

Monodisperse CoPt Nanoparticles Synthesized Using Chemical Reduction Method *

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Monodisperse CoPt nanoparticles in sizes of about 2.2 nm are synthesized by superhydride reduction of CoCl_2 and PtCl_2 in diphenyl ether. The as-prepared nanoparticles show a chemically disordered A_1 structure and are superparamagnetic. Thermal annealing transforms the A_1 structure into chemically ordered $L1_0$ structure and the particles are ferromagnetic at room temperature.

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Chemically synthesized magnetic nanoparticles have drawn much attention due to the unique magnetic properties derived from small particle sizes and uniform size distribution.^[1-7] Like FePt, $L1_0$ ordered CoPt alloys are also magnetically hard and are alternative candidates for permanent magnetic and information storage applications. CoPt nanoparticles (NPs) have been successfully synthesized by the diol reduction of $\text{Pt}(\text{acac})_2$ with the concurrent thermal decomposition of $\text{Co}_2(\text{CO})_8$ in a high boiling point organic solvent,^[2,8-9] or polyol reduction of $\text{Pt}(\text{acac})_2$ and $\text{Co}(\text{CH}_3\text{COO})_2$.^[10-12] CoPt NPs have also been made by the co-reduction of $\text{Pt}(\text{acac})_2$ and reduction of CoCl_2 using superhydride reduction (LiBEt_3H).^[13-15] In this Letter, we report a simple reduction method to synthesize monodisperse CoPt NPs. Similar to FePt NP synthesis reported in Ref. [16], the CoPt NPs are produced using readily available PtCl_2 and CoCl_2 as precursors and superhydride as the reducing agent. The synthesis allows simultaneous reduction of both metal precursors at an elevated temperature, facilitating the formation of CoPt nanoparticles. The synthesis also avoids the formation of core-shell structure that is usually observed in the reduction/decomposition process.

We used high temperature liquid reduced method to prepared monodisperse CoPt nanoparticles. Firstly, CoCl_2 (0.5 mmol), PtCl_2 (0.5 mmol) and 10 mL phenyl ether were mixed in 100 mL flask and stirred under N_2 atmosphere at 100°C for 20 min. Oleic acid (4.0 mmol) and oleylamine (4.0 mmol) were added, and the mixture was heated to 200°C for 10 min. Then, LiBEt_3H (1 M in THF, 4 mL) was dropped into the hot mixture solution over a period of 3 min. The black solution was stirred at 200°C for 5 min under N_2 to remove the lower boiling solvent and then heated to 220°C for 30 min under a blan-

ket of N_2 . The mixture was cooled down to room temperature by removing the heating source. Ethanol (40 mL) was added into this solution. The black product was precipitated and separated by centrifugation. The black product was redissolved in heptane (20 mL) in the presence of oleic acid (about $50 \mu\text{L}$) and oleylamine (about $50 \mu\text{L}$). The undissolved product was separated out by centrifugation. Ethanol (20 mL) was added into the black solution. The black product was obtained by centrifugation and redissolved in 20 mL heptane containing oleic acid and oleylamine.

Transmission electron microscopy (TEM, JEOL-200CX) and high-resolution transmission electron microscopy (HRTEM, Tecnai F20) were used to observe the morphology of CoPt nanoparticles. The structure of the nanoparticles was examined using a Rigaku D/MAX 2400 x-ray diffractometer. Magnetic properties of the particles were measured using a Physical Property Measurement System (PPMS) 6000 at 300 K. XPS analysis was carried out on the ESCA LAB5 x-ray photoelectron spectrometer. As-prepared CoPt samples were annealed in an Ar/H_2 (5% hydrogen) atmosphere at 700°C for two hours.

XRD spectra of the as-synthesized and the annealed CoPt nanoparticles are shown in Figs. 1(a) and 1(b). The diffraction peaks of the as-prepared nanoparticles show only four broad peaks corresponding to the (111), (200), (220) and (330) planes of the A_1 structure.^[15] An average diameter of 2.4 nm was estimated from the Scherrer formulation. The XRD spectrum appears differently in Fig. 1(b) when the A_1 samples were annealed under Ar/H_2 atmosphere at 700°C for two hours. The multiple diffraction peaks correspond to (001), (110), (111), (200), (220), (201), (112) and (311) planes of the $L1_0$ structure. It can be clearly observed from Figs. 1(a) and 1(b) that the intensity and shape of diffraction peaks have become

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stronger and sharper after annealed. The (001), (110) and (201) peaks of the high ordered $L1_0$ phase are also observed, indicating the thermal annealing induces the structure change of the CoPt nanoparticles from A_1 to $L1_0$. Additionally, we observe splitting of (220) peak into the (220) and (200) peaks, which is characteristic of this transformation. After CoPt NPs were annealed, an average size of 25 nm was calculated using the Scherrer equation.

TEM images of the as-prepared CoPt nanoparticles are shown in Fig. 2. It can be seen that the CoPt nanoparticles are monodisperse spherical particles. Each particle is separated from its neighbours by the organic ligand (oleic acid and oleylamine) shell. The average diameter of the particles is 2.2 nm. HRTEM reveals good crystallinity of the particles (Fig. 2(b)). The SAED ring-pattern verifies that the A_1 structure is indeed present in the particles.^[15] EDX analysis of the CoPt nanoparticles (Fig. 2(c)) shows that the molar ratio of the Co to Pt is 42: 58. This is not too

far off from the ICP analysis, which gives 49:51.

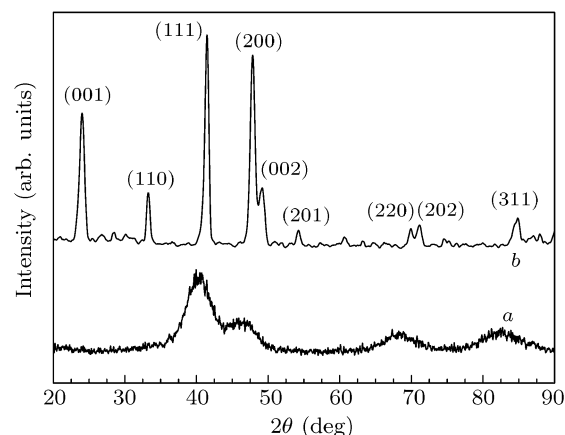


Fig. 1. XRD patterns of as-prepared and annealed CoPt nanoparticles: (a) 2.2 nm as-prepared CoPt NPs; (b) CoPt NPs annealed at 700°C for two hours under argon atmosphere.

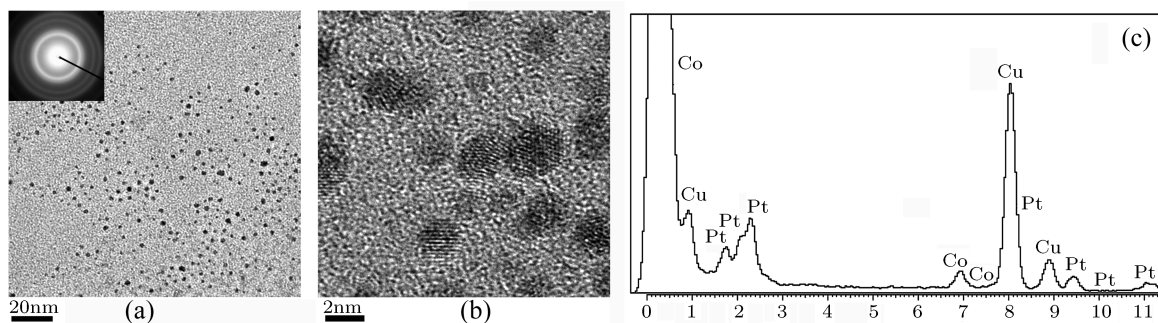


Fig. 2. TEM (a) and HRTEM (b) images, as well as EDS (c), of as-prepared CoPt nanoparticles.

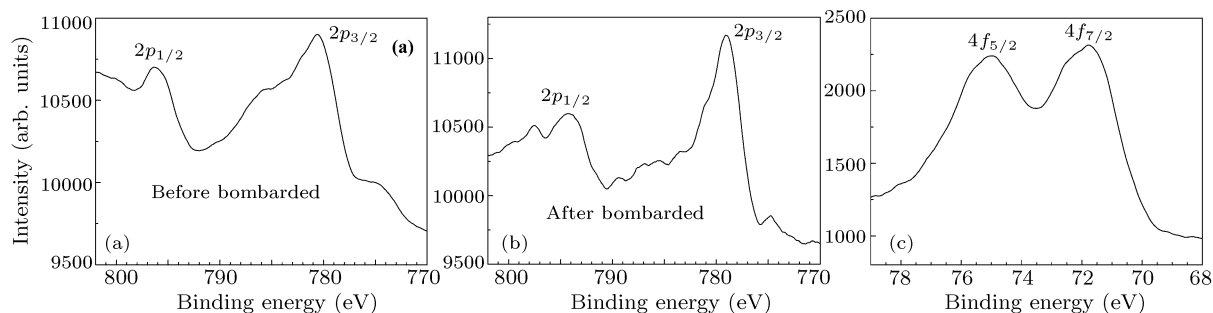


Fig. 3. XPS spectra of CoPt nanoparticles: (a) Co before bombarded using Ar^+ ion for 2 min; (b) Co after bombarded using Ar^+ ion for 2 min; (c) Pt.

In order to understand the chemical information on the nanoparticle surface, we used XPS to measure the valence state of the CoPt nanoparticles. In XPS analysis, the penetration depth of the electron beam is near 3 nm while chain length of oleic acid and oleylamine is about 2.5 nm. Therefore, the depth probed from the surface of the CoPt NPs to the core of the CoPt NPs is about 0.5 nm, which ensures that the surface valence of the molecule-coated CoPt NPs can be obtained. Figure 3(a) shows the XPS spectra of the

Co in the CoPt nanoparticles. Two peaks at 780.6 and 796.2 eV were observed, corresponding to the binding energy of CoO, and Co peaks are difficult to see. The appearance of CoO peaks indicates that the surface Co is oxidized. In order to detect the valence of the inner core of the CoPt NPs, the particles were bombarded with an argon ion beam for 2 min to remove the organic coating. The XPS spectrum of the bombarded CoPt is shown in Fig. 3(b). Two peaks at 778.9 and 794.2 eV correspond to the binding energy of the

Co within the CoPt nanoparticles (the standard values of the pure Co are at 778.3 and 793.27 eV). The slight shift of the peak position from the pure Co is likely caused by the alloying of Co with Pt within the NPs. The XPS spectrum of the Pt within the CoPt nanoparticles is shown in Fig. 3(c). The double peaks with the binding energy of 71.8 and 75.0 eV were observed, shifting also from the standard Pt $4f_{7/2}$ and Pt $4f_{5/2}$ peaks at 71.20 and 74.53 eV. These shifts of both Co and Pt are consistent with the fact that Co alloys with Pt.^[17] From XPS studies, we can see that the outer layer of the CoPt nanoparticles contains Co-O, but the inner core has metallic Co. Co-O is likely formed by the reaction between Co and COOH in oleic acid, giving Co-carboxylate ($-\text{COO}-\text{Co}$).^[18] The peak corresponding to N is also observed in the full spectrum, proving that oleylamine exists on the surface of the CoPt nanoparticles.

Figure 4 shows the typical TEM image of CoPt nanoparticles annealed in Ar/H₂ atmosphere at 700°C for two hours. The particles size of annealed sample is found to be larger than for as-prepared samples. The diameter of CoPt nanoparticles ranges from 20 nm to 30 nm. This result provides that small CoPt nanoparticles formed aggregation after annealing. The ED pattern in the inset of Fig. 4 shows that annealed CoPt nanoparticles became single crystal structure. The EDX analysis result indicates that the atomic ratio of Co to Pt was 1:1.06.

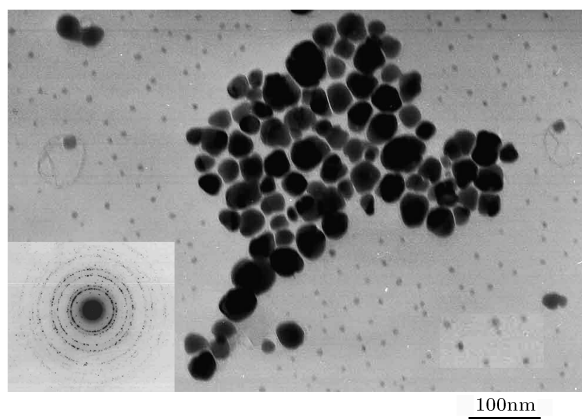


Fig. 4. TEM images of CoPt nanoparticles annealed in Ar/H₂ atmosphere at 700°C for two hours.

Figure 5 shows room temperature magnetic hysteresis loops of the as-synthesized and the annealed CoPt nanoparticles. From Fig. 5(a), it can be seen that the as-synthesized CoPt NPs are superparamagnetic at room temperature. After annealing under Ar/H₂ atmosphere at 700°C for two hours, the CoPt nanoparticles are ferromagnetic. The coercivity value is 1.25 kOe for the samples annealed at 700°C for two hours. The higher value of coercivity was due to the presence of a large number of *fcc* crystals after the thermal treatment that induced high magnetocrystalline anisotropy.

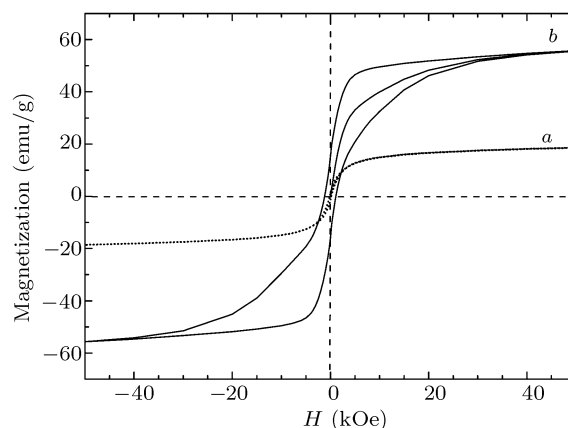


Fig. 5. Room temperature magnetic hysteresis loops of CoPt NPs after annealing at 700°C for two hours in argon atmosphere.

In summary, we have prepared ultrafine CoPt NPs using superhydride reduction of CoCl₂ and PtCl₂. As prepared, the particles have chemically disordered *fcc* (A₁) structure and are superparamagnetic at room temperature. The A₁ structure can be converted into chemically ordered *fcc* (L1₀) structure after thermal annealing, and the *fcc* structured CoPt NPs are ferromagnetic at room temperature. These particles can be used as models for nanomagnetism studies and as basic building blocks for magnetic nanodevice fabrications. The authors are grateful to Shouheng Sun for critical reading of the manuscript.

References

- [1] Sun S, Murray C B, Weller D, Folks L and Moser A 2000 *Science* **291** 2115
- [2] Shechtno E V *et al* 2002 *J. Am. Chem. Soc.* **124** 11480
- [3] Yang T Z, Shen, C M, Gao H -J *et al* 2005 *J. Phys. Chem. B* **109** 23233
- [4] Zeng H, Rice P M, Wang S X and Sun S H 2004 *J. Am. Chem. Soc.* **126** 11458
- [5] Yang H T, Shen C M, Yang T Z, Gao H -J *et al* 2004 *Nanotechnology* **15** 70
- [6] Klemmer T J *et al* 2002 *Appl. Phys. Lett.* **81** 2220
- [7] Yang H T, Shen C M, Su Y K, Yang T Z and Gao H J 2003 *Appl. Phys. Lett.* **82** 4729
- [8] Park J I and Cheon J 2001 *J. Am. Chem. Soc.* **123** 5743
- [9] Chen M and Nikles D E 2002 *J. Appl. Phys.* **91** 8477
- [10] Chinnasamy C N, Jeyadevan B, Shinoda K and Tohji K 2003 *J. Appl. Phys.* **93** 7583
- [11] Yu A C C, Mizuno M, Sasaki Y, Kondo H and Hiraga K 2002 *Appl. Phys. Lett.* **81** 3768
- [12] Gibot P, Tronce E, Chanéac C, Jolivet J P, Fiorani D and Testa A M 2005 *J. Magn. Magn. Mater.* **290** 555
- [13] Sun X C, Jia Z Y, Huang Y H, Harrell J W, Nikles D E, Sun K and Wang L M 2004 *J. Appl. Phys.* **95** 6747
- [14] Fang J Y, Tung L D, Stokes K, He J B, Caruntu D, Zhou W L and O'Connor C J 2002 *J. Appl. Phys.* **91** 8816
- [15] Tzitzios V, Niarchos D, Margariti G, Fidler J and Petridis D 2005 *Nanotechnology* **16** 287
- [16] Sun S *et al* 2003 *J. Phys. Chem. B* **107** 5419
- [17] Lee Y S, Lim K Y, Chung Y D, Whang C N and Jeon Y 1999 *Surf. Interface Anal.* **30** 475
- [18] Wu N Q, Fu L, Su M, Aslam M, Wong K C and Dravid V P 2004 *Nano Lett.* **4** 383