

Synthesis and magnetic properties of CoPt nanoparticles

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High magnetocrystalline anisotropy CoPt particles with an average size of 8 nm were synthesized by the superhydride reduction of CoCl_2 and $\text{Pt}(\text{acac})_2$ at a high temperature. As-made particles showed a disordered face-centered cubic lattice and were superparamagnetic. Upon heat treatment at temperatures above 600 °C, the particles transformed to the $L1_0$ phase, as indicated by the appearance of the superlattice peaks in the x-ray diffraction and high magnetocrystalline anisotropy. The temperature dependence of the coercivity of nanoparticles annealed at 650 °C was measured from 10 to 300 K and analyzed using a Sharrock formula. After annealing at 650 °C, the anisotropy of the nanoparticles was $K \sim 1.7 \times 10^7 \text{ erg/cm}^3$. © 2004 American Institute of Physics.
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CoPt alloy films with a face-centered tetragonal $L1_0$ -ordered structure have long been considered attractive candidates for ultrahigh-density magnetic recording media due to the high anisotropy, chemical stability, and corrosion resistance of the alloy.¹⁻³ CoPt nanoparticles have been chemically synthesized and studied in recent years following IBM's work on chemically synthesized, self-assembled FePt nanoparticles.^{4,5} However, unlike the FePt systems, comparatively low coercivity values (usually in the range from several hundred to a few thousand oersted) have been reported. By comparison, coercivity values exceeding 10 kOe have been reported in sputtered CoPt granular thin films with similar grain sizes.^{6,7} This discrepancy is mostly due to the difficulties involved in preparing samples with a uniform composition around 50:50 using chemical synthesis. A deviation as small as 5% from this composition can result in a large fraction of fcc CoPt phase in the nanoparticles, which results in soft magnetic properties even after high temperature and long time heat treatment.^{2,6} This soft phase may be ordered ($L1_2$)CoPt₃, which has a much lower anisotropy than the $L1_0$ phase.⁸⁻¹¹

In this study, we report a simple chemical process for synthesizing 8 nm rodlike CoPt nanoparticles by the superhydride reduction of CoCl_2 (anhydrous), and $\text{Pt}(\text{acac})_2$ at 200 °C in the presence of oleic acid, oleylamine, and 1,2-hexadecanediol, followed by refluxing at 260 °C. The initial molar ratio of the metal precursors is carried over to the final product, and the CoPt composition is easily tuned. For example, the $\text{Co}_{50}\text{Pt}_{50}$ particles were prepared with 197 mg of $\text{Pt}(\text{acac})_2$ (0.5 mmol), 65 mg CoCl_2 (anhydrous, 0.50 mmol), 520 mg of 1,2-hexadecanediol (2 mmol), and phenyl ether (25 ml). The reaction was performed under an inert flowing nitrogen atmosphere, in a three-neck round bottom flask fitted with a rubber septum, mercury thermometer, and water-cooled condenser. The mixture was heated to 100 °C for 10 min. Oleic acid (0.16 mL, 0.5 mmol) and oleylamine (0.17 mL, 0.5 mmol) were added, and the mixture was continu-

ously heated to 200 °C for 20 min. A superhydride, LiBEt_3H (1M THF solution, 2.5 mL), was slowly dropped into the mixture. The black dispersion was then heated to reflux at 260 °C for 30 min under flowing nitrogen gas. After the heating source was removed, the black reaction mixture was cooled to room temperature. Ethanol (50 mL) was then added, and the particles were precipitated and separated by centrifugation. The final black product, $\text{Co}_{50}\text{Pt}_{50}$, was dispersed in hexane (~10 mL) in the presence of oleic acid (~0.05 mL) and oleylamine (~0.05 mL). For the microstructure study, the dispersion was further diluted with hexane, a drop was placed on a carbon-coated copper transmission electron microscopy (TEM) grid, and the solvent was allowed to evaporate at room temperature.

A JEOL 2010 scanning TEM (STEM)/TEM analytical electron microscope operating at 200 kV was used to record high-angle annular dark-field (HAADF) images, and the particle composition was determined by energy dispersive x-ray (EDX) analysis using a Philips model XL 30 scanning electron microscope. X-ray diffraction (XRD) data were obtained on a Rigaku D/MAX-2BX Horizontal XRD Thin Film Diffractometer using $\text{Cu } K\alpha$ radiation. Room temperature magnetic hysteresis curves were measured using a Princeton Micromag 2900 alternating gradient magnetometer (AGM) using an 18 kOe saturating field. Variable temperature, high-field hysteresis loops were obtained using an Oxford Instruments vibrating sample magnetometer (VSM) with fields of up to 7 T and at temperatures from 10 to 300 K. All measurements were made with the applied magnetic field in the plane of the films. The coercivity of CoPt nanoparticle films annealed at 650 °C for 1 h was 12 kOe at 300 K and 18 kOe at 10 K.

The crystal structure and size of the CoPt nanoparticles were determined by XRD. Figure 1 shows XRD spectra of the as-made particles and after annealing at temperatures from 500 to 700 °C for 1 h. The spectrum of the as-made CoPt particles is characteristic of the chemically disordered

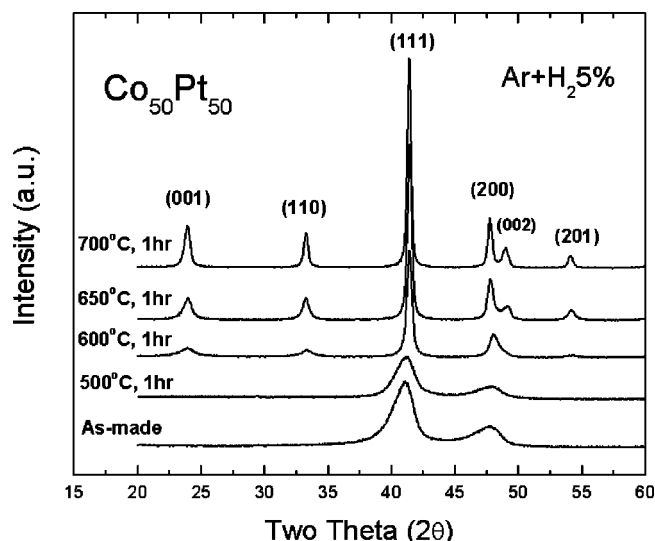


FIG. 1. XRD patterns for CoPt particles as-made and after annealing.

fcc structure. From a Scherrer analysis of the linewidth, the particle size was estimated to be ~ 8 nm. The overlaid XRD patterns show the appearance of the $L1_0$ (001), (110), and (201) superlattice peaks with increasing annealing temperature and the clear splitting of the (200) and (002) peaks at 650 and 700 °C, indicating a highly ordered $L1_0$ phase.

The HAADF [Fig. 2(a)] and high-resolution (HR)-TEM images [Fig. 2(b)] show rod-shaped particles that have partially self-assembled. The HAADF images suggest a homogeneous CoPt alloy with no core-shell structure. The observed particle length of ~ 8 nm is in agreement with XRD analysis. From EDX analysis the cobalt to platinum composition ratio was found to be 50:50 before and after annealing.

Samples were prepared for magnetometry by drying a drop of a dispersion of the CoPt particles on a silicon substrate and annealing under an Ar+5% H_2 flowing atmosphere at various temperatures for 1 h. Figure 3 shows hysteresis loops measured with an AGM for the as-made sample and for samples that were annealed from 500 to 700 °C. The as-made and 500 °C annealed samples are essentially superparamagnetic, which is consistent with the XRD spectra that show only the soft $L1_2$ phase. (The small coercivity could be due to a small fraction of particles above the superparamagnetic limit.) Large coercivities were obtained after annealing at 600 °C and above, with a maximum room temperature value of 12 kOe after annealing at 650 °C. To our knowledge, this coercivity is much higher than what has been previously reported in chemically synthesized CoPt nanoparticle systems.^{12–14} The small soft component seen in the loops may be due to the presence of a small amount of $L1_2$ CoPt₃ or fcc CoPt, although these phases cannot be detected in the XRD spectra.

Figure 4 shows the temperature dependence of the coercivity for the sample annealed at 650 °C. The smooth curve through the data is a fit using Sharrock's formula,¹⁵

$$H_c = H_0 \left[1 - \left(\frac{k_B T}{K_u V} \ln(f_0 t) \right)^{2/3} \right], \quad (1)$$

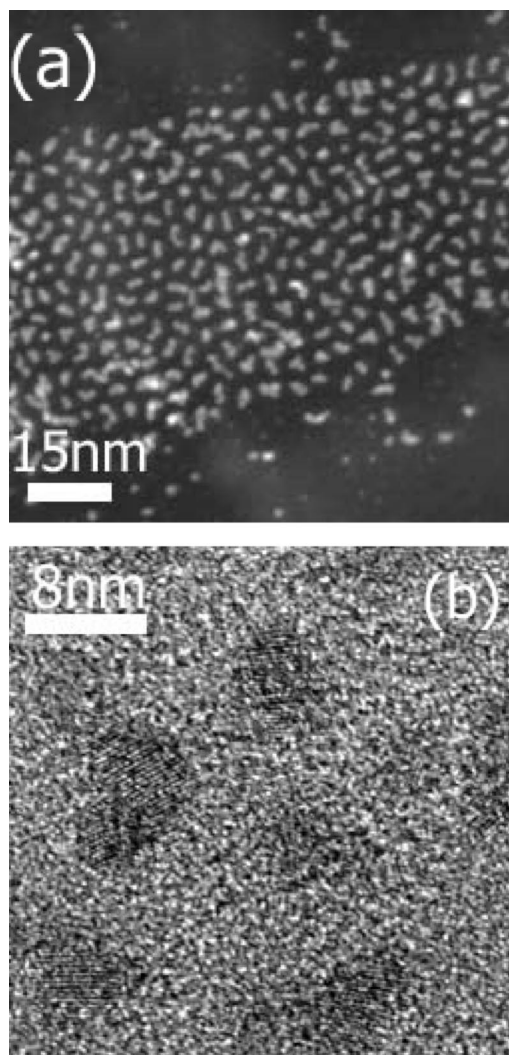


FIG. 2. (a,b) High-angle annular dark-field (HAADF) and high-resolution TEM images that show CoPt particle with rod-like shape with 8 nm average length.

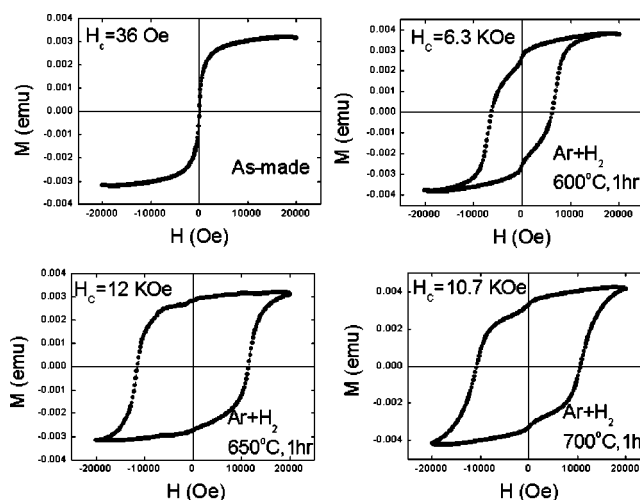


FIG. 3. Magnetic hysteresis loops for CoPt particles as-made and after annealing at different temperatures under Ar+5% H_2 for 1 hr.

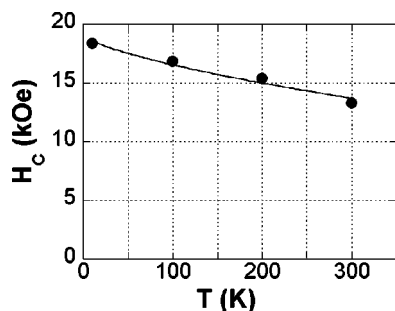


FIG. 4. Temperature dependence of coercivity for CoPt nanoparticles annealed at 650°C.

where H_0 is the zero-temperature coercivity, K_u the anisotropy energy density, V the particle volume, k_B Boltzmann's constant, T the absolute temperature, f_0 the attempt frequency ($\sim 10^{10}$ Hz), and t the effective wait time (related to the sweep rate). The $2/3$ exponent is appropriate for randomly oriented easy axes. From the fit parameters, $K_u = \frac{1}{2}M_s H_k \approx M_s H_0 = 1.7 \times 10^7$ erg/cm³ and $V = 4.3 \times 10^{-19}$ cm³ = (7.6 nm)³. (The analysis neglects the temperature dependence of K_u and M_s .) By comparison, the reported bulk value of K_u is 4.9×10^7 erg/cm³.¹⁶ The switching volume is substantially larger than the volume of the as-made particles. This may be due in part to exchange interactions between particles that have sintered during annealing, as suggested by the large remanence values seen in the hysteresis loops.

In summary, we have reported the synthesis of rod-like 8 nm CoPt nanoparticles by the superhydride reduction of CoCl₂ (anhydrous) and Pt(acac)₂. The procedure allows ac-

curate control of the composition of the particles. Thermal annealing of as-made Co₅₀Pt₅₀ particles transformed the particles from the disordered fcc phase to the $L1_0$ phase with high chemical ordering and large magnetocrystalline anisotropy.

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