

Full Length Research Paper

Shape and composition study of iron-platinum (FePt) nanoalloy prepared by polyol process

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Metal nanoparticles have been attracting intensive interest because of potential applications in the areas of magnetism, electronics, etc. In this paper, Fe and Pt nanoparticles were first synthesized by decomposition of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and reduction of $\text{Pt}(\text{acac})_2$, respectively with 1,2-hexadecanediol and LiBEt_3H superhydride as the reducing reagent at high temperature in polyol process. Similarly, FePt nanoparticles were fabricated by Fe and Pt precursors in the presence of oleic acid, oleylamine and 1,2-hexadecanediol at 200°C , followed by refluxing at 250°C . Transmission electron microscopy (TEM) images showed that self-assembled 7 nm Fe nanoparticles are formed as polygon with good size distribution and closed to each other because of magnetic interactions dominance, whereas shapeless 2 to 6 nm Pt nanoparticles have broad size distribution about 18%. On the other hand, 4 nm iron-platinum (FePt) nanoparticles have dot shape with standard division about 10% in the same condition. The results of energy-dispersive X-ray spectroscopy (EDS) analysis indicated that the composition of FePt nanoparticles gives $\text{Fe}_{52}\text{Pt}_{48}$ stoichiometry. The X-ray diffraction (XRD) spectrums show that the structure of FePt nanocomposites change from face-centred-cubic (FCC) to face-centered tetragonal (FCT) phase by annealing process.

Key words: Reducing agent, iron-platinum (FePt) nanoparticles, equilibrium interactions, polyol method.

INTRODUCTION

The study of magnetic nanostructures is attracting much interest from both fundamental and applied point of views. Novel outstanding properties of such nanostructures can be directly correlated to their nanoscale in one or more dimensions (Martin et al., 1999). Iron-platinum (FePt) hard magnetic nanoparticles are of special interest as they may be used for future ultrahigh-density magnetic recording media (Murray et al., 2000).

Chemically synthesized magnetic nanoparticles have drawn much attention (Weller et al., 2000; Sun et al., 2000) due to the unique magnetic properties derived from small particle sizes and uniform size distribution. Chemical approach is a better way to fulfill this compared with physical ways, since particle size, shape and size distribution can be better controlled in chemical synthesis

(Chen and Nikles, 2002).

Nanocrystals of various shapes have been successfully synthesized over the past years. In particular, dot (Murray et al., 2000), rod (Peng, 2003; Peng and Burda, 2001; Link et al., 2000), spindle (Peng, 2003; Peng and Burda, 2001) and tetrapod-shaped (Peng, 2003; Peng and Burda, 2001; Manna et al. 2003) nanoparticles have been fabricated. The properties of nanosized materials are strongly influenced by their shape, it is very important to explore the growth mechanisms that lead to a particular nanocrystal shape to systematically produce the desired material. The solubility of particles of the critical size equals exactly the monomer concentration in the solution. Any crystals with smaller sizes will have higher solubility and, thus, will dissolve in the solution. The distribution can be refocused by injection of additional monomer, which compensates for the depletion due to the growth and shifts the critical size back to a smaller value. In this step of nanocrystal growth, the focusing time as well as the focused size changes with the different initial

concentration of the monomer as the time for depleting the monomer concentration varies (Burda et al., 2005).

The nucleation stage for the growth of anisotropic shapes plays a key role in determining the size/shape of the resulting nanocrystals. In the extremely small size range, the relative chemical potential is highly size-dependent, and even very sensitive to the configuration of the nuclei. Thermodynamically, all of the nanocrystals will grow toward the shape having the lowest energy at equilibrium. However, the formation dynamics can affect the shape of the formed nanocrystals. In principle, before the reaction reaches the equilibrium stage, any metastable nanocrystal shapes can be arrested by tuning the reaction conditions. Even spherical or dot-shaped nanocrystals are not thermodynamically stable unless they are arrested or capped by different protecting groups, which is true in the case of most nanocrystal systems (Peng, 2003; Peng et al., 1998). In summary, essentially at low monomer concentrations or long enough growth time, all nanocrystals grow toward the lowest chemical potential environment, and this leads to the generation of only dots. On the other hand, a median monomer concentration can support only an isotropic growth in a three dimensional growth stage and produces spindle shaped nanocrystals. At high monomer concentrations, the magic-sized nanoclusters promote the formation of rods or other elongated structures having metastability (Peng, 2003). In reality, the monomer concentration remaining in the reaction solution is always depleted by the nucleation and growth of the nanocrystals. If the reaction time is sufficiently long, the monomer concentration should drop to a level lower than that required for a given shape, and the nanocrystals should eventually evolve to the most stable dot shape if no additional monomers are added to the reaction system (Burda et al., 2005).

In the present work, first Fe and Pt nanoparticles were synthesized by chemical reduction of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{Pt}(\text{acac})_2$ at 250°C under N_2 atmosphere, respectively and then were dispersed in hexane solution after purification. After that, 4 nm FePt nanoparticles were fabricated with similar route. The shape, size and composition of nanoparticles during synthesis were studied by transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDS) analysis. The structure analysis was accomplished by X-ray diffraction (XRD) analysis.

EXPERIMENTALS

The Fe and Pt nanoparticles with size of 7 and 2 to 6 nm and FePt nanoparticles with size of 4 nm were prepared similarly using the synthesis described by Sun et al. (2003). Synthesis of the nanoparticles involves the reduction of platinum (II) acetylacetonate, $\text{Pt}(\text{acac})_2$ (197 mg, 0.5 mmol), and iron (II) chloride tetrahydrate ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$) in phenyl ether (25 ml) solvent in the presence of 1,2-hexadecanediol (520 mg, 2 mmol). Oleic acid (0.16 ml, 0.5 mmol) and oleylamin (0.17 ml, 0.5 mmol) surfactants

were added to the solvent at 100°C as a protective agent, in order to prevent agglomeration and oxidation. By adding LiBEt_3H superhydride under a blanket of N_2 at 200°C , followed by refluxing, the FePt nanoparticles were formed. The refluxing temperature was fixed at 250°C . The black reaction mixture was cooled to room temperature and then combined with ethanol to remove the impurity. The product was precipitated and separated by centrifugation (10000 rpm, 10 min). Any undissolved material was removed by centrifugation because of nanoparticles purification. Then, nanoparticles were dispersed in hexane solution in the presence of surfactants.

To determine the composition of FePt nanoparticles in nucleation and growth stage, EDS analysis (15 kV) was carried out. The XRD measurement was done by Seifert with Cu-K_α (wavelength = 1.54 Å) radiation after evaporation of hexane solution. The specification of the size and shape of nanoparticles were examined by TEM analysis using a Philips EM 208 TEM (100 kV) with a resolution of 200 kX.

RESULTS AND DISCUSSION

Figure 1a shows XRD patterns of the as-synthesized and annealed FePt nanoparticles. The annealing was done at 780°C for 3 h. The as-synthesized 3.5 nm particles exhibit a disordered face center cubic (FCC) structure with lattice constant 3.86 Å. The X-ray patterns in Figure 1b, confirm that the annealing process changes the disordered FCC structure into the tetragonal L1_0 structure. Figure 2 indicate the TEM images of the as-synthesized nanoparticles. In Figure 2a, the 2 to 6 nm Pt nanoparticles were created with broad size distribution of about 18% at 160°C by 1,2 hexadecanediol as reducing reagent. As shown in Figure 3a, the shapeless Pt nanoparticles have a broad size distribution. In Figure 2c, by adding intense LiBEt_3H superhydride to the reaction solution at 200°C , the Fe atoms were released from $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and attached to Pt core as a shell and 4 nm FePt nanoparticles were made because of core-shell formation for FePt nanoparticles. Finally, in Figure 2b, polygon 7 nm Fe nanoparticles were made by similar route with $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ precursor in the same condition. The distance between Fe nanoparticles is closed to each other because of magnetic interaction. In fact, the magnetic interactions dominant to the dipole-dipole attractive and steric repulsive interactions are decreased, because of surfactants and the distances between Fe nanoparticles.

Figure 3 shows the size measurement of 100 randomly selected particles fitting with a log normal curve. Figure 3a shows a broad size distribution of 2 to 7nm Pt nanoparticles with deviation of about 18% via one step growth process. Figure 3b indicates the self-assembled 4 nm FePt nanoparticles histogram as core-shell formation which has a narrow size distribution because of magnetic interactions stability with standard deviation of about 10%.

Figure 4 shows a characteristic spectrum collected by EDS analysis. By comparing the area under each peak to a set of standards with known element concentrations,

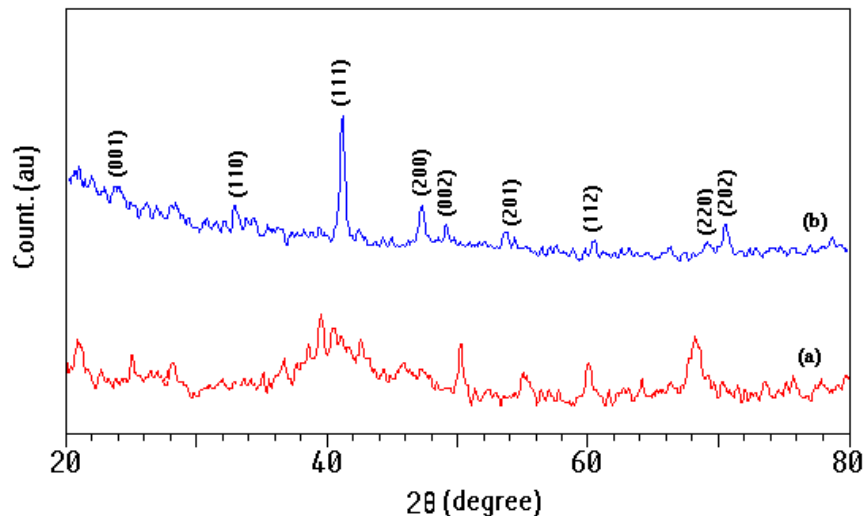


Figure 1. XRD patterns of the (a) as-synthesized and (b) annealed FePt nanoparticles at 780°C for 3 h.

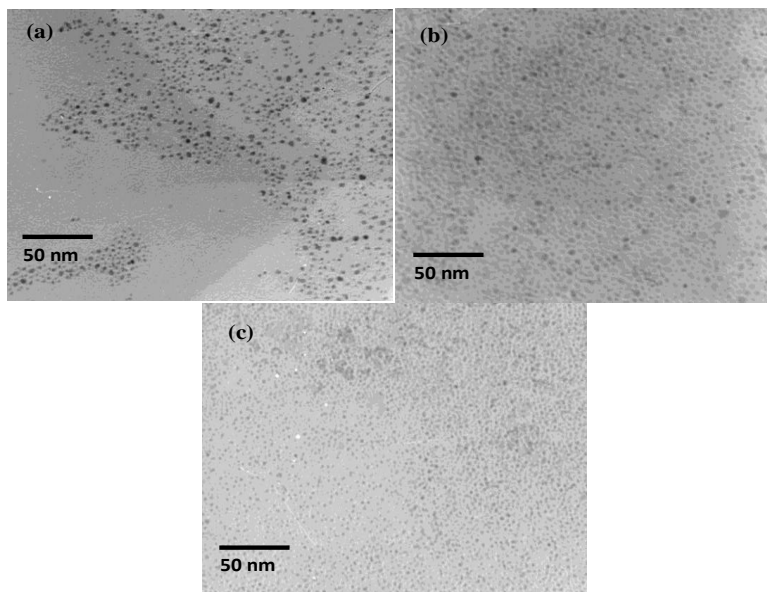


Figure 2. TEM images of the as-synthesis (a) Pt, (b) Fe and (c) FePt nanoparticles.

the concentration of the elements could be quantified, and the compositions gave Pt, Fe and $\text{Fe}_{52}\text{Pt}_{48}$ stoichiometry. Figure 3a shows the EDS diagram of Pt nanoparticles. Figure 4b indicates the element analysis of 7 nm Fe nanoparticles stoichiometry. By adding Fe precursor to the Pt, the FePt nanoparticles were made. It is realized that the Pt atoms are released by 1,2 hexadecadeniol as reducing reagent at 160°C and the core of FePt are constituted by Pt. As you can see in Figure 4c, by adding intense LiBEt₃H superhydride at

200°C, the Fe atoms are released from $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and attached to Pt core and form a shell quickly around the pt and the composition of nanoparticles changes to $\text{Fe}_{52}\text{Pt}_{48}$.

Conclusion

FePt nanoparticles were successfully synthesized with mean diameter of 4 nm by polyol method. The study of

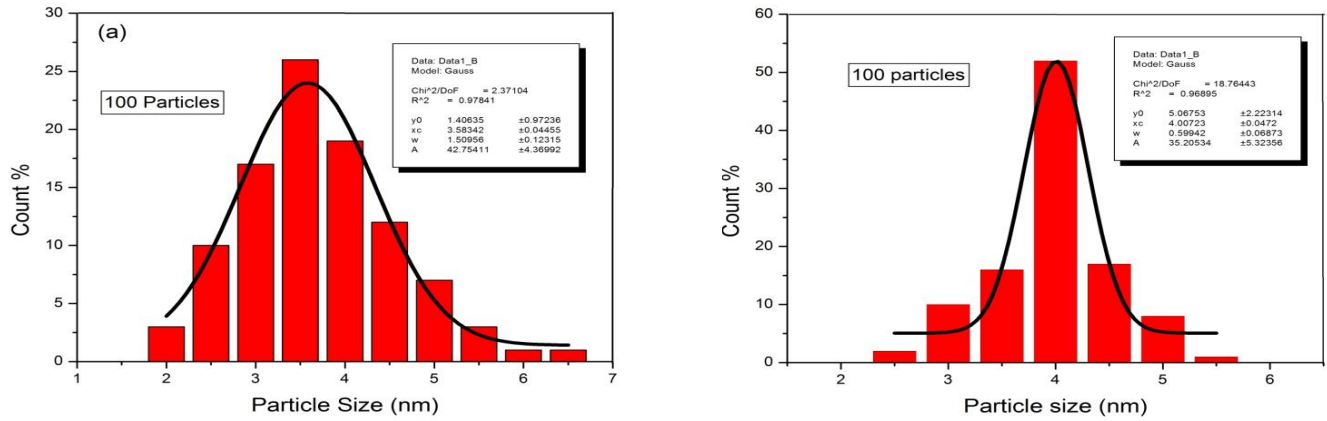


Figure 3. Particle diameter histogram of (a) Pt and (b) FePt nanoparticles; the line plotted corresponds to fit using a log normal distribution.

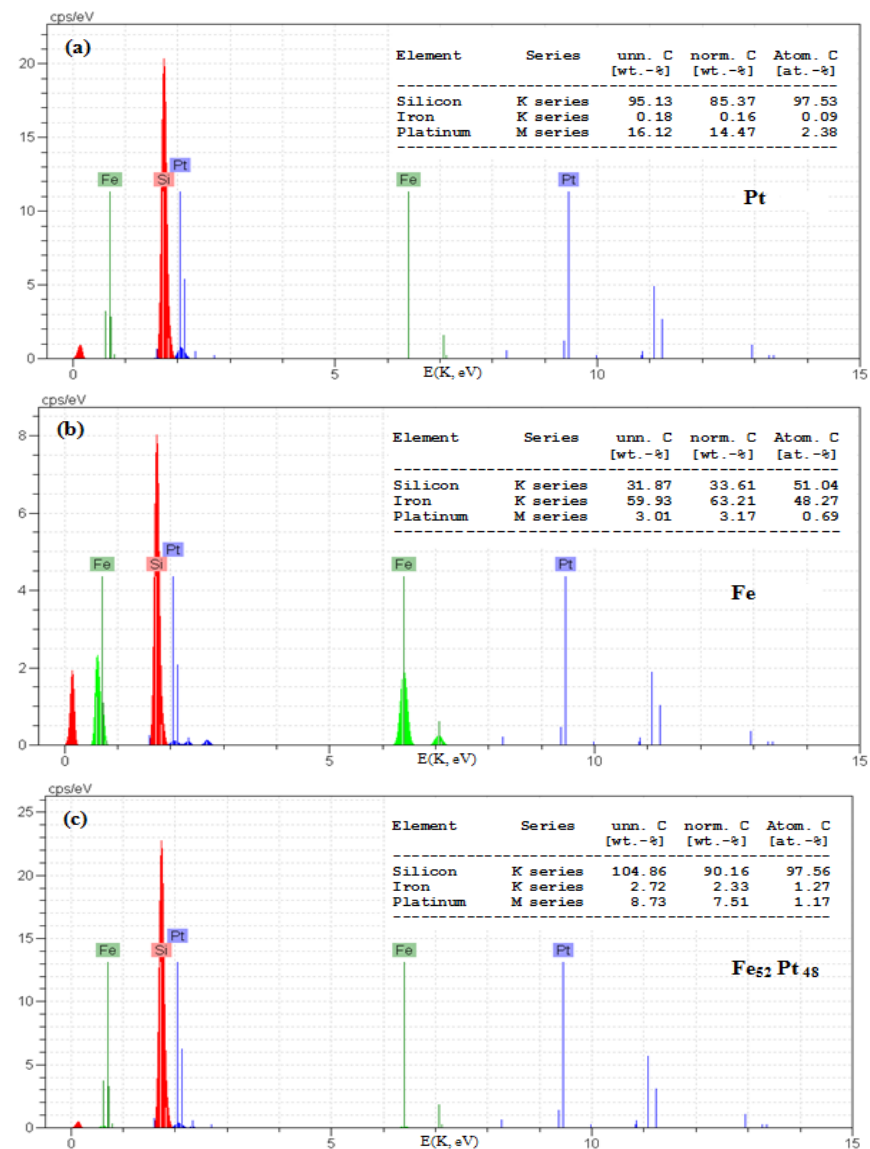


Figure 4. Energy dispersive spectroscopy (EDS) pattern of nanoparticles.

Pt, Fe and FePt nanoparticles was investigated. The TEM results demonstrated that 2 to 7nm Pt nanoparticles have disorder shape with unspecified distances between nanoparticles because of non equilibrium interactions. On the other hand, self-assembled 7 nm Fe nanoparticles have the regular polygon shape by magnetic interactions. For this case, the magnetic interactions dominant to the dipole-dipole attractive and steric repulsive interactions and the distances between nanoparticles are decreased and then closed to each other. Finally, by core-shell mechanism, the 4 nm FePt nanoparticles were achieved with 3.5 nm equilibrium distances between particles.

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