

Preparation of Larger FePt Nanoparticles by Reduction of Metal Salts

Masafumi Nakaya and Toshiharu Teranishi*

Graduate School of Pure and Applied Sciences, University of Tsukuba, 1-1-1 Tennodai, Tsukuba, Ibaraki 305-8571, Japan
Fax: +81-29-853-6503, e-mail: teranisi@chem.tsukuba.ac.jp

$L1_0$ ordered FePt nanoparticles have a potential to be applied to ultra high-density magnetic recording media, because they have very large coercivity and uniaxial magnetocrystalline anisotropy. In this regard, the size effect of FePt nanoparticles on the changes in their crystal structure and magnetic property during an annealing process should be investigated systematically. By changing the kind of precursor or the reaction sequence, the size of FePt nanoparticles could be controlled from 3.1 to 4.6 nm.

Key words: FePt nanoparticle, size control, minimal stable grain size, $L1_0$ -ordered structure

1. INTRODUCTION

Metal nanoparticles are of great interest with respect to their potential applications to optical, electronic, catalytic and magnetic devices. Since the physical properties of metal nanoparticles greatly depend on their sizes, the control of particle size is very important for these applications [1-4]. Progress in nanomagnetic devices is due in part to the development of metal thin film media with smaller particles, narrower size distribution, and optimized compositions. $L1_0$ phase materials (e.g. FePt, CoPt, FePd) are an important class of materials in permanent magnetic application because of their high uniaxial magnetocrystalline anisotropy (K_u) and high coercivity (H_c) [5]. As the magnetic stability of individual particle scales with the K_u , $L1_0$ phase materials are suitable for ultrahigh-density magnetic media application. Chemically prepared FePt nanoparticles have attracted much attention recently because of their ease of synthesis, narrow size distribution, chemical stability, and potential applications in high-density data storage and high performance permanent magnets [5,6]. The particles are commonly synthesized via co-reduction of iron salt and platinum acetylacetonate, Pt(acac)₂, decomposition of iron pentacarbonyl, Fe(CO)₅, and reduction of Pt(acac)₂, or seed-mediated growth where smaller FePt nanoparticles are used as seeds and more FePt is coated over the seeds [6-10]. By using these syntheses, the size of the resulting FePt nanoparticles was restricted to be smaller than 4 nm. For instance, only 3.1 nm FePt nanoparticle have been obtained by the co-reduction of iron acetylacetonate, Fe(acac)₃, and Pt(acac)₂ [10]. After annealing 3.1 nm FePt nanoparticle assemblies at 600 °C under vacuum to change the crystal structure from chemically disordered fcc to chemically ordered $L1_0$, the large coercivity is provided to the particles, but the coalescence of the FePt nanoparticles is always observed. This dramatic change in the magnetic properties

resulting from the crystal structural change of nanoparticles is owing to the coalescence of the 3.1 nm nanoparticles during an annealing process,

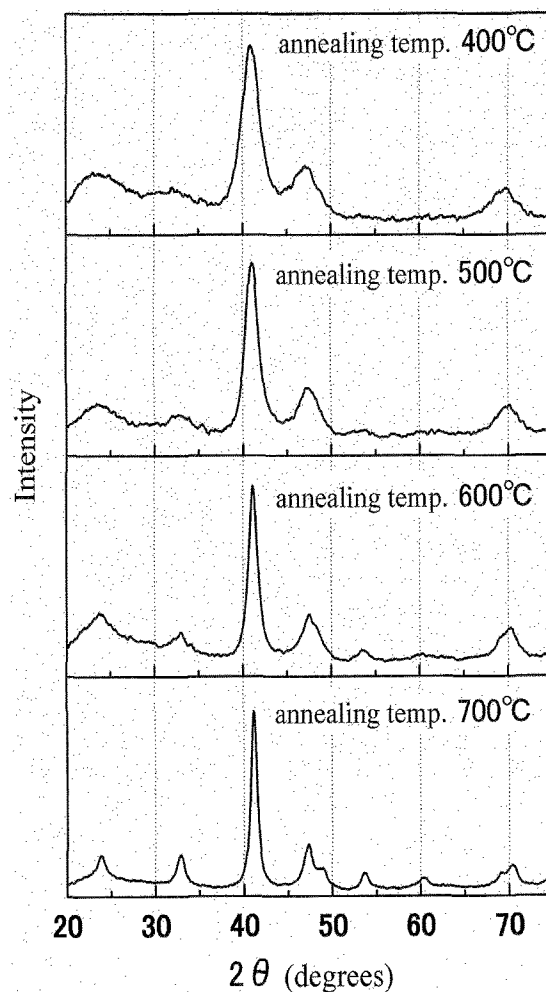


Figure 1 XRD patterns of 3.1 nm Fe₅₃Pt₄₇ nanoparticle assemblies after annealing at 400, 500, 600, and 700 °C.

as show in Fig.1. Since the minimal stable grain size to change the crystal structure from fcc to $L1_0$ has been reported to be around 4 nm [11], the novel synthesis of FePt nanoparticles larger than 4 nm is required to study the size effect on the change of crystal structure and the magnetic property. Chen et al. have reported the one-step synthesis of FePt nanoparticles with tunable size up to 9 nm using $\text{Fe}(\text{CO})_5$ as the Fe precursor [4]. This is the first method for the formation of large FePt nanoparticles, although $\text{Fe}(\text{CO})_5$ is not only toxic and inflammable, but also has a low boiling point (103 °C), which makes it difficult to control the precise composition of FePt nanoparticles during the hot synthesis.

Here, we present the synthetic procedures of FePt nanoparticles larger than 4 nm using iron salt as an Fe precursor. One is the polyol reduction of iron acetate, $\text{Fe}(\text{OAc})_2$, and $\text{Pt}(\text{acac})_2$, and the other is the addition of the powdery mixture of $\text{Fe}(\text{acac})_3$ and $\text{Pt}(\text{acac})_2$ into high temperature solvent.

2. EXPERIMENTAL

2.1 Synthesis of FePt nanoparticles using polyol reduction of $\text{Fe}(\text{OAc})_2$ and $\text{Pt}(\text{acac})_2$

The FePt nanoparticles were chemically synthesized by modifying our previous procedure [7], i.e., by a polyol-reduction of $\text{Fe}(\text{OAc})_2$ and $\text{Pt}(\text{acac})_2$. First, both precursors (total amount was 1.0 mmol) were added to di-n-octylether (10 mL), and the dissolved oxygen was removed from the solution under the reduced pressure for 5 min. The vigorously-stirred solution was heated up to 150–170 °C under N_2 atmosphere to completely dissolve the precursors. The solution was kept stirring for 30 min after an addition of reductant, 1,2-hexadecanediol (1.5 mmol), and the mixture of oleic acid (0.5 mmol) and oleylamine (0.5 mmol) was then injected into the solution and stirred for 30 min at this temperature (solution temperature was ca. 230 °C). The solution was cooled down to room temperature and the resulting particles were precipitated with ethanol for purification. The black precipitate was redispersed in hexane (50 mL) containing oleic acid (100 μL) and oleylamine (100 μL).

2.2 Synthesis of FePt nanoparticles by adding the powdery mixture of $\text{Fe}(\text{acac})_3$ and $\text{Pt}(\text{acac})_2$ into high temperature solvent

1-Octadecene (non-coordinating solvent with a high boiling point (>300 °C)) was kept under reduced pressure for 5 min to remove the dissolved oxygen, and then heated up to ca. 300 °C under N_2 atmosphere. The powdery mixture of $\text{Fe}(\text{acac})_3$, $\text{Pt}(\text{acac})_2$, 1,2-hexadecanediol, oleic acid and oleylamine was added into hot solvent, and the solution was kept for 30 min with vigorous stir. The solution was then cooled down to room temperature and the resulting particles were separated from 1-octadecene by centrifugation after an addition of chloroform and methanol. The black

precipitate obtained was redispersed in hexane (50 mL) with oleic acid (100 μL) and oleylamine (100 μL).

2.3 Measurements

The sizes of FePt nanoparticles were estimated with a Hitachi H-7100 transmission electron microscope (TEM) operating at 100 kV. The percentage of reduced Fe ions was measured by a Hitachi U-3310 UV visible spectroscopy (UV-vis). The compositions of the FePt nanoparticles were determined by a Hitachi S-3500N scanning electron microscopy (SEM) equipped with a HORIBA EMAX-7000 energy dispersive X-ray spectroscopy (EDX) operating at 20 kV. The diffraction patterns of FePt nanoparticles were collected on a Mac Science M18XHF-SRA X-ray diffractometer (XRD) under a $\text{Cu K}\alpha$ radiation.

3. RESULTS AND DISCUSSION

In our previous report, only 3.1 nm FePt nanoparticles with a narrow size distribution were obtained by the polyol reduction of $\text{Fe}(\text{acac})_3$ and $\text{Pt}(\text{acac})_2$, and larger FePt nanoparticles were not generated. That is probably because $\text{Fe}(\text{acac})_3$ is relatively stable and the Fe ions partially

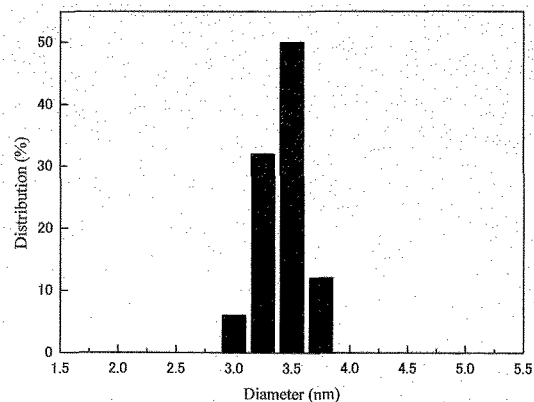
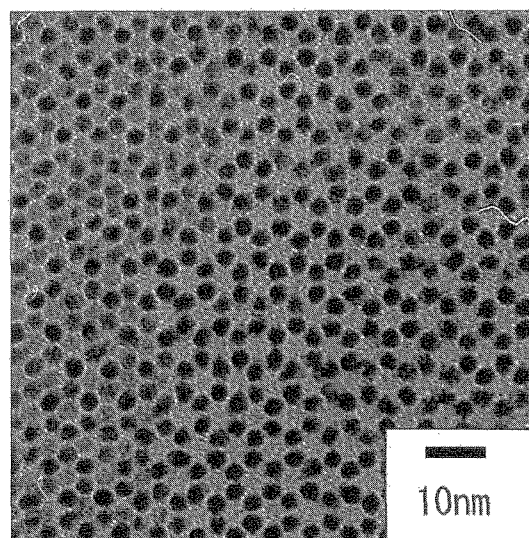


Figure 2 TEM image of 3.4 ± 0.3 nm $\text{Fe}_{39}\text{Pt}_{61}$ nanoparticles and the size distribution.

remained to be unreduced. In order to proceed the reduction of Fe ions, the kind of Fe salt was changed from $\text{Fe}(\text{acac})_3$ to $\text{Fe}(\text{OAc})_2$. By using a polyol reduction of $\text{Fe}(\text{OAc})_2$ and $\text{Pt}(\text{acac})_2$ ($\text{Fe}(\text{OAc})_2 / \text{Pt}(\text{acac})_2 = 1 \text{ mol} / 1 \text{ mol}$), monodisperse $3.4 \pm 0.3 \text{ nm}$ $\text{Fe}_{39}\text{Pt}_{61}$ nanoparticles were obtained (Fig. 2). Not only the particle size but also the Fe content became slightly larger than those by the previously synthesized particles. The Fe contents of FePt nanoparticles are 34 and 39 atom % at the initial feeding ratio of $\text{Fe}(\text{acac})_3 / \text{Pt}(\text{acac})_2 = 1/1$ and $\text{Fe}(\text{OAc})_2 / \text{Pt}(\text{acac})_2 = 1/1$, respectively. The percentages of the reduced Fe ions evaluated by the UV-vis spectroscopy are 68 % and 78 % for $\text{Fe}(\text{acac})_3$ and $\text{Fe}(\text{OAc})_2$, respectively, indicating that the increase in the percentage of reduced Fe ions contributes the growth of FePt nanoparticles. Figure 2 also indicates that these monodisperse 3.4 nm $\text{Fe}_{39}\text{Pt}_{61}$ nanoparticles self-assemble into the hexagonal close-packed (hcp) 2D superlattice and 3D AB and ABC stacking superlattices, as observed previously [10]. The 3D superlattice consists of AB stacking of hcp 2D superlattices of FePt nanoparticles forming the quasi-honeycomb structure, where the nanoparticles at the second layer occupy the three-fold hollow sites of the

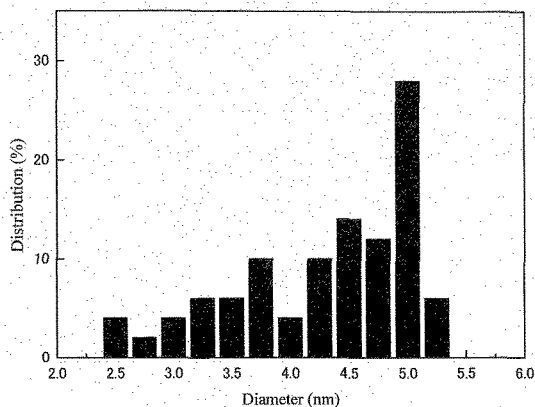
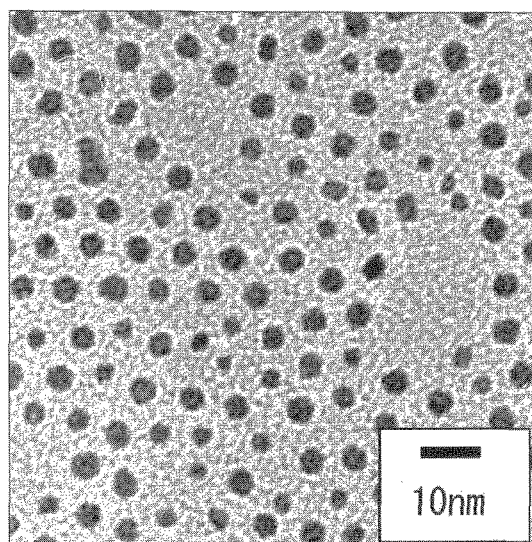


Figure 3 TEM image of $4.6 \pm 1.5 \text{ nm}$ FePt nanoparticles and the size distribution.

first layer (right part in Fig.2). The particles further assemble to give a thick superlattice with an ABC close-packed (fcc-type) structure (left part in Fig.2). Using this method, however, the FePt nanoparticles larger than 3.4 nm could not be obtained.

In the liquid phase synthesis, the solution is gradually heated up from room temperature to the reaction temperature. During the heating process, the Pt ions are first reduced at lower temperature and a lot of Pt-rich small FePt nuclei are then formed. The shortage of atoms to be used to grow the particles leads to the formation of small particles. In order to suppress the formation of many Pt-rich nuclei, the powdery mixture of $\text{Pt}(\text{acac})_2$ and $\text{Fe}(\text{acac})_3$ was added into high temperature solvent aiming the simultaneous and gradual reduction of Fe and Pt ions. The TEM image of the resulting FePt nanoparticles is shown in Fig.3, the size being $4.6 \pm 1.5 \text{ nm}$, which is larger than the minimal grain size of FePt nanoparticle. In this method, since the reaction rate was faster than the dissolving rate of the powdery mixture to the solvent, the FePt particle size was increased due to a stepwise growth. The size distribution of the resulting FePt nanoparticles was wide, which should be improved to make the size distribution narrow.

4. CONCLUSIONS

By changing the kind of precursor or the reaction sequence, the size of FePt nanoparticles could be controlled from 3.1 to 4.6 nm. In order to study the size effect of FePt nanoparticles on the change in their crystal structure and magnetic property during an annealing process, however, the larger FePt nanoparticles can be synthesized. Now, the development of a synthetic method to form the FePt nanoparticles larger than 5 nm by slowing the nucleation speed is in progress.

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6. References

- [1] A. P. Alivisatos, *Science*, **271**, 933-937 (1996).
- [2] J. Shi, S. Gider, K. Babcock, and D. D. Awschalom, *Science*, **271**, 937-941 (1996).
- [3] T. Teranishi, S. Hasegawa, T. Shimizu, and M. Miyake, *Adv. Mater.*, **13**, 1699-1701 (2001).
- [4] M. Chen, J. P. Liu, and S. Sun, *J. Am. Chem. Soc.*, **126**, 8394-8395 (2004).
- [5] D. Weller, A. Moser, L. Folks, M. E. Best, W. Lee, M. F. Toney, M. Schwickert, J. -U. Thiele, and M. F. Doerner, *IEEE Trans. Magn.*, **36**, 10-15 (2000).
- [6] S. Sun, C. B. Murray, D. Weller, L. Folks, and A. Moser, *Science*, **287**, 1989-1992 (2000).

- [7] S. Sun, S. Anders, T. Thomson, J. E. E. Baglin, M. F. Toney, H. F. Hmann, C. B. Murray, and B. D. Terris, *J. Phys. Chem. B*, **107**, 5419-5425 (2003).
- [8] B. Jeyadevan, A. Hobo, K. Urakawa, C. N. Chinnasamy, K. Shinoda, and K. Tohji, *J. Appl. Phys.*, **93**, 7574-7576 (2003).
- [9] T. Iwaki, Y. Kakihara, T. Toda, M. Abdullah, and K. Okuyama, *J. Appl. Phys.*, **94**, 6807-6811 (2003).
- [10] M. Nakaya, Y. Tsuchiya, K. Ito, Y. Oumi, T. Sano, and T. Teranishi, *Chem. Lett.*, **33**, 130-131 (2004).
- [11] Y. K. Takahashi, T. Ohkubo, M. Ohnuma, and K. Hono, *J. Appl. Phys.*, **93**, 7166-7168 (2003).

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