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Journal of Colloid and Interface Science 308 (2007) 564–567

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Note

Direct synthesis of fct-structured FePt nanoparticles at low temperature with assistance of poly(*N*-vinyl-2-pyrrolidone)

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Received 10 November 2006; accepted 16 January 2007

Abstract

Direct synthesis of fct-structured FePt nanoparticles was successfully achieved by using poly(*N*-vinyl-2-pyrrolidone) as a protective reagent at lower temperature than the case using low molecular weight ligands as a protective reagent. Experimental data suggest that a transformation of FePt nanoparticles from face-centered cubic to face-centered tetragonal (fct) structure takes place at reaction temperature of 261 °C. The results of XRD and the magnetic properties exhibit that the FePt nanoparticles synthesized at 261 °C have partially ordered fct-structure and a ferromagnetic behavior at room temperature.

Keywords: FePt nanoparticles; Direct synthesis; Poly(*N*-vinyl-2-pyrrolidone); XRD pattern; fct-Structure; Phase transformation; Coercivity; Ferromagnetism

1. Introduction

Chemical and physical researchers have a great interest in FePt nanoparticles easily synthesized by a chemical route [1–7], because the nanoparticle is a promising candidate for ultra-high density magnetic recording media based on the fact that FePt in a bulk state has a large uniaxial magnetocrystalline anisotropy ($K_u = 6.6 \times 10^7\ \text{erg/cm}^3$) [8]. In 2000, Sun and co-workers succeeded in synthesizing FePt nanoparticles by a liquid phase process [1]. In Sun's method, annealing the as-synthesized FePt nanoparticles is necessary to transform the crystal structure from a face-centered cubic (fcc) phase to a face-centered tetragonal (fct) one, and the magnetism from superparamagnetism to ferromagnetism, respectively. However, the annealed FePt nanoparticles often sinter by the post-annealing and some nanoparticles are aggregated each other.

In recent years, direct chemical syntheses of fct-structured FePt nanoparticles by a polyol process have been conducted to prevent nanoparticles from sintering by the heat treatment at high temperature [9,10]. In the previous works by other groups [9,10], direct syntheses of FePt nanoparticles were carried out over 300 °C, and the agglomeration of fct-structured FePt nanoparticles directly synthesized was observed in photographs of transmission electron microscopy (TEM). It is thought that a surfactant as a protective agent is thermally decomposed during reaction, and consequently the nanoparticles become a free-standing state without the surfactant and are aggregated each other. Thus, it is required to possess thermal stability for surfactants. Based on such consideration, we have focused a polymer as a protective agent in order to keep nanoparticles separated [11–15] and chosen poly(*N*-vinyl-2-pyrrolidone) (PVP) by confirming that PVP keeps thermal stability up to 400 °C in a thermogravimetric (TG) analyzer. Whereas low molecular weight ligands such as oleic acid, oleylamine, etc. have been used as protective reagents in the previous papers [9,10], PVP, which is very common as a polymeric protective reagent for the syntheses of metal nanoparticles in wet chemical methods [11–15], is used in the present study. If the reactions are performed at lower temperature than 300 °C in the presence of PVP instead of oleic acid and oleylamine, the thermal decomposition of protective reagents may be prevented, which may avoid agglomeration of nanoparticles.

On the basis of these considerations, we tried to directly prepare fct-structured FePt nanoparticles protected by PVP and

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doi:10.1016/j.jcis.2007.01.049

succeeded in the direct synthesis. This is the first report with regard to direct synthesis of fct-structured FePt nanoparticles protected by PVP, although FePt nanoparticles coated by PVP have already been described [16,17]. At the moment, there have remained such many unresolved issues as the fct-ordering mechanism and the magnetic phase-transformation process in the directly synthesized FePt nanoparticles with fct-structure, although their direct syntheses by chemical reduction [9,10] and He-ion irradiation [18] have already been reported. The structural and magnetic transformation mechanisms of FePt nanoparticles during the reaction may be elucidated by directly preparing them at relatively low temperature and by examining characterization of those thus prepared. In this paper, we describe for the first time the formation of the fct-structured FePt nanoparticles at relatively low temperature with assistance of PVP and refer to polymer effect on direct synthesis of the FePt nanoparticles with fct-structure.

2. Experimental procedure

$Fe(acac)_3$ and $Pt(acac)_2$ (acac = acetylacetonate, $[CH_3CO–CHCOCH_3]^-$) were used as metallic precursors. Poly(N-vinyl-2-pyrrolidone) (PVP) and tetraethylene glycol (TEG) were adopted as a protective polymer and a reducing agent, respectively. The amounts of $Fe(acac)_3$, $Pt(acac)_2$ and TEG were settled at 353.2 mg (1.0 mmol), 354.0 mg (0.9 mmol) and 50 ml, respectively. The amount of PVP was changed in a wide range (21.1–2112.0 mg) to control the size of FePt nanoparticles. In general method, the TEG solution was stirred with $Fe(acac)_3$, $Pt(acac)_2$ and PVP, and heated up to ca. 300 °C in an Ar gas. The solution was kept refluxing for several hours and then spontaneously cooled down to room temperature. Then, the atmosphere filled by the Ar gas could be opened to an ambient environment. The black precipitate separated from ethanol (∼400 ml) was purified by washing with ethanol and gathered as powder.

The structure of FePt nanoparticles was investigated by powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). The elemental composition measurement of FePt nanoparticles was carried out by an inductively coupled plasma (ICP) spectroscopy. Magnetic property of FePt nanoparticles was measured by a superconducting quantum interference device (SQUID) magnetometer.

3. Results and discussion

Fig. 1 shows various properties of PVP-protected FePt nanoparticles synthesized by refluxing at 300 °C for 3 h. Figs. 1A and 1B show a TEM photograph and a size distribution histogram, respectively. The size distribution histogram was obtained based on the TEM photograph by counting over 100 of FePt nanoparticles to calculate the mean diameter and standard deviation. $Fe_{52}Pt_{48}$ nanoparticles, the composition of which is determined by an ICP spectrometer, have a mean diameter of 5.1 nm and a standard deviation of 0.9 nm. By using 15 g/cm^3 of a density of FePt in a bulk state [19], the real number of atoms (Fe and Pt) in the $Fe_{52}Pt_{48}$ nanoparticle with 5.1 nm in diameter was estimated to be 2700 and 2500, respectively. Figs. 1C and 1D exhibit XRD patterns and a magnetic hysteresis loop at 300 K of the FePt nanoparticles, respectively. In the XRD profile, superlattice peaks of (001) and (110) planes at 24° and 33°, respectively, indicate that the crystal structure of as-synthesized nanoparticles is the fct-structure [1]. The FePt nanoparticles have a coercivity of 750 Oe and a saturation magnetization of 39.0 emu/g at 300 K as shown in Fig. 1D. The results seen in Fig. 1 definitely suggest that ferromagnetic FePt nanoparticles with the fct-structure have been directly synthesized without any post-synthesis annealing even in the case that PVP is used as a protective reagent.

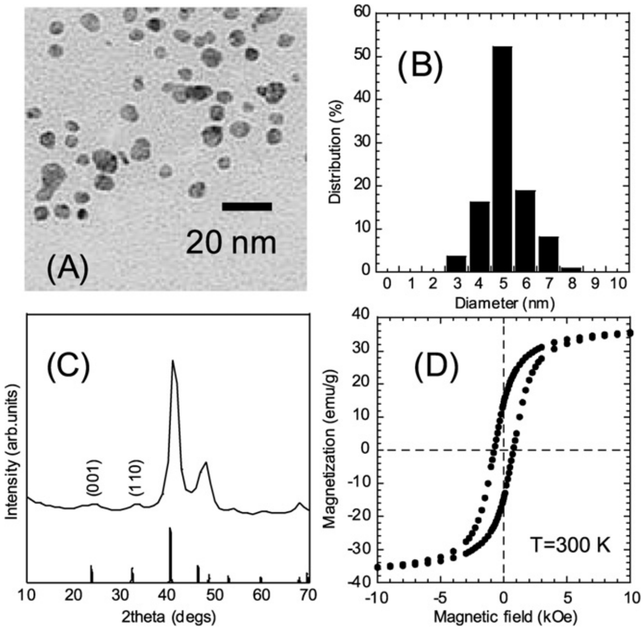

Fig. 1. (A) TEM photograph, (B) size distribution histogram, (C) XRD pattern and (D) magnetic hysteresis loop at 300 K of PVP-protected $Fe_{52}Pt_{48}$ nanoparticles synthesized by refluxing at 300 °C for 3 h. The mean diameter is 5.1 nm and standard deviation is 0.9 nm.

To investigate the lowest temperature required for the phase-transformation from the fcc-structure to fct-one during the solution-based chemical reaction, we synthesized FePt nanoparticles at various reaction temperatures of 213–293 °C without refluxing when 1055.8 mg (9.5 mmol in monomer unit) of PVP was added to 50 ml of TEG solution with 353.2 mg (1.0 mmol) of $Fe(acac)_3$ and 354.0 mg (0.9 mmol) of $Pt(acac)_2$. Fig. 2A displays the mean diameter and Fe composition for PVP-protected FePt nanoparticles as a function of the reaction temperature for the synthesis. The mean diameter and standard deviation of FePt nanoparticles were evaluated from TEM photographs. The error bar means the standard deviation of the particle's size. The diameter of FePt nanoparticles increases with increasing reaction temperature, while the Fe composition is kept constant. These Fe compositions of the FePt nanoparticles as shown in Fig. 2A are included in the range between $Fe_{35}Pt_{65}$ and $Fe_{60}Pt_{40}$ to transform the crystal structure from fcc to fct.

Fig. 2B shows XRD patterns of PVP-protected FePt nanoparticles synthesized at various reaction temperatures without refluxing. A strong (111) peak is observed at 41° for FePt