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Composition controlled synthesis of fcc-FePt nanoparticles using a modified polyol process

R. Justin Joseyphus · K. Shinoda · Y. Sato · K. Tohji · B. Jeyadevan

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Abstract A low temperature synthesis method using a modified polyol process is employed to synthesize FePt nanoparticles even at 393 K. The composition could be controlled using the above process by varying the reaction conditions to obtain $Fe_{50}Pt_{50}$ nanoparticles at 473 K. The magnetic properties of the fcc-FePt nanoparticles indicate that they are not completely superparamagnetic in spite of the smaller particle size.

Introduction

Ordered FePt nanoparticles of equi-atomic Fe and Pt are an important class of magnetic nanomaterials used for high density recording applications [1, 2]. The ordered fct-FePt nanoparticles are obtained from the disordered fcc-FePt on annealing at high temperatures [3]. $L1_0$-ordered FePt nanoparticles assume importance due to their large uniaxial magnetocrystalline anisotropy ($K_1 = 7 \times 10^6$ J/m^3) and chemical stability [4]. Most of the reported methods of synthesis use techniques like thermal decomposition of iron pentacarbonyl, which is environmentally unfriendly. However, the synthesis of FePt nanoparticles using much simpler process like polyol process has also been undertaken [5, 6]. In such cases FePt nanoparticles are synthesized using platinum acetylacetonate and $Fe(acac)_3$ at the boiling point of a polyol. The authors have already demonstrated that fct-FePt nanoparticles could be obtained without the requirement of a post-annealing step through slow reaction process at 573 K in tetraethylene glycol for a reaction duration of 3.5 h [7]. However, the particles obtained were polycrystalline and also the polymerization of polyol stained the surface of the particles and prevented their dispersion in organic solvent. The low temperature synthesis of FePt is suggested as an alternate to overcome the above drawbacks. Until now, the low temperature synthesis of FePt was found difficult due to the requirement of high temperatures for the reduction of Fe. Komarneni et al. have shown that microwave polyol process could be utilized to synthesis metals, alloys and compounds with controlled size and shapes at temperatures below 473 K [8–11]. Recently, we have successfully synthesized Fe in liquid polyols at temperatures as low as 393 K using a modified polyol process [12]. In polyol process, the metal salts are reduced to their corresponding metals in a polyol such as ethylene glycol. However, our studies have revealed that the properties of the particles such as size, structure, shape etc are controlled by the type of polyol, heating rate, type of metal precursors, additives etc [12–14] which could be utilized in modifying the conventional polyol process to obtain metals and alloys hitherto found difficult. In this study, we have incorporated the above parameters during the synthesis of FePt, one of which is the requirement of high concentration of NaOH. This has also paved the way for the low temperature synthesis of fct-FePt nanoparticles. In this paper, we present the composition-controlled synthesis of fcc-FePt nanoparticles using iron chloride ($FeCl_2 \cdot 4H_2O$) and hexacholoroplatinate ($H_2PtCl_6 \cdot 6H_2O$) as metal salts using a modified polyol process.

Experimental procedures

The precursors used in the synthesis of FePt are $FeCl_2 \cdot 4H_2O$ and $H_2PtCl_6 \cdot 6H_2O$. In a typical reaction, the Fe and

R. J. Joseyphus · K. Shinoda · Y. Sato · K. Tohji · B. Jeyadevan (✉)
Graduate School of Environmental Studies, Tohoku University, Aramaki, Aoba-ku, Sendai 980-8579, Japan
e-mail: jeya@mail.kankyo.tohoku.ac.jp

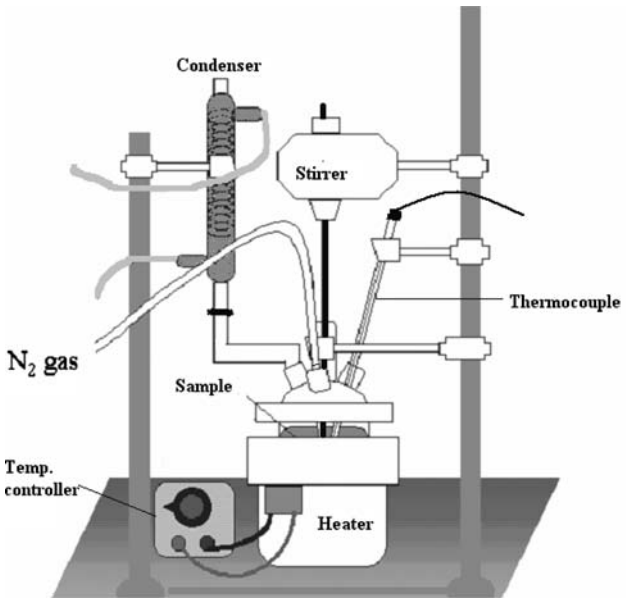

Fig. 1 The polyol process experimental set up

Pt salts along with NaOH are introduced in 100 mL of trimethylene glycol (TMEG) at room temperature in to the reaction vessel. Then, the vessel is placed in a mantle heater and heated at a rate of 15 K/min to specific temperatures under N_2 purging. The reaction temperature is monitored using a thermocouple. The metal ion-polyol solution was refluxed at the required temperatures (323–473 K) under constant mechanical stirring (160 rpm) at normal atmospheric pressure for a reaction duration of 1 h. The details of the experimental set up is shown in Fig. 1. The molar concentration of Fe and Pt salts are 0.01 M and 0.005 M, respectively and NaOH of varying molar concentration is used in TMEG at various reaction temperatures. The synthesized nanoparticles are characterized by X-ray diffraction (XRD) using a Cu target (Rigaku) for phase analysis and transmission electron microscopy (Hitachi) to determine the morphology. The grain sizes are estimated from the XRD line profile using the Scherrer's formula. The composition analysis was performed in a transmission electron microscope (Hitachi) in the energy dispersive mode. The magnetic characterization was undertaken in a SQUID magnetometer (Quantum design) at 5 and 300 K.

Results and discussion

Synthesis of FePt in polyols

The synthesis of FePt at low temperatures can be achieved only if both Fe and Pt are co-reduced. As iron chloride is reduced at 393 K in the presence hydroxyl ion, the selection of suitable Pt salt to be reduced under the above experimental conditions is very much necessary. Thus, FePt nanoparticles synthesis using iron chloride and platinum salts such as, $Pt(AcAc)_2$ *cis*-$Pt(Cl_2)(NH_3)_2$, H_2PtCl_6 and *cis*-$Pt(NO_2)(NH_3)_2$ was carried out in trimethylene glycol (TMEG). Among the platinum salts used in the above study, H_2PtCl_6 was found to be a better choice as the reduction without hydroxyl ions is found to occur at 423 K. Furthermore, platinum particles were formed even at temperatures as low as 343 K depending on the hydroxyl ion concentration. Thus it may be possible to obtain FePt particles at low temperatures and the FePt synthesis was attempted at various temperatures below 393 K. The hydroxyl ion concentration of 0.05 M was chosen so that the platinum particles were reduced at temperatures close to that of iron, for a Fe/Pt molar ratio of 2. Table 1 shows the variation in the grain size and composition of the FePt nanoparticles synthesized in TMEG at various temperatures upto 393 K. At 323 K, the particles are rich in Pt as seen from the composition which is Fe_9Pt_{91}. The Fe content in the sample increases with temperature drastically from 9 to 43 at.% when the temperature is increased to 393 K. The XRD pattern of the FePt nanoparticles synthesized at 393 K in TMEG is shown in Fig. 2. The grain size of the sample found from XRD pattern is around 2.4 nm and the particle size is around 2–3 nm as observed from the TEM micrograph shown in Fig. 3. The samples

Table 1 The variation in the grain size and composition of the FePt nanoparticles synthesized in TMEG at various reaction temperatures

Temperature (K)	Grain size (nm)	Composition
323	1.7	Fe_9Pt_{91}
353	2.3	$Fe_{27}Pt_{73}$
393	2.4	$Fe_{43}Pt_{57}$

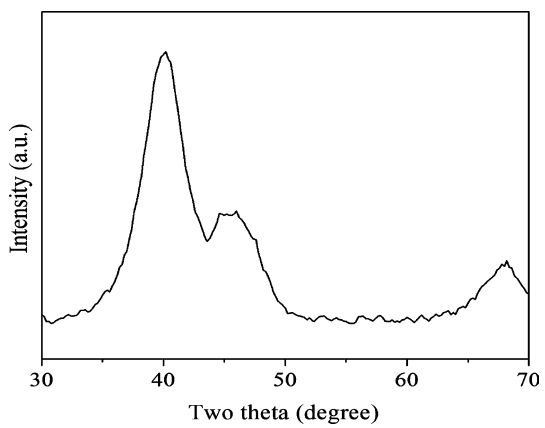

Fig. 2 The XRD pattern of the FePt nanoparticles synthesized in TMEG at 393 K

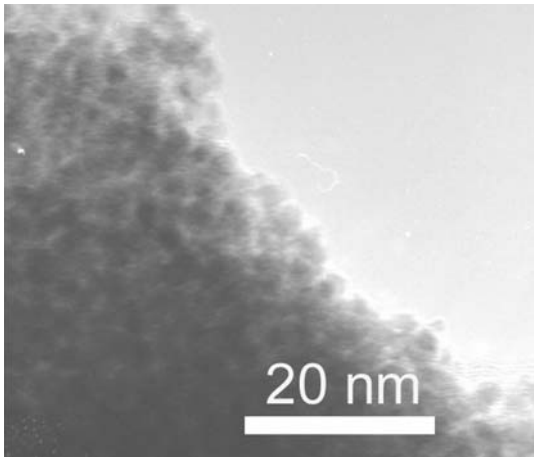

Fig. 3 The TEM micrograph of the FePt nanoparticles synthesized in TMEG at 393 K

also exhibited a saturation magnetization of 10 emu/g and coercivity of nearly 70 Oe which suggests that they are magnetic. Eventhough the composition analysis of the sample revealed $Fe_{43}Pt_{57}$ which indicated the formation of FePt phase at 393 K, the particles are not homogeneous and FePt particles rich in Fe are also present. The $Fe_{50}Pt_{50}$ composition is required to obtain fct-FePt [15] and hence for recording applications, homogeneous $Fe_{50}Pt_{50}$ composition is necessary. The inhomogeneity in the FePt composition at 393 K may be due to the mismatch in the reduction potential of polyols on Fe and Pt. In the presence of hydroxyl ions at 393 K, the reduction of Fe is found to occur within 2–3 min whereas all the Pt ions are reduced to Pt in 10–15 min. However, at higher temperature the entire Pt may be reduced along with Fe. The synthesis at 473 K may enable the complete reduction of Fe and Pt for a particular hydroxyl ion concentration which may result in homogeneous composition. Hence the reaction was carried out at 473 K in order to obtain homogeneous $Fe_{50}Pt_{50}$.

Composition controlled fcc-$Fe_{50}Pt_{50}$

Since it was suggested that the homogeneous composition could be obtained at 473 K, the reaction was carried out at this temperature for a Fe/Pt molar ratio of 2. The coreduction can be fine tuned by either varying the temperature or hydroxyl ion concentration. For complete reduction, the reaction has to be carried out at 473 K and hence the hydroxyl ion concentration is varied.

Table 2 shows the lattice parameter, grain size and phases present for the samples synthesized in TMEG at 473 K on varying the $[OH^-]$/Fe ratio. Without hydroxyl ions the FePt nanoparticles are Pt rich whereas with increasing hydroxyl ions the composition of FePt could be controlled. The lattice parameter obtained without hydroxyl

Table 2 The lattice parameter, grain size and phases present for the FePt samples synthesized in TMEG at 473 K on varying the $[OH^-]$/Fe ratio

$[OH^-]$/Fe ratio	Lattice parameter, a (±0.005 Å)	Grain size, D (nm)	Phases
0	3.916	8.2	Pt rich
2.5	3.892	3.3	Fe + $Fe_{30}Pt_{70}$
5	3.892	2.4	$Fe_{50}Pt_{50}$
10	3.917	2.2	$Fe_{70}Pt_{30}$ + Fe
20	3.913	2.0	FePt + Fe + Fe_3O_4

ions is 3.916 Å, which is close to the cubic Pt (PDF # 040802). The composition of the FePt nanoparticles obtained from EDX analysis is $Fe_{13}Pt_{87}$. When the $[OH^-]$/Fe ratio is further increased to 2.5 both Fe and FePt are found to be present. This may be due to the insufficient hydroxyl ion concentration required to coreduce both Fe and Pt. Here, Pt is reduced faster compared to Fe and hence all the Fe are not combined with Pt resulting in Pt rich FePt and Fe. However, when the $[OH^-]$/Fe ratio is increased to 5, Fe and Pt are reduced in equal amount to form $Fe_{50}Pt_{50}$ nanoparticles. The equiatomic composition of $Fe_{50}Pt_{50}$ thus achieved is almost homogeneous with a variation of only ±3 at.%. The lattice parameter is found to decrease to 3.892 Å which is close to that of fcc-FePt (PDF # 290718). The grain size is also found to decrease from 8.2 nm without hydroxyl ions to 2.4 nm for a $[OH^-]$/Fe ratio of 5. When the OH/Fe ratio is increased further the grain size decreases further and other phases such as Fe and Fe_3O_4 begin to appear. This is due to the fact that with increasing $[OH^-]$/Fe ratio, the coreduction of Fe and Pt could not be achieved due to the decrease in the reduction temperature of Pt and increasing volume fraction of Fe which subsequently gets oxidized. The increase in the lattice parameter is due to the formation of Fe rich phase. Figure 4 shows the XRD pattern of the FePt nanoparticles synthesized in TMEG at 473 K (a) without hydroxyl ions and (b) with $[OH^-]$/Fe ratio 5. The XRD pattern confirmed that oxides or Fe phase are absent in both cases. The XRD line broadening for the samples with a $[OH^-]$/Fe ratio of 5 suggested that the grain size decreases with the presence of hydroxyl ions. The TEM analysis of the particles synthesized with hydroxyl ions showed particle size in the range 2–3 nm as shown in Fig. 5. The particle size is closer to the average grain size obtained from XRD. This indicates that the particles are single crystalline and are single domain. The above studies indicate that fcc-FePt nanoparticles of the composition $Fe_{50}Pt_{50}$ could be obtained in TMEG with a $[OH^-]$/Fe ratio of 5. The magnetic properties of the $Fe_{50}Pt_{50}$ will be interesting to know if the particle posses high coercivity due to ordering or particle size.

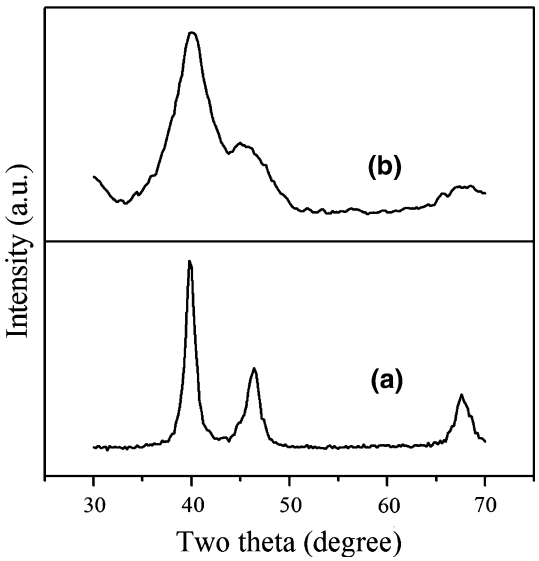

Fig. 4 The XRD pattern of the FePt nanoparticles synthesized in TMEG at 473 K (**a**) without hydroxyl ions (**b**) with $[OH^-]$/Fe ratio 5

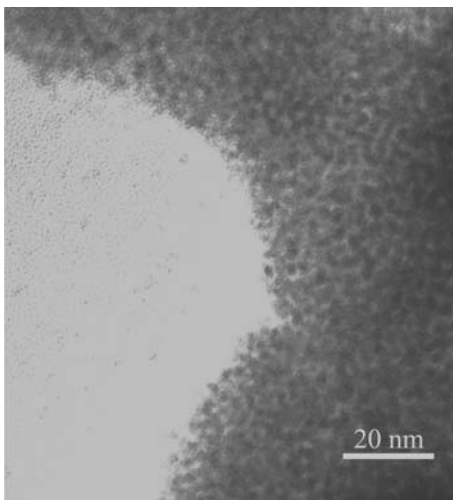

Fig. 5 The TEM micrograph of the $Fe_{50}Pt_{50}$ nanoparticles synthesized in TMEG at 473 K

Magnetic properties of $Fe_{50}Pt_{50}$

The coercivity of a magnetic material is a function of the particle size. In FePt nanoparticles, the coercivity depends on (a) ordering parameter and (b) particle size. The disordered fcc FePt nanoparticles are magnetically soft and hence show low coercivity. Figure 6 shows the hysteresis loop of the $Fe_{50}Pt_{50}$ nanoparticles measured in a SQUID at 300 and 5 K. The coercivity of the 2–3 nm particles is around 250 Oe at room temperature as shown in the inset of Fig. 5. The presence of nonzero value for the coercivity indicates that all the particles are not completely superparamagnetic whereas such disordered fcc FePt nanoparticles of 4 nm are found to

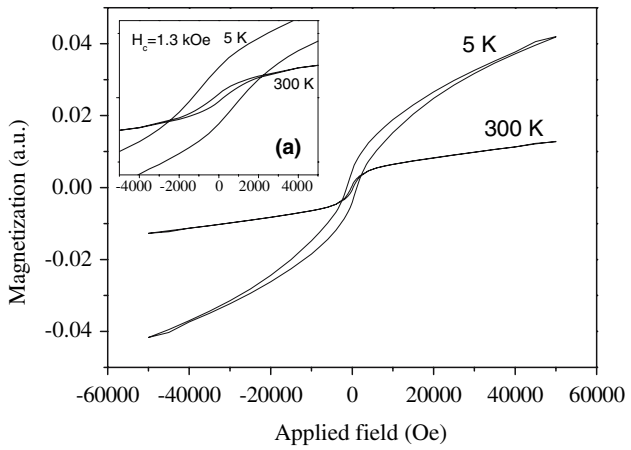

Fig. 6 The hysteresis loop of the $Fe_{50}Pt_{50}$ nanoparticles synthesized in TMEG at 473 K. (**a**) portion of the hysteresis loop showing the coercivity at 300 and 5 K

show zero coercivity [16]. This suggests that some amount of ordering should be present in the sample which is also confirmed from the coercivity of 1.3 kOe at 5 K. However, the ordering could not be much pronounced in these samples as particles size above 4 nm is required to obtain significant ordering [17]. Further work is in progress to obtain particles of diameter larger than 4 nm. The above studies have also opened up the possibility that ordered FePt could be formed at low temperatures in polyols. Further improvement in the coercivity of the nanoparticles could be obtained on increasing the particle size.

Conclusions

Composition controlled $Fe_{50}Pt_{50}$ nanoparticles were synthesized using a modified polyol process by reducing Fe and Pt at low temperatures. The fcc-$Fe_{50}Pt_{50}$ nanoparticles are not completely superparamagnetic at room temperature inspite of their smaller size of 2–3 nm. Partial ordering is also expected to be present in the as-synthesized FePt nanoparticles which exhibit coercivity at low temperature.

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