Synthesis and kinetic shape and size evolution of magnetite nanoparticles

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Abstract

Eleven nanometers of magnetite nanoparticles were synthesized by using 6 nm magnetite nanoparticles as seeds and Fe(acac)3 as precursor at high temperature. Growth kinetics of magnetite nanoparticles was studied during the progress of reaction. Magnetite nanoparticles with different shapes including near-sphere, tetrahedral, truncated tetrahedral and cubic were observed at different reaction time. Transmission electron microscopic results show that the shape and size distributions are time- and temperature-dependent. Hydrodynamic diameter results give the kinetic size distribution changes of magnetite nanoparticles during the reaction, which suggest that this synthesis underwent a “growth-controlled nucleation”.

1. Introduction

Magnetic nanoparticles (MNPs) have been of great interests because of their extensive applications in high-density data storage, biochemistry, hyperthermia, in vivo drug delivery, and MR contrast reagent [1–7]. Their magnetic properties are size- and shape-dependent, and therefore, the synthesis of well-controlled shapes and size of MNPs is important for their applications. However, MNPs prepared by conventional chemical co-precipitation synthesis [8] display a rather broad particle size distribution. Size- and shape-control of MNPs is surely an experimental challenge [9].

Recently, shape-control studies are actively being pursued on the semiconductor and metal nanocrystals [10–12], but little work exists for MNPs system despite their unique nanomagnetism and important technological applications. For example, iron oxide nanopyrramids via a polymer assisted synthetic approach [13] has been reported, their structural characterizations were not clearly elucidated. Shape-controlled cobalt ferrite nanoparticles were obtained through controlling nanocrystals growth rate [14]. Cheon et al. reported the shape revolution of iron oxide nanocrystals by changing the capping reagents and delay the reaction time [15]. However, there is still no detailed report about the shape and size formation mechanism of the magnetite nanoparticles.

In this work, we report the kinetic shape and size evolution of magnetite (Fe₃O₄) nanoparticles utilizing the seed-mediated high-temperature thermal decomposition of iron(III) acetylacetonate (Fe(acac)₃) precursor method. Fe₃O₄ nanoparticles with 6 nm were used as seeds to grow larger nanoparticles. During the reaction process, the shape of the
nanoparticles transform from near-sphere, cubic, tetrahedral to truncated tetrahedral (TT) morphology. Fe₃O₄ nanoparticles with mean diameter of 11 nm were obtained after the anneal treatment. The shape formation mechanism and nucleation mode of Fe₃O₄ nanoparticles are also discussed in this study.

2. Experimental

2.1. Preparation of 6 nm seeds and 11 nm magnetite nanoparticles

Fe₃O₄ nanoparticles were prepared according to the Sun’s method [16]. The strategy is using Fe(acac)₃ thermal decomposed in the high-temperature organic solution containing the reducing reagent and surfactants to synthesis magnetite with a mean diameter of 6 nm. Subsequently, further size-selection was applied to get the monodispersed Fe₃O₄ nanoparticles. Such 6 nm nanoparticles then were served as seeds to grow larger nanoparticles in the seed-mediated growth process.

In a typical synthesis, Fe(acac)₃ (2 mmol), 1,2-hexadecanediol (10 mmol), benzyl ether (20 ml), oleic acid (2 mmol), and oleylamine (2 mmol) were mixed and magnetically stirred under a flow of nitrogen. Forty-two milligrams of 6 nm Fe₃O₄ seeds nanoparticles dispersed in hexane (4 ml) was added. The mixture was first heated upto 80 °C for 30 min to remove hexane, then upto 200 °C for 1 h. Under a blanket of nitrogen, the mixture temperature was raised upto 300 °C at a rate of 10 °C/min and kept at reflux at 300 °C for 30 min before being cooled down to room temperature. During the growth process (200–300 °C), aliquots (each withdrawn every 15 min) were taken to investigate the crystal shape and size of the nanoparticles. Each sample was cooled to room temperature and quenched from the reaction with excess of ethanol and washed with magnet separate method several times to remove surfactant residue completely, and dispersed into hexane without size-selection process.

2.2. Nanoparticle characterization

Transmission electron microscopic (TEM) analysis and high-resolution transmission electron microscopy (HRTEM) were performed with a Hitachi 600 microscope operating at 80 kV and a JEOL electron microscope operating at 200 kV, respectively. Samples were prepared by drying a drop of the dilute solutions of nanoparticles onto 300-mesh carbon-coated copper grids and allowed to dry completely at room temperature. Nanoparticles shape and size distributions were obtained by measuring each of the TEM image in which had more than 300 nanoparticles.

Hydrodynamic diameter of magnetite nanoparticles were measured with a high-performance particle sizer (HPPS, Malvern Instrument, λ = 632.8 nm, T = 25 °C). The concentration of each sample was 3 mg Fe₃O₄/ml hexane.

X-ray diffraction (XRD) were recorded on a Rigaku Dmax-r C X-ray diffractometer using Cu Kα ration (λ = 1.540 Å) operated at 40 KV and 100 mA.

3. Results and discussion

3.1. Kinetic mechanism for shape formation

Fig. 1 shows six TEM images of Fe₃O₄ nanoparticles taken from different reaction time (0 (seeds), 15, 30, 45, 60, 90 min) during the synthesis. Fig. 2 gives the size and shape distributions of Fe₃O₄ nanoparticles according to the TEM images in Fig. 1A–E. There was no near-sphere nanoparticles in the seeds solution (these particles were observed as highly faceted shape by enlarging the image (Fig. 1A)), but as the reaction processing, near-sphere nanoparticles began presenting in the initial reaction stage (15 min after the seed-mediated growth reaction, 200 °C), as shown in Figs. 1B and 2B. Near-sphere, cubic, tetrahedral, TT nanoparticles presented together in the next reaction stages (30 min and 45 min after the seed-mediated growth reaction, 200 °C) in Figs. 1C, D and 2C, D. Few of the sphere and cubic nanoparticles appeared at the end of the reaction stages (60 min after the seed-mediated growth reaction, 200 °C, Figs. 1E and 2E, and 30 min after the thermal anneal treatment, 300 °C, Figs. 1F and 2F).

Fig. 3 shows the time-dependent percentages of the different shapes of nanoparticles taken from different reaction time. Fifteen minutes after the growth reaction (200 °C), the percentages of the near-sphere nuclei rapidly increased to 33% from 0%; at the same time, ratio of the TT nanoparticles decreased sharply. At 15 min, the cubic nanoparticles
were dominating in the reaction solution. At 30 min, the small near-sphere nuclei grew larger and transformed to other shaped nanoparticles. The tetrahedral became the most at this reaction stage. In 30–45 min, the percentage of cubic and tetrahedral changed slightly. The near-sphere nanoparticles disappeared at the 45 min. With the reaction process, the percentage of the TT increased rapidly, but the amount of other shape decreased. After an anneal at 300 °C for

Fig. 1. TEM images of magnetite nanoparticles with different reaction stages: (A) seeds of 6 nm magnetite nanoparticles, (B) 15 min, (C) 30 min, (D) 45 min, (E) 60 min, after the seed-mediated growth reaction (200 °C), (F) 30 min after anneal treatment (300 °C).
30 min, the percentage of the TT nanoparticles increased to 86%, and the percentage of the tetrahedral and the cubic decreased to about 10%.

From the shape distribution and the TEM images shown in Figs. 1–3, the main feature of the shape evolution during the synthesis process was seen. The relative percentages of all kinds of shapes of nanoparticles in the solution strongly depended on the reaction time and temperature. The percentages of cubic and tetrahedral first increased then decreased with time. However, the percentage of TT in seeds decreased first then increased dramatically, and then the TT became the dominating shape in the last reaction stage. In this reaction conditions, the TT was the dominating shape in the final products.
Based on the above phenomena observed, the kinetic shape evolution mechanism can be accounted as the nanoparticle faceted from sphere, to cubic, tetrahedral and TT during the whole reaction. As fcc crystal, a general sequence of surface energies of Fe$_3$O$_4$ nanoparticles may hold, $\gamma\{111\} < \gamma\{100\} < \gamma\{110\}$ [17]. Based on surface free energy minimization principle, the equilibrium morphology of magnetite is expected to be a cubic-octahedron, and indeed, this is the most common form in which nanocrystalline magnetite is observed [18]. In this study, oleic acid and oleyamine, as the capping agent, tended to adsorb on the particular high-energy facets of the nanoparticles. Their overall specific surface energy was more or less reduced, and the surface reaction rate would be decreased. The ratio between growth rates in different direction can be varied by special adsorption of organic surfactants onto particular crystallographic facets inhibiting the growth of a particular crystallographic direction [19]. The capping reaction was dominating in the initial reaction time when the concentrations of the surfactants were high enough. Cubic particles formed if the growth rate in the $\{111\}$ direction is much higher than that in $\{100\}$ direction [20]. The small near-sphere nanoparticle transformed to cubic nanoparticle having six $\{100\}$ surfaces in this reaction stage. The cubic nanoparticles having six $\{100\}$ facets of high surface energies were less stable in the high temperature. It was observed that annealing at $\sim 300^\circ C$ resulted in the edge of the cubic nanoparticles formed at $200^\circ C$ were smoothed. This phenomenon was also observed in the work of Shevchenko et al. [21]. However, mechanism responsible for the phenomena of edge smoothed during the anneal process is not clear and require further investigation.

The difference among the surface energies of the facets reduced gradually for the adsorption effect. The tetrahedral nanoparticles having four $\{111\}$ facets transformed from the near-sphere emerged in the reaction solution. The growth rates of $\{100\}$ and $\{111\}$ balanced when the surfactant molecular were volatilized at this anneal temperature. Amount of larger TT nanoparticles having both $\{100\}$ and $\{111\}$ facets presented in the final sample, and there were less cubic and tetrahedral nanoparticles in the Fig. 1F.

A tetrahedral particle is defined by four $\{111\}$ facets and it usually gives a triangular shape in HRTEM [17]. Fig. 4 shows the hexagonal-shaped atom-resolution image of Fe$_3$O$_4$ nanoparticle taken from the final product. Two $\{111\}$ facets and one $\{001\}$ facet (as a result of truncation of a tetrahedral) are imaged edge-on. The distance between two adjacent planes is measured to be 4.85 Å with their separation angle of 70.53° along the $\langle110\rangle$ zone axis, corresponding to $\langle111\rangle$ planes in the spinel-structured Fe$_3$O$_4$ [22].

### 3.2. Kinetic size-control growth mechanism

XRD patterns in Fig. 5 reveal the nanocrystal nature of the samples taken from different reaction stages. The position and relative intensity of all peaks match well with standard Fe$_3$O$_4$ powder diffraction data, indicating that each sample is Fe$_3$O$_4$ crystal.
Fig. 6 shows the results of HPPS for Fe$_3$O$_4$ nanoparticles taken from different reaction time. Along with the reaction procedure, hydrodynamic diameter of the nanoparticles increased and the polydispersity index (PI) of the nanoparticles decreased. The hydrodynamic diameter of the sample was composed of core Fe$_3$O$_4$ nanoparticle diameter and the size of the absorbed surfactant molecule. Noticeably, there were two peaks of the size distribution appeared at 30 min after the seed-mediated growth reaction. The smaller peak spaced from 5 nm to 7 nm, and the larger peak spaced from 8 nm to 50 nm. The small size peak suggests that the small nuclei particles formed in this reaction stage, and then transformed to other shape of particles in the next reaction stage, which is consistent with Figs. 2 and 3.

Fig. 4. HRTEM image of truncated tetrahedral Fe$_3$O$_4$ nanoparticle. The particle was imaged along its [1 1 0] zone axis.

Fig. 5. X-ray diffraction patterns of magnetite nanoparticles taken from different reaction time: (A) seeds of Fe$_3$O$_4$ nanoparticles, (B) 30 min, (C) 60 min after the seed-mediated growth reaction (200 $^\circ$C), (D) 30 min after an anneal treatment (300 $^\circ$C). The characteristic peaks of Fe$_3$O$_4$ were labeled.
In general, the synthesis of colloidal crystalline particles from a solution involves two consecutive stages: formation of nuclei with sizes larger than the critical one (nucleation stage) and growth of these nuclei (growth stage) [23].

In this synthesis, the Fe\textsuperscript{2+}/Fe\textsuperscript{3+} decomposed from the Fe(acac)\textsubscript{3} were independent on the nucleation and growth process. The seed-mediated growth of Fe\textsubscript{3}O\textsubscript{4} in this study was a “growth-controlled nucleation” process. The nucleation process was controlled by the growth of the nuclei and virtually terminated in the early stage of the particles formation. In our case, the broader size distribution in the Fig. 2B and the two peaks of size distribution in Fig. 6, and the distribution shift toward to higher value indicating small amount of nucleation was formed and particle size increased during the early 200 °C series, which means a superposition of growth and nucleation occurred during the reaction stage. The ration of the particle to metal ion increased after the short time nucleation burst, and growth predominated over nucleation. It suggests that if adding seeds to a system of the growth-dependent nucleation, the seeds will reduce the spontaneous nucleation, and the size of the final product can be controlled systematically by changing the number of the seeds.

In the growth stage, the following mechanisms were proposed to occur: (i) growth consuming molecular precursor from surrounding solution; (ii) Oswald ripening or coarsening when larger particles grow at the expense of dissolving smaller ones; and (iii) fusion of several particles (oriented attachment) [24]. If nanoparticles grow via Oswald ripening, the particle size distribution tends to be uniform irrespective of the initial shape of the size distribution. On the other hand, if nanoparticles grow by consuming molecular precursors from surrounding solution, the size of smaller particles increases faster than that of the larger ones. In Fig. 6, the hydrodynamic diameter of the nanoparticles increased and PI of the nanoparticles decreased especially at the 300 °C reaction stage. It was so-called “focusing” size distribution growth regime observed in CdSe, CoPt\textsubscript{3} nanoparticles [21,25]. As discussed above in this study, the monodispersed Fe\textsubscript{3}O\textsubscript{4} nanoparticles can be obtained by ending the nucleation in the early reaction stage, and then the particles grew by consuming the monomers in the solution at higher temperature. It accounts for broader size distribution in the Fig. 1A–E and a narrower distribution for Fig. 1F.

4. Conclusion

Time-dependent shape and size evolution of Fe\textsubscript{3}O\textsubscript{4} nanoparticles synthesized by seed-mediated method were studied. The seeds added in the reaction solution of the growth-controlled nucleation, urged the spontaneous nucleation end at the early reaction stage and further growth by consuming the monomers in the solution at higher temperature to get the monodisperse nanoparticles. The truncated tetrahedral particles were dominating in the final reaction solution when the particles were prepared using the seed-mediated growth. The special shape Fe\textsubscript{3}O\textsubscript{4} nanoparticles can be obtained by simply tuning the growth time. The detailed study with the kinetic shape and size evolution process supply new way to synthesis the shape- and size-controlled nanoparticles.

Fig. 6. Time-dependent hydrodynamic diameters of the Fe\textsubscript{3}O\textsubscript{4} nanoparticle taken from different reaction time: the PI decreased from 0.430 (15 min) to 0.325 (60 min), 0.115 (90 min).
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