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Growth mechanism and magnetic properties of magnetite nanoparticles during solution process

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ABSTRACT

We investigated the growth mechanism of magnetite nanoparticles during chemical synthesis by analyzing their physicochemical properties. The transformation from metallic precursor to particles and the growth of the particle occurred during chemical synthesis. During the transformation process, $Fe(acac)_3$, which was used as a metallic precursor, was decomposed, fabricating an Fe oleate. The Fe oleates then agglomerated to each other to form Fe oleate clusters. Finally, the Fe oleate cluster was reduced, and a magnetite nanoparticle was fabricated. During the growth process of the magnetite nanoparticle, the diameter of the magnetite nanoparticles increased as the reaction temperature increased. Then, the Fe oleates on the surface of the magnetite nanoparticle were reduced at a constant rate, and as a result, the magnetite nanoparticle grew significantly.

1. Introduction

Elemental iron (Fe) constitutes 5.0% of the Earth's crust, which is large compared with other metallic elements [1]. Fe exhibits ferromagnetic behavior at room temperature, which is a property that is limited to only elemental Fe, Co, and Ni. However, Fe tends to oxidize easily, generating Fe oxides. Fortunately, Fe oxides (e.g., Fe_3O_4 and Fe_2O_3) also exhibit ferromagnetic behavior and are commonly studied in multiple disciplines.

Recently, chemical and physical researchers have begun to investigate metal nanoparticles. Many researchers have synthesized various types of nanoparticles using chemical and physical methods, and investigated the characteristics of these materials because nanoparticles exhibit novel properties due to the quantum size effect. As a result, it has been predicted that Fe oxide nanoparticles can be applied in the fields of data storage, magnetic resonance imaging (e.g., as a contrast agent), hyperthermia therapy and drug delivery [2–6]. There have been many reports on various chemical synthesis procedures and physicochemical properties of Fe oxide nanoparticles [7–16]. A polyol process is one of the most useful chemical synthesis procedures, and various types of nanoparticles (e.g., Ni, CoPt, FePt, FePd, and Fe oxide) have been prepared easily with this process [17–23].

Generally, in the case of Fe oxide nanoparticles prepared via chemical synthesis, oleic acid is often chosen as a ligand [7,24–27]. Additionally, Fe oleates are also often used as metallic precursors [14,28,29]. Thus, it is thought that the Fe atom is miscible with carboxylic acid and carboxylate; however, the reaction or growth mechanism of Fe oxide nanoparticles via chemical synthesis has not yet been studied in detail, although Zhao has reported that there are nucleation and growth processes in magnetite nanoparticles prepared via the thermal decomposition of iron(III) acetylacetonate as a metallic precursor [23]. If the growth mechanism of this material is clearly described, it is expected that the size and shape of the nanoparticles will be easily manipulated, and their yields will be high. However, it is difficult to obtain clear evidence of the transformation of a metallic precursor into Fe oxide nanoparticles because we cannot directly measure what types of intermediate products are prepared during chemical synthesis. Although some reports have explained growth process of magnetite nanoparticles [13,23], the authors have not identified intermediate products in the process. Thus, it is worthy to investigate the intermediate products and it is a big theme to elucidate them and solve the growth mechanism of magnetite nanoparticles. So, we must describe the growth mechanism of Fe oxide nanoparticles by preparing the intermediate products and verifying their physicochemical properties.

In this study, we examine the growth mechanism of magnetite nanoparticles prepared via a polyol process based on their physicochemical properties because the growth mechanism is not

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studied in detail. We separately explain the transformation of the metallic precursors into the nanoparticles and the growth of the particles during chemical synthesis similarly to the previous reports [13,23]. Herein, we first find intermediate products from magnetic properties, and discuss them and the growth mechanism of magnetite nanoparticles.

2. Experimental procedures

2.1. Materials

Iron(III) acetylacetonate (=Fe(acac)$_3$) was used as a metallic precursor and was purchased from Dojindo. Tetraethylene glycol (TEG) was used as a reducing reagent and was obtained from Wako. Oleic acid and oleylamine were used as ligands to protect the samples and were purchased from Wako and Aldrich, respectively.

2.2. Synthesis of magnetite nanoparticles

In a typical procedure [15], 706.4 mg of Fe(acac)$_3$ was mixed in 50 mL of TEG solution, and the TEG mixtures were vigorously stirred. Protective reagents (0.16 mL of oleic acid and 0.17 mL of oleylamine) were added to the TEG mixtures at approximately 100 °C. The mixtures were elevated to a reaction temperature and allowed to reflux at the reaction temperature for several hours. After the reaction had completed, the mixtures were automatically cooled to room temperature. The products were then purified by washing with acetone and filtered to produce the final powder.

2.3. Synthesis of Fe oleate

To compare the intermediate products generated during the chemical synthesis of magnetite nanoparticles, we prepared the Fe oleate. In 60 mL of distilled water, 3.04 g of sodium oleate, which was purchased from Wako, was resolved at 80 °C. 0.892 g of $FeCl_3 \cdot 6H_2O$, which was purchased from Wako, in 60 mL of

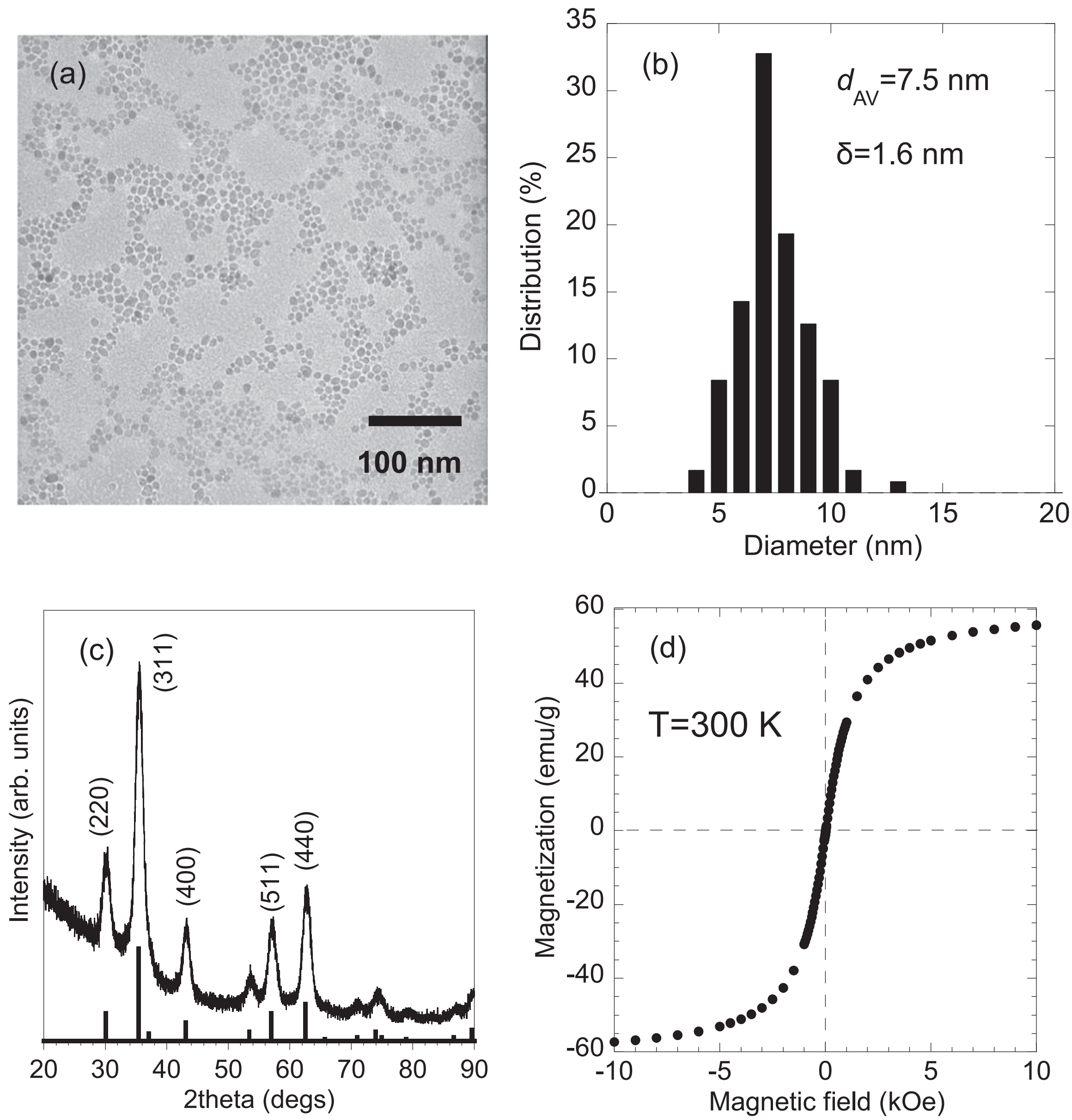

Fig. 1. (a) TEM photograph, (b) size distribution histogram, (c) XRD pattern, and (d) magnetization curve at 300 K of the typical magnetite nanoparticles prepared via a polyol process. The standard XRD pattern of (c) is taken from PDF no. 00-019-0629.