Preparation of FePt Nanoparticles with a Narrow Size Distribution in Ionic Liquids

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Nanoparticles of FePt were prepared in two different ionic liquids (ILs). Because IL serves not only as a solvent but also as a surfactant, the particles prepared could be dispersed stably in hexane without adding other surfactants. The size distribution of the particles was found to be narrow without depending on a size-selection process such as centrifugation. In addition, the particle sizes and composition were found to depend on the kind of IL employed.

Nanoparticles of FePt attract much attention as a promising material for high density magnetic recording and hyperthermia. The chemical preparation of face-centered cubic (fcc) structured FePt nanoparticles in an organic solvent such as dioctyl ether (DOE) is a well-established method,[1] in which the addition of oleic acid and oleylamine enables the nanoparticles to be redispersed in hexane, and the monodispersed nanoparticles are obtained by using a size selection process with centrifugation. Thermal annealing converts the fcc FePt to face-centered tetragonal (fct) FePt, which has magnetic properties attractive as a material for recording media. To simplify the preparation process and to obtain the desired product in a high yield, many studies for the direct preparation[2,3] of fct FePt nanoparticles and the optimization of preparation conditions[4,5] have been carried out in recent years. In previous study, we focused on the crystal growth temperature of the formation of FePt alloy structure in chemical process.[6] It was confirmed that the nanoparticles which contain not only fcc phase but also fct phase can be obtainable by chemical process controlling the temperature.

We focused our attention on the use of ionic liquid (IL) not only as a solvent but also as a dispersant for the preparation of FePt nanoparticles. As the preparation of monodispersed Ir, Ag, Pt, and CoPt nanoparticles in ILs[7] was reported in the past, IL is considered to be a feasible solvent for preparing a dispersed solution of FePt nanoparticles with a controlled size distribution. The technique of producing monodispersed FePt nanoparticles without using centrifugation is expected to simplify the process and reduce the loss of materials. In this study we examined the size and composition of FePt nanoparticles prepared by using ILs instead of DOE.

In the preparation of FePt nanoparticles, 1-ethyl-3-methylimidazilium tetrafluoroborate (EMI-BF_4) or 1-butyl-1-methylpyrrolidinium trifluoromethanesulfonate (BMP-TF) was used as a solvent. These ILs were synthesized by Toyo Gosei Co., Ltd. First, $Pt(acac)_2$ (98.5 mg, 0.25 mmol), 1,2-hexadecanediol (198 mg, 0.75 mmol), and IL (20 mL) or dioctyl ether (DOE) (10 mL) were mixed and stirred in a flask under Ar gas atmosphere. After the resulting solution was heated to 100 °C, $Fe(CO)_5$ (0.07 mL, 0.5 mmol) was added. This mixture was then heated to 190 °C and kept at that temperature for 30 min. After particles were produced, the reaction mixture was allowed to cool to room temperature. Finally, the particles produced in the ILs were washed three times with acetone and collected in hexane. Essentially the same procedure was employed for the preparation of FePt nanoparticles in DOE, except for the addition of oleic acid (0.08 mL) and oleylamine (0.08 mL) as surfactants, the reaction temperature of 230 °C, and the washing once with ethanol and twice with acetone. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were obtained by JEM-1011 at an accelerating voltage of 100 kV. The particle size distribution curve of FePt nanoparticles were obtained from measurements of 100 particles in TEM images. Powder X-ray diffraction (XRD) patterns were recorded by Rigaku RINT-TTR with Cu Kα radiation (λ = 1.5405 Å). The sample for the XRD analysis was prepared by a drop of the hexane solution on a glass substrate and evaporating the hexane. The composition of the particles was measured by energy dispersive X-ray spectroscopy (TEM-EDX: HITACHI H8100A).

The size and morphology of the nanoparticles produced in DOE and ILs were examined by TEM and SAED images of each sample (Shown in Figure 1).

The particles produced in both ILs were well dispersed, like the particles produced in DOE with the addition of oleic acid and

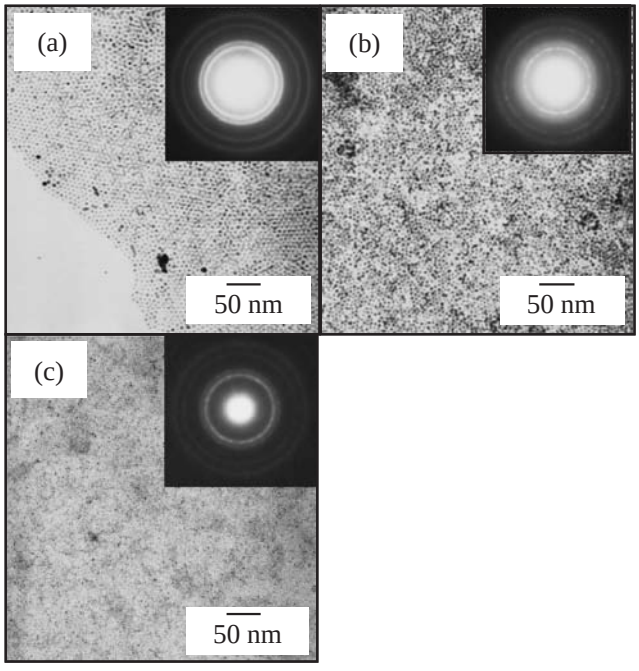

Figure 1. TEM images and SAED patterns of FePt nanoparticles made in (a) DOE, (b) EMI-BF_4, and (c) BMP-TF.

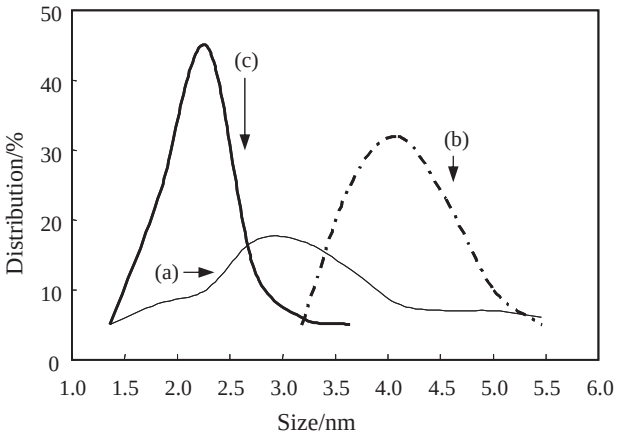

Figure 2. The particle size distribution curve of FePt nanoparticles chemically produced in (a) DOE, (b) EMI-BF_4, and (c) BMP-TF. The curves were estimated by measuring diameter of 100 particles in TEM image, i.e., 1% equal to number of particles.

oleylamine, suggesting a high redispersibility of the nanoparticles in hexane. Because no surfactants were added during the preparation in the ILs, it is suggested that IL serves not only as a solvent but also as a stabilizer.[8] The four rings observed in the SAED patterns are assigned to (111), (200), (220), and (311) reflections of the fcc structure of the FePt alloy. The XRD patterns (not shown) were also indicative of the formation of fcc FePt.

Figure 2 shows the particle size distribution of FePt nanoparticles chemically produced in each solution. The values of standard deviation for the particles made in EMI-BF_4, BMP-TF, and DOE were 0.55, 0.63, and 1.16 nm, respectively. The particles formed in ILs showed a size distribution narrower than that of the particles formed in DOE. This result indicates that the ionic species of ILs interact with the surface of growing FePt nanoparticles more strongly than oleic acid and oleylamine, because the stabilizers are known to control the growth of FePt nanoparticles.[4,5] Based on the fact that IL behaves both as solvent and as stabilizer in the present case, interionic interactions of ILs are assumed to narrow down the size distribution of grown particles. Our results show that the use of IL as a solvent resulted in the narrow size distribution of the particles without depending on the size-selection process involving centrifugation. Thus, the new method simplifies the preparation procedure of FePt nanoparticles and contributes to ca. 70% yield.

The mean diameters of the particles made in EMI-BF_4, BMP-TF, and DOE estimated by TEM micrographs were 4.3, 2.4, and 3.2 nm, respectively. This solvent dependency was also confirmed by XRD. Although the preparation in EMI-BF_4 and BMP-TF was carried out at the same temperature of 190 °C, the sizes of the nanoparticles produced in the two different ILs were different. Some properties of ILs such as viscosity, heat capacity, conductivity, and their dependence on temperature[9–11] are considered to influence the particle formation mechanism proposed by Sun et al.,[1,4] in which the reduction of $Pt(acac)_2$ to Pt leads to the formation of Pt-rich nuclei, and Fe atoms from thermally decomposed $Fe(CO)_5$ contribute to the particle growth. Thus, the size of FePt nanoparticles prepared in ILs can be controlled by the combination of anion and cation of ILs. The compositions of the particles formed in EMI-BF_4 and BMP-TF were $Fe_{30}Pt_{70}$, and $Fe_{50}Pt_{50}$, respectively. From the observation that a cloud of smoke caused by thermal decomposition of $Fe(CO)_5$ appeared in the flask during the reaction in EMI-BF_4,[12] we assumed that the coating of Pt-rich nuclei by Fe atoms in the growth process of FePt nanoparticles[4] did not proceed efficiently. As the thermal decomposition of $Fe(CO)_5$ occurs in gas phase, the difference in efficiency of Fe coating is considered to be originated from the differences in gas solubility, viscosity, or density depending on the kind of IL employed.[9] Further, smaller Pt nuclei may become richer in Fe compared to the larger Pt nuclei because of a surface area per Pt atom.[13] We obtained particles with the composition of nearly Fe:Pt = 50:50, which is desirable for conversion to fct structure, by the preparation in BMP-TF.

In conclusion, FePt nanoparticles with a narrow size distribution were successfully prepared in ILs of EMI-BF_4 and BMP-TF without using centrifugation. The nanoparticles prepared by this method can be redispersed in hexane without adding surfactants. The application of other ILs to the preparation of FePt nanoparticles is now being explored.

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References and Notes

1 S. Sun, C. B. Murray, D. Weller, L. Forks, A. Moser, *Science* **2000**, *287*, 1989.
2 M. S. Wellons, W. H. Morris, Z. Gai, J. Shen, J. Bentley, J. E. Wittig, C. M. Lukehart, *Chem. Mater.* **2007**, *19*, 2483.
3 I. Zafiropoulou, E. Devlin, N. Boukos, D. Niarchos, D. Petridis, V. Tzitzios, *Chem. Mater.* **2007**, *19*, 1898.
4 M. Chen, J. P. Liu, S. Sun, *J. Am. Chem. Soc.* **2004**, *126*, 8394.
5 H. L. Nguyen, L. E. M. Howard, G. W. Stinton, S. R. Giblin, B. K. Tanner, I. Terry, A. K. Hughes, I. M. Ross, A. Serres, J. S. O. Evans, *Chem. Mater.* **2006**, *18*, 6414.
6 T. Hachisu, T. Yotsumoto, A. Sugiyama, H. Iida, T. Nakanishi, T. Asahi, T. Osaka, *Chem. Lett.* **2008**, *37*, 840.
7 G. S. Fonseca, G. Machado, S. R. Teixeira, G. H. Fecher, J. Morais, M. C. M. Alves, J. Dupont, *J. Colloid Interface Sci.* **2006**, *301*, 193; Y. Wang, H. Yang, *Chem. Commun.* **2006**, 2545; C. W. Scheeren, G. Machado, J. Dupont, P. F. P. Fichtner, S. R. Texeira, *Inorg. Chem.* **2003**, *42*, 4738; Y. Wang, H. Yang, *J. Am. Chem. Soc.* **2005**, *127*, 5316.
8 Y. Zhou, *Curr. Nanosci.* **2005**, *1*, 35; A. B. McEwen, H. L. Ngo, K. Lecompte, J. L. Goldman, *J. Electrochem. Soc.* **1999**, *146*, 1687.
9 B. G. Trewyn, C. M. Whitman, V. S. Y. Lin, *Nano Lett.* **2004**, *4*, 2139.
10 L. Cammarata, S. G. Kazarian, P. A. Salter, T. Welton, *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192.
11 C. P. Fredlake, J. M. Crosthwaite, D. G. Hert, S. N. V. K. Aki, J. F. Brennecke, *J. Chem. Eng. Data* **2004**, *49*, 954.
12 Practically no smoke generation occurred during the reaction in BMP-TF.
13 H. G. Bagaria, D. T. Johnson, C. Srivastava, G. B. Thompson, M. Shamsuzzoha, D. E. Nikles, *J. Appl. Phys.* **2007**, *101*, 104313.

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