

Full Length Research Paper

Two step growth process of iron-platinum (FePt) nanoparticles

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In this paper, FePt nanocrystals have been prepared by adding LiBEt₃H to the phenyl ether solution of FeCl₂·4H₂O and Pt(acac)₂ precursors in the presence of oleic acid and oleylamine surfactants and 1,2-hexadecanediol as the reducing reagent at 195°C, followed by refluxing at 245°C by sol process. Similarly, Pt nanoparticles were made by adding 1, 2-hexadecanediol as the reducing reagent to the phenyl ether solution of Pt (acac)₂. The results of Transmission electron microscopy (TEM) images showed that 2 to 7 nm Pt nanoparticles are formed via one step growth whereas, bimetallic 4 nm magnetic FePt nanocrystals are formed by two step growth as core-shell with good uniformity in size and shape. The size measurement results indicated that the standard deviation of FePt nanoparticles improves to 8% because of two step growth process. In order to phase transition from fcc to L₁₀ structure, the FePt nanoparticles were annealed at 750°C for 4 h. The structural properties of FePt nanoparticles were analyzed by XRD spectra. To prevent FePt nanoparticles from sintering, NaCl particles were used as the separating media. SEM and TEM observations of FePt show the salt-matrix FePt nanoparticles with size of 40 nm after annealing.

Key words: Growth, iron-platinum (FePt) nanoparticles, equilibrium interactions, sol process.

INTRODUCTION

The study of magnetic nanostructures is attracting much interest from both fundamental and applied point of views (Jia and Misra, 2011). Novel outstanding properties of such nanostructures can be directly correlated to their nanoscale in one or more dimensions (Martin et al., 1999). Chemically synthesized magnetic nanoparticles have drawn much attention (Sun et al., 2000; Chen and Nikles, 2002; Shevchenko et al., 2002) 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. FePt hard magnetic nanoparticles are of special interest as they may be used for future ultrahigh-density magnetic recording media (Weller et al., 2000) and high performance permanent magnetic nanocomposites (Zeng et al., 2002). Previous work on the synthesis of FePt nanoparticles involved the reduction of Pt (acac)₂ and the decomposition of Fe(CO)₅

(Sun et al., 2001) and other works included addition of Ag, Co to the FePt nanoparticles to improve their physical and magnetic properties (Chen and Nikles, 2002; Kang et al., 2002). Recently, the formation of 4 nm FePt nanoparticles via the simultaneous reduction of FeCl₂ and Pt(acac)₂ as well as Fe and Pt acetylacetonate has also been reported (Sun et al., 2003; Jeyadevan et al., 2003).

The systematic adjustment of the reaction parameters, such as reaction time, temperature, concentration, and the selection of reagents and surfactants, can be used to control the size, shape, and quality of nanoparticles. During nanocrystals growth, the surfactants in solution adsorb reversibly to the surfaces of the nanocrystals, providing a dynamic organic shell that stabilizes the nanoparticles in solution and mediates their growth. Surfactants that bind more tightly to the nanoparticle surface or larger molecules providing greater steric hindrance slow the rate of materials addition to the nanoparticle, resulting in smaller average nanoparticle

size. When the nanoparticle sample reaches the desired size, further growth is arrested by quickly cooling the solution. The nanoparticles are then isolated from their growth solution (Burda et al., 2005).

$L1_0$ type materials have attracted more and more attention for ultra-high-density magnetic recording media (McCurrie and Gaunt, 1966; Bolzoni et al., 1984), which needs smaller particle size and very high uniaxial anisotropy ($K_u = 7 \times 10^6 \text{ J/m}^3$) materials to maintain thermal stability. Monodisperse assemblies of high anisotropy $L1_0$ FePt nanoparticle with diameters of the order of 4 nm are considered potential data storage medium beyond 1 Tbit/in² (Jia et al., 2011). However, annealing at temperatures $>500^\circ\text{C}$ is required to convert the as-deposited, chemically disordered face-centered cubic (fcc) FePt into the chemically ordered, high anisotropy $L1_0$ phase (Klemmer et al., 2002; Ding et al., 2003; Nakaya et al., 2004). This annealing step potentially allows a number of undesirable, thermally activated processes to occur including particle agglomeration and changes in oxidation state. To solve this dilemma, extensive efforts have been made to obtain monodisperse fct FePt nanoparticles. Doping by elements such as Ag, Au, and Cu in the FePt phase and mixing by NaCl salt particles with as-synthesis FePt nanoparticles has been tested since 2000, resulting in the onset of the fct phase problem (Mizuno et al., 2004; Yamamoto et al., 2005; Aslam et al., 2005; Zeng et al., 2003; Saita and Maenosono, 2004; Elkins et al., 2005). Recently investigations have been improved by chemical synthesis and magnetization behavior of FeRh–FePt nanostructures fabricated using a two-step procedure. The first step involved chemical synthesis of FeRh nanoparticles using a polyol co-reduction process accompanied by the second stage of encapsulation of FeRh nanoparticles with FePt. The FeRh–FePt nanoparticles were subsequently annealed in a salt matrix at 600°C for 3 h (Jia et al., 2010).

In present work, first 4 nm FePt nanoparticles were synthesized by sol process. After that, 2 to 7 nm Pt nanoparticles were made by Pt (acac)₂ precursor with similar route. The two step growth process was studied by TEM analysis by shape and size study of FePt nanoparticles during synthesis. The crystal structure of FePt before and after annealing has been investigated by XRD spectra. To prevent from agglomeration after annealing, the as-synthesis FePt were mixed with salt particles and the results were observed by SEM observations.

EXPERIMENTAL DETAILS

The Pt nanoparticles with size of 2 to 7 nm and FePt nanocrystals with size of 4 nm were made using the synthesis described by sol-gel process (Sun et al., 2003). Synthesis of the nanoparticles involves the reduction of Pt (acac)₂ (197 mg) and FeCl₂·4H₂O (139 mg) in phenyl ether solvent (25 ml) in the presence of 1,2-hexadecanediol (250 mg). Oleic acid (0.16 ml) and oleylamin (0.17

ml) surfactants were added to the solvent at 100°C as a protective agent, in order to prevent agglomeration and oxidation. By adding superhydride (LiBEt₃H) (2 ml) under a blanket of N₂ at 195°C , followed by refluxing, the FePt nanoparticles were formed. The refluxing temperature was fixed at 245°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 (8000 rpm, 15 min). Any undissolved material was removed by centrifugation because of nanoparticles purification. Then FePt nanoparticles were dispersed in hexane solution (40 ml) in the presence of surfactants. The 2 to 7 nm Pt nanoparticles were synthesis by Pt (acac)₂ with similar route.

The specification of the size and shape of the as-synthesis and annealed nanoparticles were examined by transmission electron microscopy (TEM) analysis using a Philips EM 208 (100 kV) with a resolution of 200 kX. The microstructure of annealed FePt nanoparticles was studied using a VEGA field emission scanning electron microscopy (SEM) (15 Kv). X-ray diffraction measurements (XRD) were performed to determine the crystallinity of $L1_0$ FePt nanoparticles structure, using a Seifert system with Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$).

RESULTS AND DISCUSSION

Figure 1 shows the XRD spectra of the FePt nanoparticles before and after annealing. The large width of the peaks indicates as-synthesis FePt nanoparticles superparamagnetism with fcc structure as shown in Figure 1a. Extra peaks appeared after annealing at 750°C for 4 h under a flow of 90% Ar + 10% H₂ as shown in Figure 2a. These peaks provide evidence of a chemical ordering phase ($L1_0$) transition.

The Pt nanoparticles were formed according to one step growth mechanism as follows. After the nuclei are formed from the solution, they grow via molecular addition. When the concentration drops below the critical level, nucleation stops and the particles continue to grow by molecular addition until the equilibrium concentration of the precipitated species is reached. Uniformity of the size distribution is achieved through a short nucleation period that generates all of the particles obtained at the end of the reaction followed by a self-sharpening growth process. At this stage, the smaller particles grow more rapidly than the larger ones because the free energy driving force is larger for smaller particles than for larger ones (Peng et al., 1998). Production of monodisperse colloids requires a temporally discrete nucleation event followed by slower controlled growth on the existing nuclei. A general scheme for preparing monodisperse nanostructures requires a single, temporally short nucleation event followed by slower growth on the existing nuclei (Murray et al., 1993). As long as the consumption of the reactants by the growth of the particles is not exceeded by the rate of precursor addition to the solution, no new nuclei form and the additional material can only add to the existing nuclei. Because the growth of any one nanocrystal is similar to that of all others, the initial size distribution is largely determined by the time over which the nuclei are formed and begin to grow.

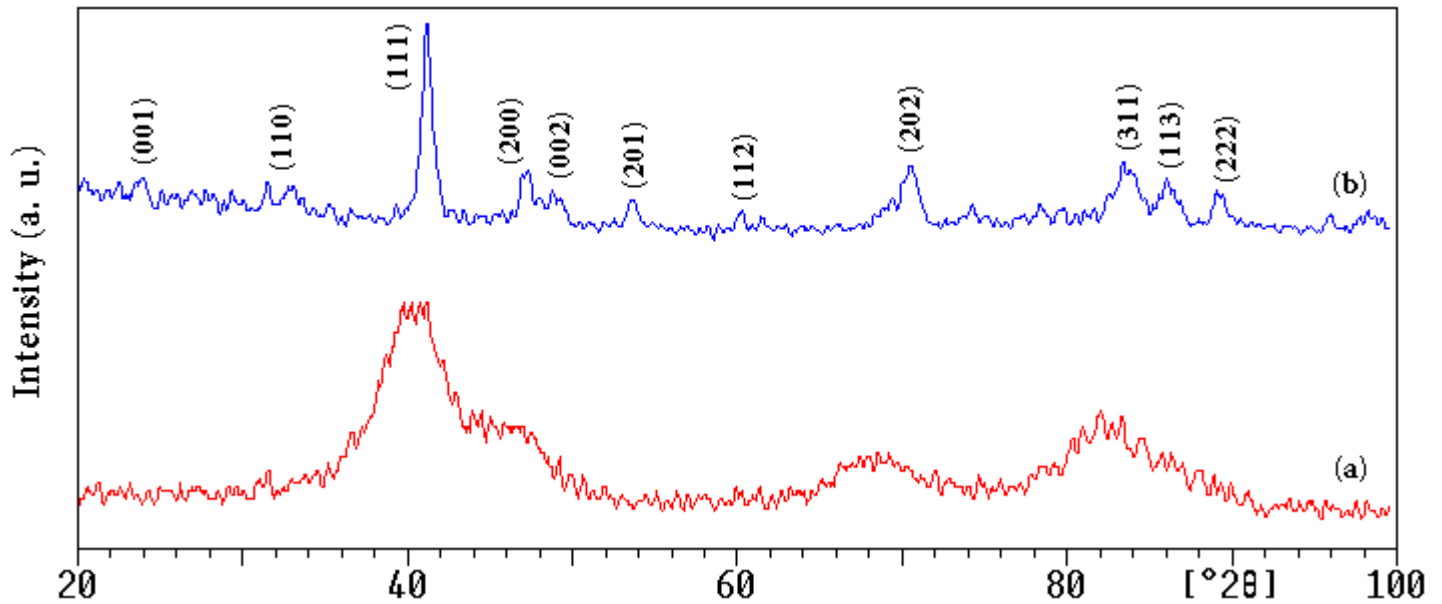


Figure 1. X-ray diffraction ($\lambda = 1.54 \text{ \AA}$, Cu-K α radiation) pattern of a) as-prepared and b) annealed FePt.

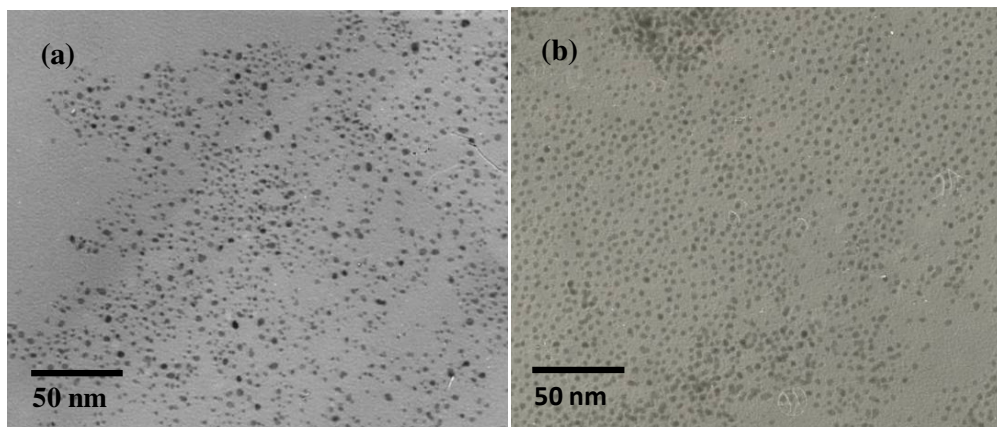


Figure 2. TEM images of the as-synthesis FePt nanoparticles after evaporation of hexane a) 2-7 nm Pt at 195°C (b) 4 nm FePt at 245°C.

Figure 2 shows TEM images of the as-synthesized Pt and FePt nanoparticles. In Figure 2a, the 2-7 nm Pt nanoparticles were made by 1, 2 hexadecadienol as reducing reagent at 190°C via one step growth process. As you can see the broad distribution of Pt nanoparticles is originated from nonmagnetic equilibrium interaction by one step growth. On the other hand in Figure 2b, 4 nm FePt nanoparticles with good size distribution were formed by two step growth process. In order to formation of FePt nanoparticles, the Pt atoms is first made by 1,2 hexadecadienol as reducing reagent at 195°C and then by adding intense LiBEt₃H supehydride to the reaction solution at 210°C, the Fe atoms are released from the FeCl₂·4H₂O and form a shell around the Pt core in the

second growth process. By formation of Fe shell around Pt atoms, the equilibrium interactions between FePt nanoparticles are increased regarding to magnetic interactions and stability of the FePt nanoparticles improves by two step growth.

Figure 3 shows the size measurement of 100 randomly selected particles fitting with a log normal curve. Figure 3(a) shows a broad size distribution of 2 to 7 Pt nanoparticles with deviation of about 18% via one step growth process whereas FePt nanoparticles with size of 4 nm prepared by two step growth growth have a narrow size distribution because of interactions with standard deviation of about 8% as shown in Figure 3(b).

In order to phase transition from fcc to L1₀, FePt

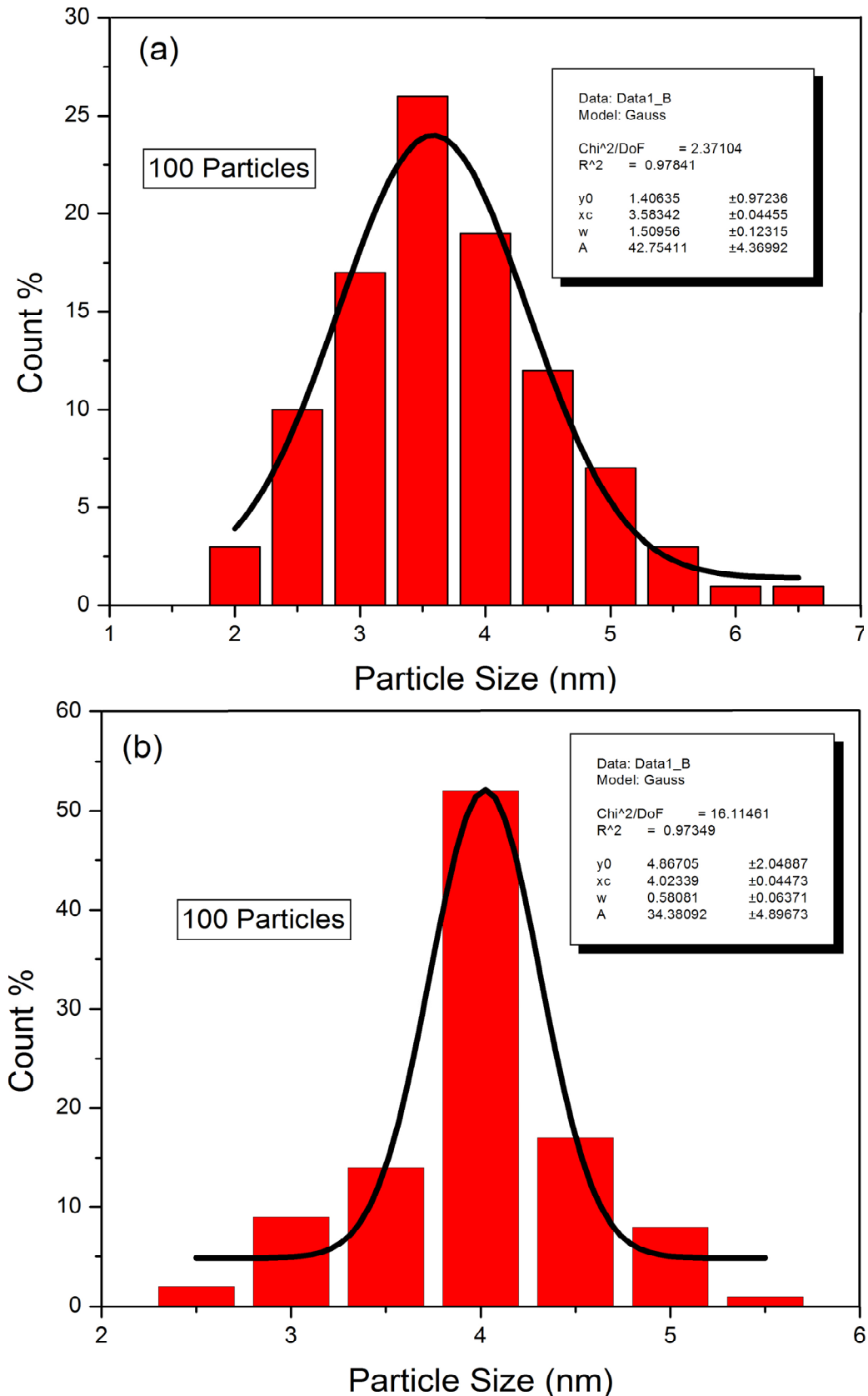


Figure 3. Particle diameter histogram of (a) Pt and (b) FePt nanoparticles; the line plotted corresponds to fit using a log normal distribution.

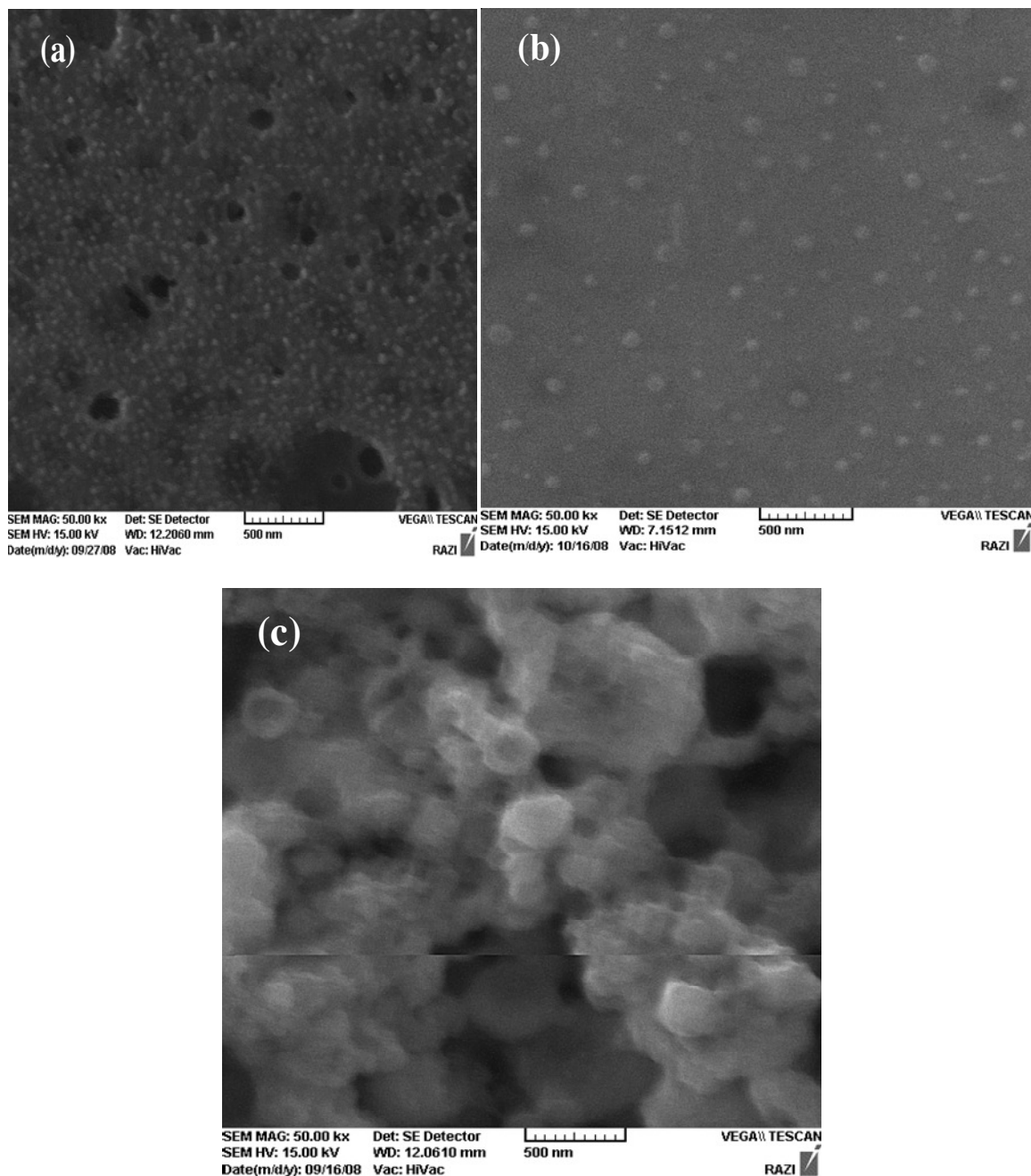


Figure 4. The SEM images of annealed FePt after (a) 15 min, (b) 30 min and (c) 4 h annealing.

nanoparticles were annealed at 750°C for different time. Figure 4(a) shows the SEM analysis of 50 nm FePt nanoparticles after 15 min annealing. In Figure 4(b), the size of FePt nanoparticles increases to 120 nm by increasing annealing time to 30 min. It seems that the size of annealed FePt increases with increasing annealing time because the oleic acid and oleylamine surfactants remove by increasing temperature which leads to nanocrystals agglomeration. Figure 4(c) shows the sintering FePt nanoparticles with size of 250 nm after

4 h annealing.

In order to prevent FePt agglomeration, the as-synthesis FePt nanoparticles, were mixed with 1 micron NaCl salt particles prepared by ultrasonic vibrations and then annealed at 750°C. After removing impurity, the L_{10} -FePt nanocrystals were dispersed in hexane solution (Farahmandjou and Sebt, 2009). Figure 5 indicates the TEM images of separated 5 to 40 nm L_{10} FePt nanoparticles prepared by NaCl salt-matrix method after annealing at 750°C for 4 h under a flow of 90% Ar +

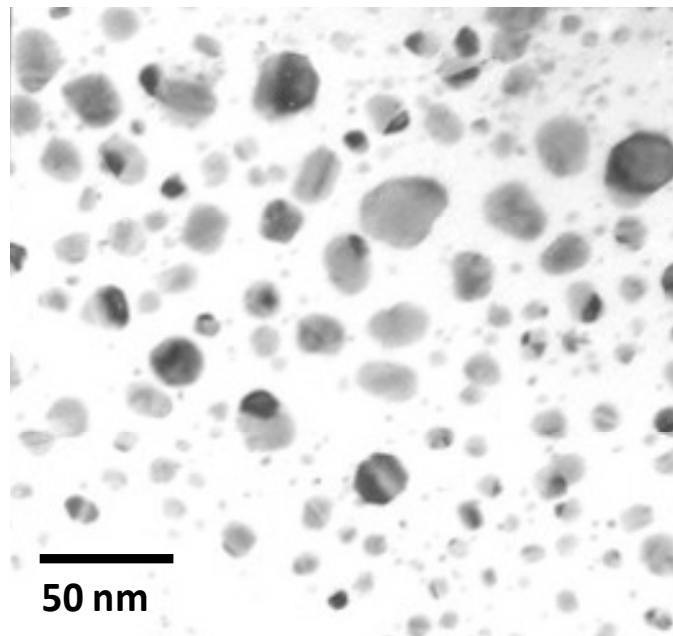


Figure 5. TEM images of isolated annealed FePt nanoparticles.

10% H₂.

CONCLUSION

Uniform as-synthesized FePt nanoparticles were successfully synthesized with mean diameter of 4 nm by sol process via two step process. The TEM results showed that 2 to 7 nm Pt nanoparticles have not good uniformity in size and shape because of one step growth process. On the other hand, FePt nanoparticles were formed as core-shell by two step growth with size distribution about 8%. The SEM results indicated an increase of the FePt agglomeration when the annealing temperature increases. The XRD spectra indicated the L₁₀ structure of FePt nanoparticles. Finally, TEM image of salt-matrix FePt showed the isolated nanocrystals after annealing process.

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