

Composition study of FePt nanoparticles synthesized from modified polyol process

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Five different conditions for modified polyol processes using iron(III) acetylacetonate and platinum(II) acetylacetonate as starting materials reveal significantly different products in terms of composition. The initial Fe:Pt molar ratio is not retained in the final products and Pt-rich nanoparticles are obtained from 1:1 molar ratio of Fe:Pt sources. The imbalance between Fe and Pt indicate that the nanoparticles formation can be explained by the heterocoagulation mechanism rather than the binary nucleation model. The increase in refluxing time and initial Fe:Pt molar ratio improved the amount of Fe in nanoparticles. However, the highest molar ratio of 3:1 apparently affected the uniformity of particles. The co-existence of iron oxide and Pt-rich nanoparticles is clearly evident in the case of 3:1 molar ratio combined with 1,2 hexadecanediol as a reducing agent.

Keywords: Magnetic nanoparticle, FePt, Modified polyol process, Metal acetylacetonate, Molar ratio

Chemical synthesis of magnetic nanoparticles has rapidly been developed for novel technological applications in the past decade¹. Iron oxides and spinel ferrites nanoparticles are majorly implemented in medical science because of their biocompatibility and superparamagnetic characteristics^{2,3}. On the other hand, applications of iron-platinum (FePt) nanoparticles are in nanocomposite magnets and ultrahigh density bit patterned media for the next generation hard disk drives⁴. FePt nanoparticles are commonly synthesized from the thermal decomposition of iron pentacarbonyl (Fe(CO)₅) and the reduction of platinum(II) acetylacetonate (Pt(acac)₂) by polyalcohol (i.e. 1,2 hexadecanediol) in ether solvents with oleic acid and oleylamine as surfactants⁴.

In order to obtain ferromagnetism required for magnetic recording applications, the Fe:Pt atomic ratio in these nanoparticles has to be closed to 1:1. The superparamagnetic particles with comparable fractions of Fe and Pt in the disordered face-centered cubic structure can then be transformed into the ferromagnetic face-centered tetragonal ordering by the annealing process. However, typical outcomes

show a large variation in composition (ranging from 0.27:1 to 2.33:1)⁵ among nanoparticles posing a major obstacle to implement the self-assembly of annealed FePt nanoparticles in recording. The lack of homogeneity is partly due the volatility of Fe(CO)₅ during the reaction. This reason combined with the safety concern over Fe(CO)₅ led to the interest in alternative procedures including the modified polyol process⁶⁻¹¹. The process involved the co-reduction of less toxic iron(III) acetylacetonate (Fe(acac)₃) with Pt(acac)₂. Nandwana *et al.*⁷ demonstrated that monodispersed FePt nanoparticles can be obtained without any reducing agent in this reaction and suggested that 1,2 hexadecanediol may only be necessary in the case of relatively low synthesis temperature. Furthermore, Nakaya *et al.*⁸ successfully synthesized FePt nanoparticles by using excess surfactants in an absence of conventional ether solvents. To improve a control over the composition of FePt nanoparticles, the evolution in size and composition was studied by Beck Jr *et al.*¹¹ and the heterocoagulation model of nanoparticles formation from the modified polyol process was verified. In contrast to the binary nucleation model proposed for the Fe(CO)₅ reaction¹², the heterocoagulation mechanism consists of two stages¹¹. In the former

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stage, Pt-rich nuclei are mostly formed and their surfaces are adsorbed by Fe₃O₄ clusters and CO. The Fe₃O₄ clusters are reduced to Fe atoms by the virtue of the CO-spill over process and then diffused into Pt-rich nuclei at high temperature in the latter stage of FePt formation. It was also suggested by Harpeness and Gedanken that the carbon atoms which are produced from the decomposition reaction coated on FePt nanoparticle surface helps to reduce Fe ion to its metallic state¹³.

In this work, we have adopted the heterocoagulation model to explain the compositional variation in FePt nanoparticles synthesized from five different procedures using Fe(acac)₃ and Pt(acac)₂ as starting materials. The dependence of the composition of nanoparticles on the amount of reagents and the refluxing condition will also be essential information in the development of a simple, effective and environmental friendly route to synthesize FePt nanoparticles.

Experimental Procedure

Fe(acac)₃ (99.9%), Pt(acac)₂ (97%), oleic acid (90%), oleylamine (70%), 1,2-hexadecanediol (90%) were purchased from Sigma-Aldrich Company and used as received. Benzyl ether was degassed for 15 min before each use. Other AR grade organic solvents used for purification (e.g. hexane and absolute ethanol) were used as purchased. All manipulations were performed under dry nitrogen (N₂) using standard Schlenk line techniques unless otherwise stated. As shown in Table 1, five reactions differ in terms of the molar ratio of metal acetylacetonates, the use of reducing agents as well as refluxing conditions. Reactions 1 and 2 used a 1:1 molar ratio of Fe and Pt sources whereas the ratio was increased to 1.5:1 in reaction 3 and 3:1 in reactions 4 and 5. Since the reducing agents may not be necessary for the modified polyol process at high temperatures, 1,2-hexadecanediol were employed only in reaction 5. In addition to the variation of refluxing time, the refluxing temperature of 240°C is

used instead of 300°C in reaction 5 because of the low boiling point of 1,2-hexadecanediol.

The reactions between Fe(acac)₃ and Pt(acac)₂ took place in a 100 mL Schlenk flask. Oxygen was removed from the reaction flask *in vacuo* before being filled with nitrogen. Surfactants and 20 mL benzyl ether were added to the flask. Under constant stirring and nitrogen flow, the solution was heated and allowed to reflux at a temperature shown in Table 1 for 0.5-3.0 h. The product was then cooled to room temperature under N₂. The particles were precipitated by addition of ethanol and then isolated by centrifugation. The obtained precipitate was re-dispersed in hexane, followed by centrifugation. This washing procedure was repeated for three times and then, the washed particles were dispersed in hexane with the presence of small amount (*ca.* 0.05 mL) of oleic acid and oleylamine, followed by bubbling with N₂ to remove O₂. The colloids were stored in glass bottles in a refrigerator at 4°C. In the characterizations, samples were prepared by depositing the colloid on carbon-coated copper grid and evaporating the solvent at room temperature. The morphology of the products was examined by transmission electron microscopy (TEM) and the elemental composition was probed by energy dispersive spectroscopy (EDS).

Results and Discussion

The as-synthesized nanoparticles are stabilized in carrier liquids without the sedimentation for more than a year. Oleic acid and oleylamine, acting as surfactants, prevent these nanoparticles from agglomeration and regulate their size^{14,15}. In every reaction, the amount of each surfactant is constant at 5 mmol because a preliminary experiment using 0.5 mmol of oleic acid and oleylamine failed to obtain nanoparticles proving that sufficient surfactants are needed in the synthesis of nanoparticles from metal acetylacetonates. From TEM images in Fig. 1, these five reactions give rise to products of under 10 nm in size. The nanoparticles from reaction 1 (Fig. 1a) are spheroidal in shape. Interestingly, the nanoparticles

Table 1—Reaction conditions and Fe:Pt atomic ratio of nanoparticles measured by EDS

Reaction	Reagents (mmol)		Reducing agent	Refluxing		Fe:Pt atomic ratio
	Fe(acac) ₃	Pt(acac) ₂		temperature (°C)	time (h)	
1	0.5	0.5	-	300	0.5	0.11:1
2	0.5	0.5	-	300	2.0	0.37:1
3	0.75	0.5	-	300	3.0	0.69:1
4	1.5	0.5	-	300	2.0	2.94:1
5	1.5	0.5	1,2-hexa decanediol	240	2.0	2.16:1

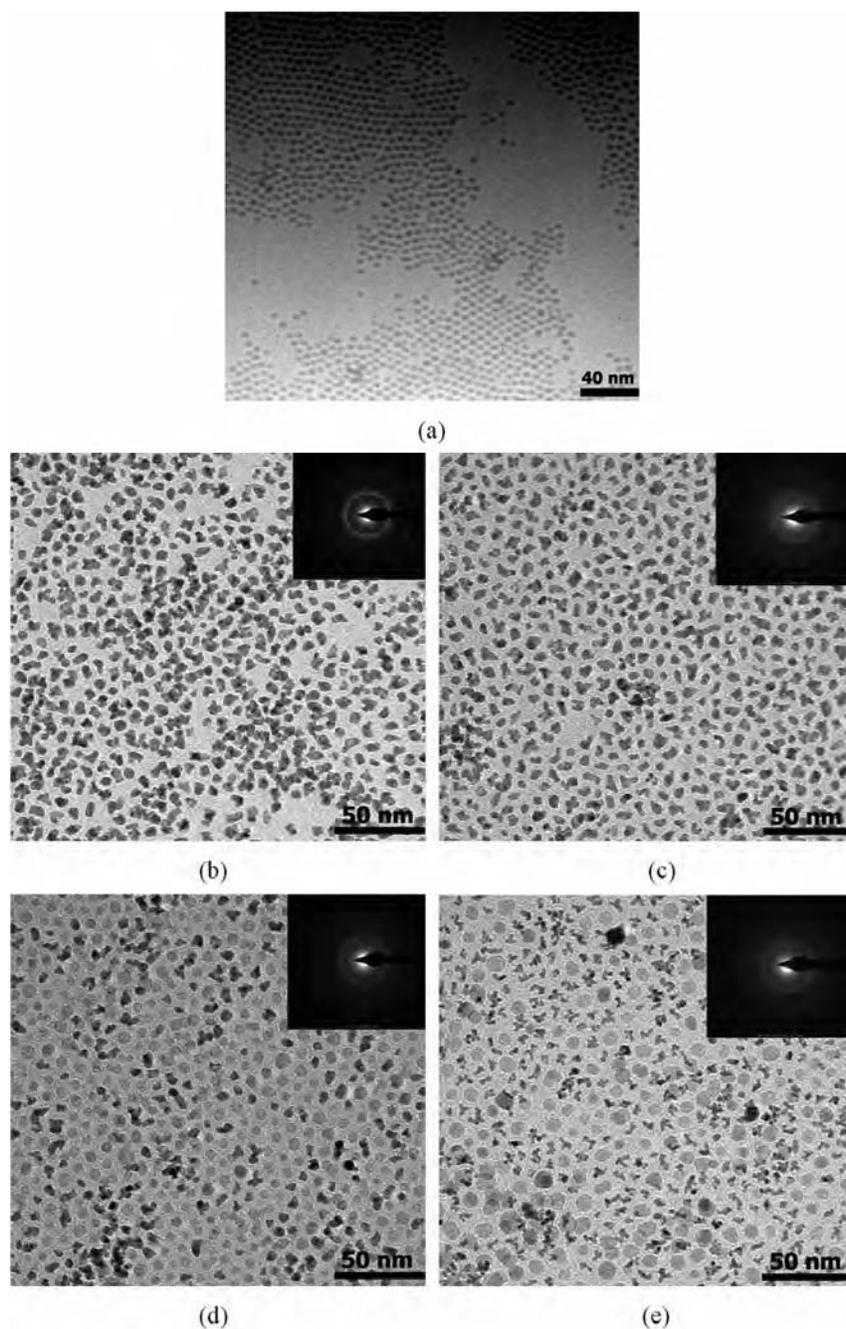


Fig 1—TEM images of nanoparticles synthesized from reactions (a) 1, (b) 2, (c) 3, (d) 4 and (e) 5

exhibit self-assemble pattern in a short range on the solid substrate because they are uniform in size and shape. It is noted that uniformity in size and shape from other reactions is degraded as the nanoparticles become more irregular. The large morphological and size variation in reaction 4 (Fig. 1d) implies the possible existence of two different groups of nanoparticles. The iron oxides appear lighter in color and spheroidal in shape whereas the smaller irregular

nanoparticles could be Pt-rich. In Fig. 1e, the addition of the reducing agent reinforces this notion by increasing the size of nanoparticles in the former group. The diffraction patterns of the nanoparticles are also shown in the insets of Fig. 1(b)-(e). The patterns clearly show the diffracted rings indicating that the crystalline phases of the nanoparticles were obtained. However, the numbers of rings are not sufficient to determine the structural phases.

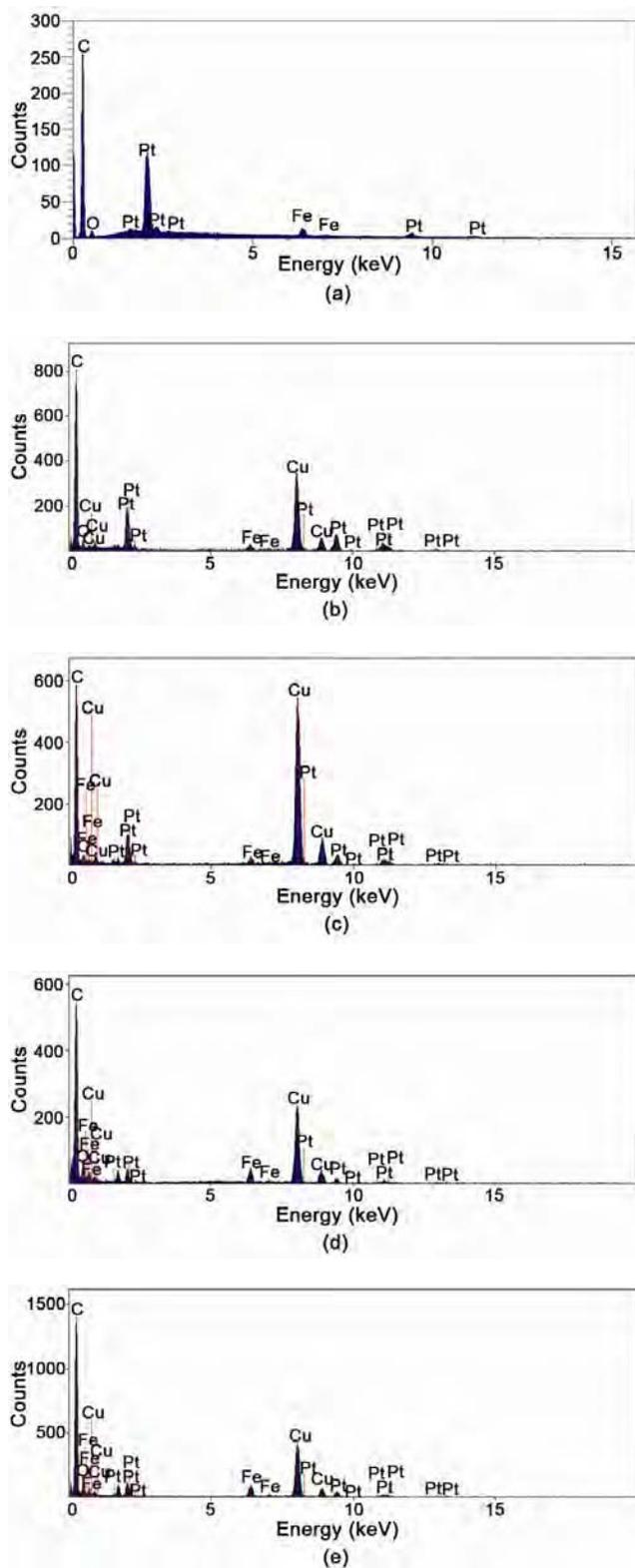


Fig 2—EDS spectra of nanoparticles synthesized from reactions (a) 1, (b) 2, (c) 3, (d) 4 and (e) 5

The EDS spectra of nanoparticles synthesized from reactions 1 to 5 are shown in Fig. 2. Elemental compositions of the colloid deposits in Table 1 show a large variation with the synthetic procedures. Initial molar ratios of metal acetylacetonates are not carried over to the final product. Reaction 1 whose refluxing time is the shortest (0.5 h) shows the most Pt rich particles even though the molar ratio of Fe:Pt sources are the same as reaction 2. A longer refluxing (2.0 h) in reaction 2 increased the Fe:Pt ratio to 0.37:1. It was previously studied using the change in color of each reagent⁷ and confirmed¹¹ that $\text{Fe}(\text{acac})_3$ and $\text{Pt}(\text{acac})_2$ could be decomposed at 180-190 and 130-140°C, respectively. The temperature used in all reactions should then be sufficiently high for both metal acetylacetonates. The low fraction of Fe in reactions 1 and 2 can be explained by using the heterocoagulation model. Fe atoms are not directly incorporated into nanoparticles but the reduction of $\text{Fe}(\text{acac})_3$ initially leads to Fe and different forms of iron oxide (e.g. Fe_3O_4 , Fe_2O_3 , FeO) on the surface of Pt-rich nuclei. The efficiency of the diffusion apparently depends on reaction conditions resulting in the compositional variation. The low Fe detection by EDS is explained by the separation between Pt-rich nuclei and large Fe-rich particles. The latter were removed by the process of centrifugation.

The Fe:Pt ratio is predictably increased by the increase in the initial molar ratio of metal acetylacetonates in reactions 3 and 4. However, an extra amount of $\text{Fe}(\text{acac})_3$ leads to the morphological variation in nanoparticles previously observed by TEM and Fe may end up in forms of excess iron oxide instead of FePt nanoparticles. Kamal *et al.*¹⁶ suggested that the further increase of iron oxide during the heat treatment may prevent the particles agglomeration. For as-synthesized nanoparticles from reaction 5, the Pt fraction is increased because the reduction $\text{Pt}(\text{acac})_2$ is facilitated by 1,2-hexadecanediol^{14,15}. However, the combination of an extra amount of $\text{Fe}(\text{acac})_3$ and the 1,2-hexadecanediol promotes the growth of separated iron oxide phase. Further treatments or condition adjustments are therefore needed to enhance the inclusion of Fe into Pt-rich nanoparticles.

Conclusions

Conditions in the polyol reduction process of $\text{Fe}(\text{acac})_3$ and $\text{Pt}(\text{acac})_2$ affect the formation of nanoparticles. The following conclusions can be drawn from this study:

- (i) Nanoparticles of comparable size can be obtained by using the benzyl ether solvent either with or without reducing agents and but their composition and homogeneity differ substantially.
- (ii) Higher fraction of Fe(acac)₃ in starting materials is recommended because the reduction to Fe and its incorporation into FePt nanoparticles are apparently more difficult to obtain than those of Pt. However, fractions of Fe are in forms of iron oxide which need further adjustment of conditions and treatments.
- (iii) Longer refluxing time at 240-300°C improves the amount of Fe in the resulting nanoparticles.

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