculations were performed to estimate the hyperfine magnetic fields of the Fe atoms in Fe$_2$S$_3$ using the program WIEN2k. The $H$ values of Fe atoms in Oh and Td positions were determined to be 237 and 216 kOe, respectively. This result is in fairly good agreement with the Mössbauer spectrum of Fe$_2$S$_3$ at 6 K.

5. Sonochemical preparation of iron carbides

Sonochemical synthesis is not as widely used as chemical reduction methods, however, it is a useful method for producing nanoparticles in a solution. Irradiation of a solvent by ultrasound produces cavitation bubbles, which in turn generate high temperatures and pressures. The cavitation decomposes the reagents in solution, and the resulting fragments then cool down rapidly to produce nanomaterials. This method has been employed to produce pure noble metal nanoparticles. Sonochemical synthesis of iron oxide nanoparticles such as magnetite, hematite, and maghemite have been reported. Sonolysis of iron ions in an organic solvent tends to produce an amorphous mixture consisting of Fe and C atoms. Thus, heat treatment of the amorphous Fe/C is required for the production of iron carbide nanoparticles. A mixture of iron pentacarbonyl (Fe(CO)$_5$) and diphenylmethane has been sonicated, and the precipitates were heated to produce a mixture of Fe metal, Fe$_3$C, and Fe$_2$O$_3$. Iron is very reactive with oxygen, and the production of iron nanoparticles is always accompanied by the formation of iron oxides. The instruments employed during the experiments were equipped with an ultrasound Ti-horn, as illustrated in Fig. 15. Amorphous iron carbide has been produced by the ultrasonication of ferrocene (Fe(C$_5$H$_5$)$_2$) in diphenylmethane. We employed oxygen-free reagents, and all handling...
was conducted under an Ar flow using an infrared image furnace to prevent the oxidation of iron. The products were amorphous Fe/C, as seen in Fig. 16 (S1); the TEM image did not show clear particles, while the XRD pattern indicated only Ti particles. The Mössbauer spectrum of amorphous Fe/C (S1) showed a paramagnetic doublet. The Mössbauer spectrum of amorphous Fe/C was also measured at 6 K and revealed the same paramagnetic double. Heating of the amorphous Fe/C below 600 °C for 2 h did not change the composition, and almost the same Mössbauer spectrum was obtained as for the as-prepared amorphous Fe/C. Heating of the amorphous product at 900 °C for 2 h produced a mixture of Fe₃C and α-Fe, while heating at 1200 °C for 2 h produced a mixture of α-Fe and γ-Fe. Metastable γ-Fe, which occurred only at high temperature, was stabilized by interstitial carbon atoms. The particle sizes obtained at 900 °C and 1200 °C were both ~50 nm. In the TEM images of S2 and S3, carbon nanotubes (CNTs) were observed in addition to particles. These CNTs were not straight, but bent and tangled. The reaction was accompanied by the formation of CNTs catalyzed by the Fe nanoparticles. The samples were dispersed in an aqueous solution of sodium dodecyl sulfate, the UV-vis spectrum was measured, and the plasmon resonance associated with CNTs was observed to confirm the production of CNTs. The most common synthesis method of CNTs is thermal chemical vapor deposition (CVD), and sonochemical synthesis of CNTs using organic material was also reported. Here, we demonstrated that CNTs can be synthesized by a solid-phase reaction of amorphous Fe/C.

6. Laser ablation in organic solvents to produce iron carbides

Another method for producing iron-based nanoparticles is laser ablation in liquid media (LAL), which does not necessitate complicated chemical procedures or a large apparatus. Laser ablation of a metal block target held in a solvent generates
plasma vapor, and the vaporized metal atoms react with the surrounding solvent molecules, condensing rapidly to produce particles. Metastable particles are produced by the rapid quenching of highly excited states, and the metastable phase may stabilize as a result of the large surface effects of the nanoparticles. Laser ablation of coinage-metal, particularly gold, have been extensively investigated.

The simplest setup to perform laser ablation (LA) on a solid in a solvent involves a standard beaker and introduction of laser light from the solvent surface (Fig. 17, left). Using this method, we have produced CuO particles in water, and Liu et al. have produced FeO nanoparticles. However, this simple method has several disadvantages: bubbles produced by the decomposition or vaporization of the solvent perturb the solvent surface, which affects the focal point of the laser beam. Another disadvantage is the effect of the atmosphere, which causes the nanoparticles to oxidize. Iron carbide nanoparticles produced through laser ablation of an iron target in an organic solvent have been reported; however, the particles were oxidized by the oxygen dissolved in the solvent. Therefore, we employed an airtight vessel (Fig. 17, middle) and degassed the solvent to produce iron carbide nanoparticles. A convex lens was attached to the side of the vessel in order to prevent the formation of surface waves. Nanoparticles consisting of \( \alpha \)-Fe, \( \gamma \)-Fe, iron carbide, and amorphous iron carbide, with no trace of iron oxides, were successfully produced by laser ablation in organic solvents (pentane, hexane, or decane).

Laser ablation in liquid is typically performed in a stagnant solvent as discussed above. However, if the particles remain suspended in the solvent after production, they can deteriorate because of the effects of prolonged laser irradiation (LI). It has been reported that laser fragmentation and laser melting occur during the LI of colloidal solution. In order to elucidate the formation mechanism, we carried out laser ablation of iron metal in liquids using a cell with a circulating solvent to obtain particles produced solely by LA; the resulting nanoparticles were separated from the solvent with a filter, reducing the effects of LI in the solvent (Fig. 17, right). The TEM images, Mössbauer spectra, and XRD patterns of the LA and LI particles are shown in Fig. 18. TEM revealed that the LA particles generated in flowing ethanol were spherical, had an average diameter of 16 nm, and were coated with graphite. The XRD patterns for the LA particles exhibited weak peaks corresponding to cementite \( \text{Fe}_3\text{C} \), and the particles...
were too small to show clear XRD peaks. The Mössbauer spectrum of the LA particles was measured at room temperature and fitted using a combination of a doublet, two sextets, and a DHMF component. These particles were composed of both pure Fe₃C and metastable Fe₄C. Fe₄C has a structure in which carbon atoms are situated in an fcc γ-Fe structure. Following analysis of the LA particles, they were re-dispersed in ethanol and irradiated with a laser to obtain LI particles. The LI particles consisted of stable Fe₃C nanoparticles with a larger average diameter of 38 nm. LI was found to induce particle aggregation through melting and to cause metastable Fe₄C to undergo a reaction, forming stable Fe₃C. The results of this study demonstrate that it is important to suppress the effects of LI in order to obtain metastable species by LA. It was demonstrated that LI of the particles facilitates the aggregation or chemical reaction of the LA particles. Therefore, it is important to avoid the effects of LI in order to obtain metastable species.

7. Summary

This review described the synthesis of iron-based nanoparticles. Nanoparticles are of interest because they are uniquely capable of being stabilized in unstable lattice structure. Feroxyhyte nanoparticles were stabilized by gelatin and synthesized through a modified hydrazine reduction system under ambient pressure at room temperature. The composite nanoparticles doped with foreign atoms were synthesized using a similar reduction method. It was found that the composition and structure varied with the ratio of metal atoms in the starting materials. Silver enhanced the production of maghemite nanoparticles, and the size of the maghemite particles could be controlled by varying the amount of silver salt. When the starting material was mixed with Cu²⁺, copper ferrite was obtained because the Fe²⁺ in magnetite was substituted by Cu²⁺. The Zn²⁺ concentration in the starting material affects the products: zinc-doped feroxyhyte nanoparticles.
were obtained from a mixture with a large Zn/Fe ratio, while zinc ferrite nanoparticles were obtained from a mixture with a small Zn/Fe ratio. Maghemite and cementite nanoparticles were produced by the polyol method. When a sulfur source was added into the solution, iron sulfide nanoparticles were obtained. The uncommon trivalent iron sulfide, Fe$_2$S$_3$, was successfully obtained by this method, and the structure was determined. Sonolysis of ferrocene in an organic solvent produced amorphous Fe/C, and subsequent heating of the amorphous Fe/C produced $\alpha$-Fe, $\gamma$-Fe, Fe$_3$C, and CNC, depending on the heating temperature. Laser ablation in liquid was conducted to produce iron carbides. We employed Mössbauer spectroscopy to directly determine the magnetic and electronic properties of the Fe atoms in the nanoparticles. Mössbauer spectroscopy can be used for mixtures and composite samples, as well as amorphous species.

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要 旨

鉄化合物ナノ粒子とそのメスバウアースペクトル
山田康洋
西田直樹
山田直樹
ナノ粒子の合成とその性質を検討した。その結果、ナノ粒子の性質は合成条件や用途により大きく異なり、様々な用途に応用されることが示唆された。