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Direct Synthesis of Partially Ordered FePt Nanoparticles

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Partially ordered FePt nanoparticles were obtained by using polyol reduction of metal salts in an autoclave at high reaction temperature. The resulting FePt nanoparticles synthesized at 400 °C had the particle sizes of 6–7 nm and could be easily redispersed into hexane, toluene and chloroform. Their crystal structure was found to be partially ordered $L1_0$ structure and the ordering degree was dependent on the reaction temperature and the reaction time.

Key words: FePt nanoparticle, crystal structural transformation, partially ordered structure

1. INTRODUCTION

The chemically ordered $L1_0$ FePt nanoparticles have a potential for an application to ultra high-density magnetic recording media because of their large coercivity and uniaxial magnetocrystalline anisotropy [1]. In the case of chemically synthesized FePt nanoparticle, as-synthesized nanoparticles have chemically disordered face-centered-cubic (fcc) phase, while annealing above 600 °C under vacuum, inert gas, or reducing atmosphere transforms the crystal structure from fcc to chemically ordered $L1_0$ phase [2–7]. However, such high ordering temperature always leads to a coalescence of nanoparticles (Figure 1) [5]. Many efforts have been dedicated to prevent the nanoparticles from the coalescence, for example, the reduction of ordering temperature by adding a third element to FePt nanoparticles [8–11] or the confinement of FePt nanoparticles into SiO_2 shell or NaCl fine powder [12,13]. However, these techniques have drawbacks, such as the contamination coming from a third element or the time-consuming treatment including the confinement and extraction of FePt nanoparticles. Here, we report the direct synthesis of partially ordered FePt nanoparticles by using polyol reduction of metal salts in an autoclave. Since only fcc-FePt nanoparticles were obtained under the reflux condition of high boiling point solvents, such as di-*n*-octylether (b.p. = ~290 °C) and octadecene (b.p. = ~317°C), we tried to synthesize the FePt nanoparticles at higher temperature using an autoclave. In this paper, we used the oleic acid and oleylamine (b.p. = ~340 °C) as both the solvent and ligand, and investigated the influence of the reduction temperature and the reduction time on the crystal structure of FePt nanoparticles.

2. EXPERIMENTAL

The FePt nanoparticles were synthesized by modifying our previously reported method [3–5]. The experimental conditions are summarized in Table 1.

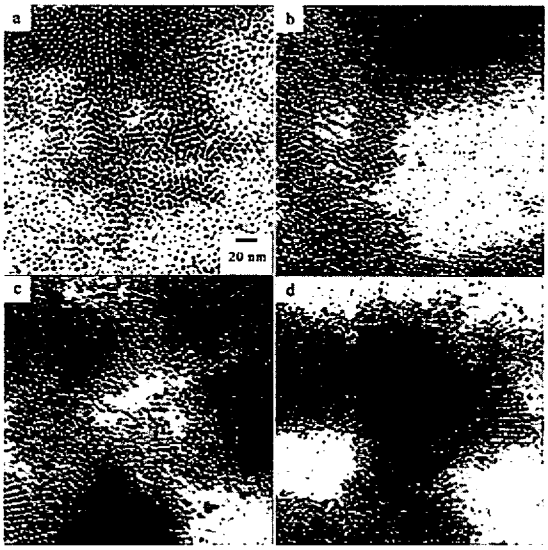

Figure 1. TEM images of 5.1 nm $Fe_{41}Pt_{51}$ nanoparticles after annealing on amorphous carbon-coated TEM grids at (a) 400, (b) 500, (c) 600, and (d) 700 °C under vacuum (ca.10^{-6} Torr). The mean diameters are (a) 5.2, (b) 5.5, (c) 5.5, and (d) 6.2 nm.

Typically, iron(III) acetylacetonate ($Fe(acac)_3$) (0.1 mmol), platinum(II) acetylacetonate ($Pt(acac)_2$) (0.1 mmol), oleic acid (1.0 mmol), oleylamine (1.0 mmol), and 1,2-hexadecanediol (0.3 mmol) were put into a sample tube (oleic acid and oleylamine were distilled under reduced pressure prior to use). The sample tube was inserted in an autoclave (Taiatsu Techno) and the dissolved oxygen was removed from the mixture under the reduced pressure. After the nitrogen gas was filled, the autoclave was set in a muffle furnace. The tube was heated up to 375–400 °C, and the reaction was kept for 30 min–5 h, followed by the removal of the autoclave from the muffle furnace to terminate the reaction. Hexane (5 mL) was then added to the resulting black precipitate formed in the

Table 1. Experimental conditions to synthesize FePt nanoparticles

Run	Temp. (°C)	Time (h)	$Fe(acac)_3$ / $Pt(acac)_2$ (mmol/mmol)
1	375	0.5	0.1 / 0.1
2	385	0.5	0.1 / 0.1
3	400	0.5	0.1 / 0.1
4	375	1	0.1 / 0.1
5	385	1	0.1 / 0.1
6	400	1	0.1 / 0.1
7	400	2	0.1 / 0.1
8	400	5	0.1 / 0.1
9	375	2	0.14 / 0.06
10	400	2	0.14 / 0.06

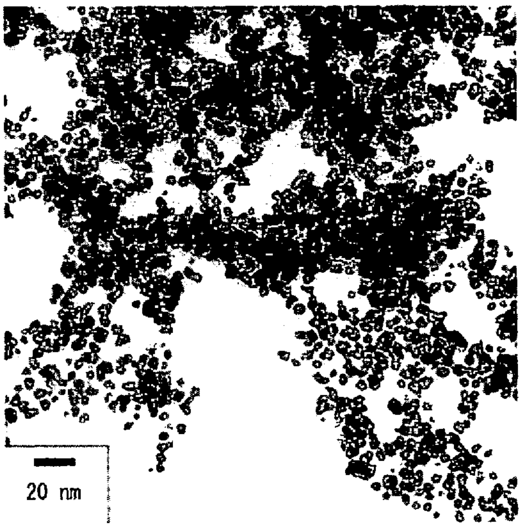

Figure 2. TEM image of FePt nanoparticles synthesized at the molar ratio of $Fe(acac)_3/Pt(acac)_2$ = 0.14/0.06 (mmol/mmol) at 400 °C for 2 h (Run 10).

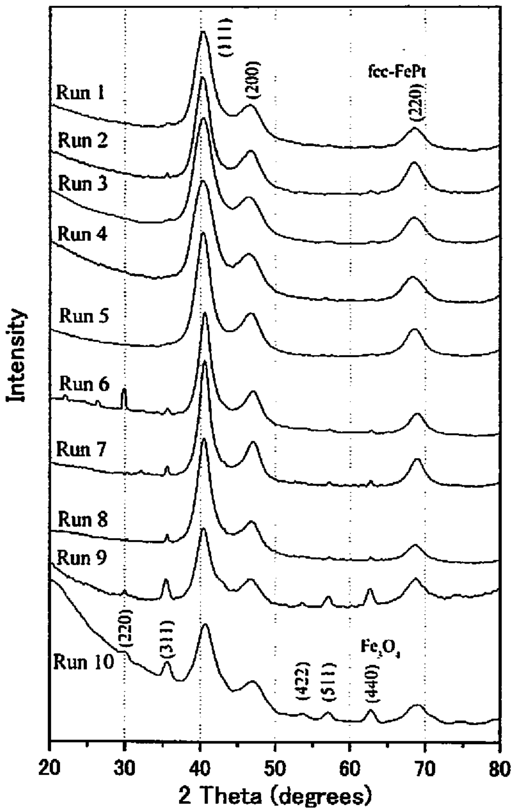

Figure 3. XRD patterns of FePt nanoparticles obtained at the experimental condition in Table 1.

sample tube, and the FePt nanoparticles were purified by pouring ethanol (20 mL) to the hexane solution of FePt nanoparticles. The obtained black FePt nanoparticles were redispersed into hexane. The size of the resulting FePt nanoparticles was estimated by transmission electron microscopy (TEM) operating at 100 kV (JEOL JEM-100). The compositions of the FePt nanoparticles were determined by X-ray fluorescence spectrometer operating at 30 kV (JEOL JSX-3202C). The X-ray diffraction patterns of the FePt nanoparticles were collected on X-ray diffractometer (XRD) under Cu Kα radiation (PANalytical X'Pert Pro MPD).

3. RESULTS AND DISCUSSION

The FePt nanoparticles were synthesized by changing the reaction temperature (375–400 °C), the reaction time (0.5–2 h), and the $Fe(acac)_3/Pt(acac)_2$ molar ratio (0.1/0.1–0.14/0.06 mmol/mmol). Figure 2 shows a TEM image of the FePt nanoparticles obtained at the molar ratio of $Fe(acac)_3/Pt(acac)_2$ = 0.14/0.06 (mmol/mmol) at 400 °C for 2 h (Run 10). The particles have the size of 6.0 ± 1.0 nm and the Fe content of 72 mol %. The resulting nanoparticles could be easily dissolved to hexane and the particle coalescence was not observed, suggesting that oleic acid and oleylamine were not decomposed during the synthesis and protecting the FePt nanoparticles. In addition, other experimental conditions (Runs 1–9) gave the similar size and size distribution of FePt nanoparticles except for the Fe content of 52 mol % at the molar ratio of $Fe(acac)_3/Pt(acac)_2$ = 0.1/0.1 (mmol/mmol). These nanoparticles have relatively wide size distribution and irregular shapes, although the formation of hexane-soluble FePt nanoparticles at around 400 °C is quite significant, because several post-annealing processes at around 400 °C lead to the transformation of the crystal structure from fcc to $L1_0$.

In order to investigate the influence of the reaction temperature, reaction time, and the molar ratio of precursors on the ordering degree of FePt nanoparticles, the XRD measurements were carried out for all samples. The XRD patterns and (111) lattice spacings of the resulting FePt nanoparticles were presented in Figures 3 and 4, respectively. In Figure 3, since the crystalline sizes estimated from the full width at half-maximum of (111) peaks were in good agreement with the sizes of FePt nanoparticles estimated from TEM, indicating the single crystalline nature of FePt nanoparticles. The $L1_0$-FePt has a structure in which the Fe and Pt atomic layers are alternately piling up. When the chemically-disordered fcc-FePt nanoparticles are transformed into chemically-ordered $L1_0$ structure, the crystal lattices shrink in the c-axis direction, leading to the decrease in the (111) lattice spacings. For the FePt nanoparticles synthesized at Fe(acac)$_3$/Pt(acac)$_2$ = 0.1/0.1 at the temperature lower than 400 °C (Runs 1, 2, 4, 5), the (111) lattice spacings are similar to that for fcc-FePt nanoparticles (40.3°, d_{111} = 0.2238 nm) and the ordering peaks were not observed. When the reaction temperature was raised at 400 °C, the short reaction time (Run 3) did not lead a significant change in the crystal structure, the 1-h reaction (Run 6) caused the (111) peak shift to the higher position (40.6°, d_{111} = 0.2229 nm). As elongating the reaction time from 1 to 5 h, the (111) lattice spacings became narrower (Runs 6–8), indicating that the synthesis of FePt nanoparticles at 400 °C promotes the diffusion of Fe and Pt atoms in the FePt nanoparticles to transform the crystal structure from fcc to partially ordered $L1_0$. In the conventional ordering technique, annealing the FePt nanoparticles at 400 °C under vacuum does not bring the crystal structural transformation at all. The crystal structural transformation of FePt nanoparticles synthesized at Fe(acac)$_3$/Pt(acac)$_2$ = 0.14/0.06, (Runs 9, 10) exhibited the similar tendency. The local structural analysis of the obtained FePt nanoparticles is under investigation to confirm the compatibility with the XRD results.

Our method proposed here is a facile approach to obtain the partially ordered $L1_0$-FePt nanoparticles without the noticeable coalescence of particles compared to the conventional post-annealing methods over 550 °C, which is usually responsible for the particle coalescence. Furthermore, the partially ordered FePt nanoparticles have a potential to align their easy axes in the same direction on the substrate with the aid of the magnetic field.

The drawback of this system is the formation of iron oxide. The (311) peaks of Fe_3O_4 were observed at 35.5° for Runs 6–10. The Fe_3O_4 species would come from the unreacted Fe precursor and the oxygen in the sample tube at high temperature condition. Especially, the formation of Fe_3O_4 becomes remarkable when increasing the content of Fe precursor (Run 10). Now, in order to prevent the formation of iron oxide, the synthesis of the FePt nanoparticles in the autoclave using the hydrogen release reagent or stronger reducing agent than 1,2-hexadecanediol is in progress.

4. CONCLUSIONS

We have succeeded to obtain partially ordered FePt nanoparticles at 400 °C using an autoclave and the resulting nanoparticles were easily dissolved in hexane. The ordering degree is found to be dependant on the reaction time and temperature. Direct synthesis of $L1_0$-FePt nanoparticles is quite important in the light of their facile application to ultra high-density magnetic recording media and nanocomposite magnets. The development of direct synthesis of high quality $L1_0$-FePt nanoparticles without iron oxide species is under investigation.

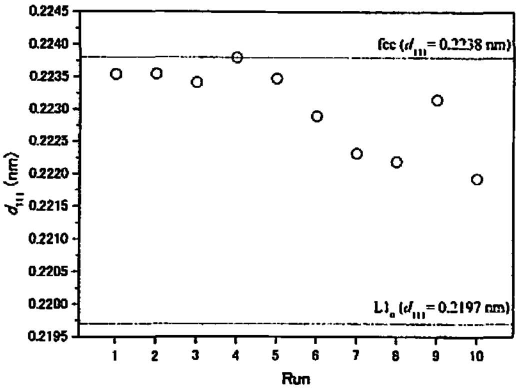

Figure 4. The (111) lattice spacings of FePt nanoparticles determined by XRD peak positions.

5. Acknowledgment

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6. References

[1] 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).

[2] S. Sun, C. B. Murray, D. Weller, L. Folks, and A. Moser, *Science*, **287**, 1989–1992 (2000).

[3] M. Nakaya, Y. Tsuchiya, K. Ito, Y. Oumi, T. Sano, and T. Teranishi, *Chem. Lett.*, **33**, 130–131 (2004).

[4] M. Nakaya and T. Teranishi, *Trans. Mater. Res. Soc.Jpn.*,**30**(2), 579–582 (2005).

[5] M. Nakaya, M. Kanehara, and T. Teranishi, *Langmuir*, **22**, 3485-3487 (2006)

[6] M. Chen, J. P. Liu, and S. Sun, *J. Am. Chem. Soc.*, **126**, 8394–8395 (2004).

[7] S. Saita and S. Maenosono, *Chem. Mater.*, **17**, 3705–3710 (2005).

[8] O. Kitakami, Y. Shimada, K. Oikawa, H. Daimon, and K. Fukamachi, *Appl. Phys. Lett.*, **78**, 1104–1106 (2001).

[9] T. Maeda, T. Kai, A. Kikitsu, T. Nagase, and J. Akiyama, *Appl. Phys. Lett.*, **80**, 2147–2149 (2002).

[10] S. Kang, J. W. Harrell, and D. E. Nikles, *Nano Lett.*, **2**, 1033-1036 (2002).

[11] H. Kura and T. Sato, *J. Appl. Phys.*, **96**, 5771–5774 (2004).

[12] S. Yamamoto, Y. Morimoto, T. Ono, and M. Takano, *Appl. Phys. Lett.*, **87**, 032503(1–3) (2005).

[13] K. Elkins, D. Li, N. Poudyal, V. Nandwana, Z. Jin, K. Chen, and J. P. Liu, *J. Phys. D: Appl. Phys.*, **38**, 2306–2309 (2005).

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