Available online at www.sciencedirect.com
ScienceDirect
Journal of Photochemistry and Photobiology A: Chemistry 182 (2006) 342–345
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

Synthesis of magnetic CoPt/SiO_2 nano-composite by pulsed laser ablation

Takafumi Seto [a,*], Kenji Koga [b], Fumiyoshi Takano [b], Hiroyuki Akinaga [b], Takaaki Orii [a], Makoto Hirasawa [a], Mitsuhiro Murayama [c]

[a] *Advanced Manufacturing Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-2-1 Namiki, Tsukuba 305-8564, Japan*
[b] *Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba 305-8565, Japan*
[c] *National Institute for Material Science, 1-2-1 Sengen, Tsukuba 305-0047, Japan*

Available online 11 July 2006

Abstract

Core–shell nanoparticles composed of ferromagnetic cobalt platinum cores covered by non-magnetic silica shells were synthesized by laser ablation of a composite target in a helium background gas. The average diameter of the CoPt core was controlled by adjusting the CoPt/SiO_2 ratio of the ablation target and size-classifying the nanoparticles by an electrical mobility classifier. The present method successfully synthesized nearly monodispersed nanoparticles with an average core diameter as small as 2 nm. The size-dependent magnetic properties of nano-composite films generated by the deposition of nanoparticles onto the substrate were investigated by a SQUID magnetometer.

Keywords: Core–shell nanoparticle; Superparamagnetism; Cobalt platinum; Laser ablation

1. Introduction

A nanoscale composite (nano-composite) composed of ferromagnetic domains dispersed in a non-magnetic matrix has unique magnetic and transport properties suitable for magnetic recording mediums [1] and giant magnetoresistance (GMR) materials [2]. Highly anisotropic materials, such as ordered face center tetragonal (fct) phase CoPt and FePt can handily compete with the thermal fluctuation of the electron spin, and this ability makes good candidates as ferromagnetic domains. Nano-composite films of this type have been conventionally fabricated by sputtering [1], molecular beam epitaxy [2] and pulsed laser deposition [3]. The magnetic exchange interactions between the domains and between the domains and matrix must be strictly controlled during the fabrication. This can be challenging, however, as the variations in the generation mechanism in response to surface nucleation and growth make it rather difficult to control the size and inter-domain distance without changing the crystal structure. As one alternative, Sun et al. developed a liquid phase method to synthesize monodispersed magnetic Pt–alloy nanoparticles and their two-dimensional array [4]. This technique, however, brings new challenges of its own: careful thermal treatment is requisite for the realization of an ordered phase, and the annealing induces the nanoparticles to agglomerate.

We recently proposed a method to fabricate core–shell nanoparticles with a changeable core size using laser ablation and electrical mobility classification (so-called laser nano-prototyping) [5,6]. In earlier studies, we fabricated surface-oxidized metal nanoparticles (e.g., Ni/NiO and CoPt/CoO) and investigated the magnetic properties of the nanoparticles thus produced. The electron spin in these systems was fixed by the weak exchange coupling at the interface between the ferromagnetic core and antiferromagnetic shell. In the present study, we apply laser nano-prototyping to fabricate nano-composite composed of ferromagnetic CoPt domains covered by non-magnetic SiO_2 shells.

2. Experimental procedures

Core–shell nanoparticles were synthesized by laser ablating a multi-component disk target composed of Co, Pt and SiO_2.

* Corresponding author. Tel.: +81 29 861 7268; fax: +81 29 861 7871.
E-mail address: t.seto@aist.go.jp (T. Seto).

1010-6030/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jphotochem.2006.04.046

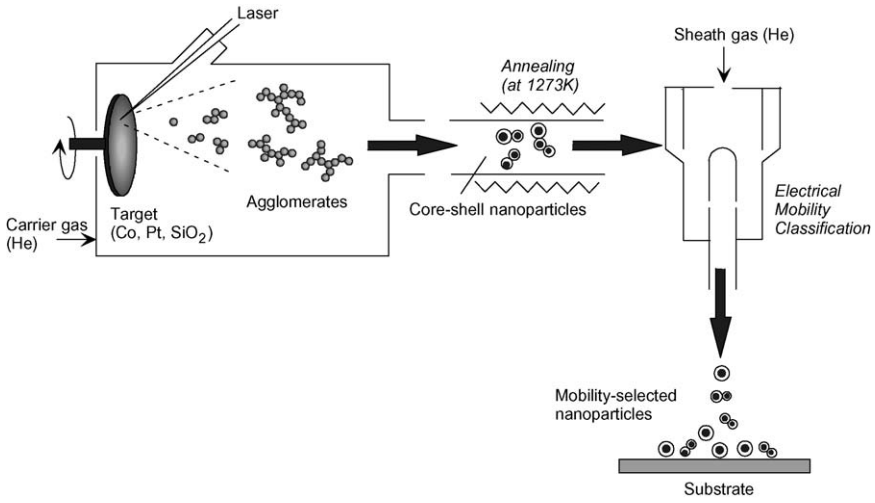

Fig. 1. Experimental setup for generating CoPt:SiO_2 core–shell nanoparticles.

The ablation targets (50 mm in diameter, 2 mm in thickness) were prepared by the hot press of Co, Pt and SiO_2 powders. Two target compositions were used to control the morphologies of the generated particles (atomic ratio, Co:Pt:SiO_2 = 75:25:10 or 75:25:30). The disk target was rotated at a rate of 20 rpm during the laser irradiation. The target materials were simultaneously vaporized and condensed into nanoparticles when the disk target was irradiated by a high-energy laser beam (Nd:YAG, wavelength 532 nm, frequency 20 Hz, pulse energy 23 mJ, spot size 2 mm, fluence 7.3 mJ/mm^2) in a helium background gas (pressure, 1000 Pa), as shown in Fig. 1. Nano-agglomerates were synthesized by the Brownian collision of primary particles. These generated nano-agglomerates (the mixture of Co, Pt and SiO_2 nanoparticles) were transported by the carrier gas and then annealed in the gas phase (an aerosol post annealing: APA) at 1273 K. The nano-agglomerates were restructured and the cores of CoPt alloy were formed during the APA process. The SiO_2 was separated out to the surface, where it formed a shell structure, which protected the cores from further agglomeration and growth. The APA temperature of 1273 K was high enough to generate CoPt alloy but too low to completely sinter the SiO_2.

An electrical mobility classifier (low-pressure differential mobility analyzer; LP-DMA) was used to select the specific mobility of the core–shell nanoparticles (8 or 15 nm in mobility-equivalent diameters). The size-classified nanoparticles were collected on the TEM microgrids and the morphology (core size, shell thickness and shape) was measured by a high-resolution transmission electron microscope (HR-TEM). Given that the electrical mobility was nearly proportional to the square of surface area of particles, the diameter of the primary particles obtained from the electron micrographs, d_{TEM}, differed from the mobility-equivalent diameter, d_m, in the case of the fractal agglomerates. We measured the core diameters and outer diameter of shell of at least 200 primary particles from TEM images in order to determine the size distribution and average core diameters and outer diameter of shell, d_{core} and d_{shell}. By tuning the target composition and mobility diameter, d_{core} and d_{shell} can be controlled. We also evaluated the magnetic properties of these core–shell nanoparticles using a superconducting quantum interference device (SQUID) magnetometer.

3. Results and discussion

Fig. 2a–d are typical TEM images of mobility-classified CoPt:SiO_2 core–shell nanoparticles. The experimental conditions for samples (a)–(d) are listed in Table 1. Two target compositions were used (atomic ratios of 75:25:30 and 75:25:10). The particles were also classified based on two mobility-equivalent diameters, i.e., 8 and 15 nm. In TEM images, the particles were composed of single crystal cores of CoPt alloy covered by SiO_2 shells. We confirmed the alloying of Co and Pt from electron diffraction. We also observed that SiO_2 was localized at the surface by elemental mapping using high resolution electron energy loss spectroscopy (HREELS) attached to the TEM.

Fig. 3 shows the size distributions of cores and shells measured from TEM images. The average diameters of the cores and shells increased as the mobility diameter increased and the

Table 1
Experimental conditions and average dimensions of synthesized nanoparticles

Sample	Target composition (Co:Pt:SiO_2 at%)	Mobility diameter (nm)	Average core diameter (nm)	Average outer diameter of shell (nm)	Average shell thickness (nm)
(a)	75:25:30	8	2.0	4.5	1.25
(b)	75:25:30	15	2.5	5.0	1.25
(c)	75:25:10	8	5.0	7.5	1.25
(d)	75:25:10	15	7.5	12.0	2.25

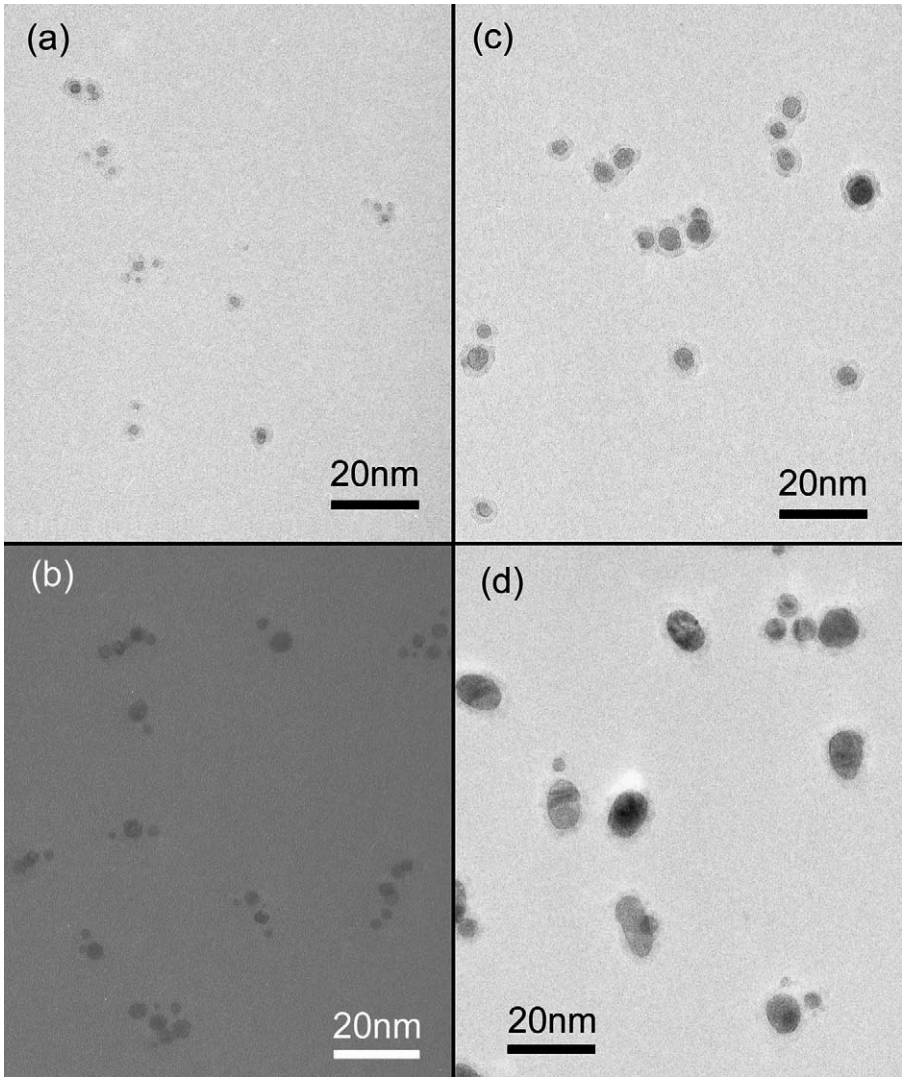

Fig. 2. Typical TEM images of core–shell nanoparticles generated by laser ablating Co:Pt:SiO_2 targets with atomic ratios of (a and b) 75:25:30 and (c and d) 75:25:10. The particle mobility-equivalent diameters were classified at (a and c) 8 nm and (b and d) 15 nm.

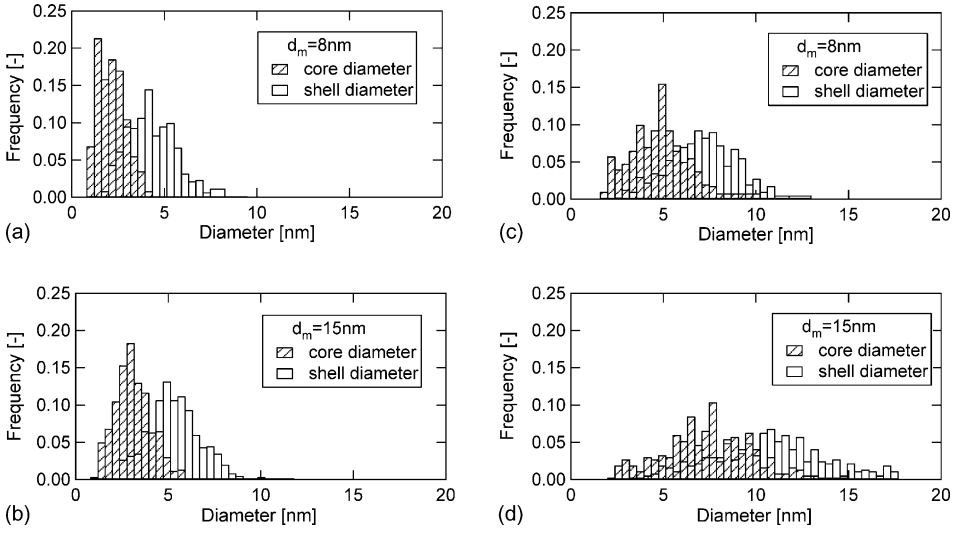

Fig. 3. Size distributions of cores and shells obtained from TEM images. The atomic ratios of the Co:Pt:SiO_2 target were (a and b) 75:25:30 and (c and d) 75:25:10. The particles were classified to mobility-equivalent diameters of (a and c) 8 nm and (b and d) 15 nm.

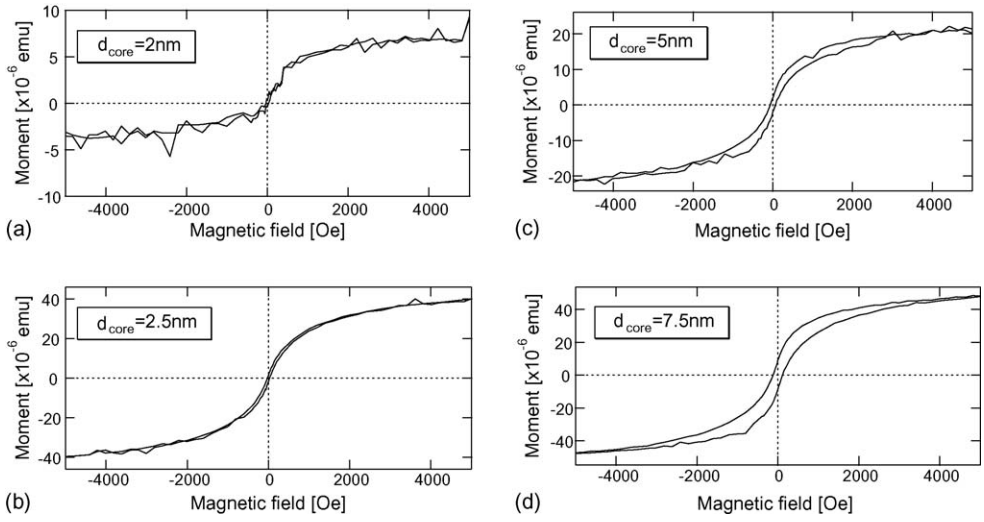

Fig. 4. Hysteresis curves of CoPt:SiO_2 core–shell nanoparticles with average core diameters of (a) 2 nm, (b) 2.5 nm, (c) 5 nm and (d) 7.5 nm. The curves were measured at room temperature.

SiO_2 composition in the target decreased. The average diameters are also listed in Table 1. The particles generated from the target containing 30 at% silica had thicker surface layers than the particles generated from the target containing 10 at% silica. The core diameter was therefore much smaller than the mobility diameter (8 or 15 nm), given that most of the particles were agglomerates and that the primary particles were protected from grain growth by the SiO_2 shells, as shown in Fig. 2a–d. We should note here that the mobility diameter coincided with the outer diameter of the core–shell nanoparticles for the sample (c) (Fig. 3(c)). In the gas phase, most of the generated particles apparently existed as single spheres. The particles were agglomerates, however, when the larger (15 nm) particles were classified or when SiO_2 composition was large (30 at%). This may have been due the action of SiO_2 in protecting against grain growth during the APA process.

Fig. 4 shows the magnetic hysteresis curves of the CoPt:SiO_2 nano-composite films measured by a SQUID magnetometer at room temperature. The nano-composites were prepared by depositing core–shell nanoparticles on the silicon substrates. Hysteresis was observed for the particles with core diameters larger than 2.5 nm, and weak ferromagnetism coupled with superparamagnetism was observed for the particles with the smallest core diameter (2 nm). The coercive force rose in parallel with the core diameter as a result of the spin ordering, reaching 100 Oe for the particles with the largest core diameter (7.5 nm). Our findings thus elucidated the effects of the core size on the magnetic properties of CoPt:SiO_2 nano-composites. It is known that coercivity depends on chemical composition and crystal structure as well as core size as observed for similar system [7,8]. One of our research goals in the future may be to analyze how the magnetic properties change in response to the crystal structure, shell material and inter-particle distance.

4. Summary

We synthesized core–shell nanoparticles by laser ablating a multi-component disk target composed of Co, Pt and SiO_2. The diameters of the CoPt core were adjusted to 2, 2.5, 5 and 7.5 nm by controlling the target composition and performing electrical mobility classification. The core size dependency of the magnetic property was measured at room temperature.

Acknowledgement

This study was supported in part by the New Energy and Industrial Technology Development Organization (NEDO) under the Nanotechnology Materials Program.

References

[1] M. Watanabe, T. Masumoto, D.H. Ping, K. Hono, Appl. Phys. Lett. 76 (2000) 3971–3973.
[2] H. Akinaga, J. Mag. Mag. Mater. 239 (2002) 145–148.
[3] S. Stravroyiannis, I. Panagiotopoulos, D. Niarchos, J.A. Christodoulides, Y. Zhange, G.C. Hadjipanayis, J. Mag. Mag. Mater. 193 (1999) 181–184.
[4] S.H. Sun, C.B. Murray, D. Weller, L. Folks, A. Moser, Science 287 (2000) 1989–1992.
[5] T. Seto, H. Akinaga, F. Takano, K. Koga, T. Orii, M. Hirasawa, J. Phys. Chem. B 109 (2005) 13403–13405.
[6] T. Seto, K. Koga, H. Akinaga, F. Takano, T. Orii, M. Hirasawa, J. Nanoparticle Res., in press.
[7] A.C.C. Yu, M. Mizuno, Y. Sasaki, M. Inoue, H. Kondo, I. Ohta, D. Djayaprawira, M. Takahashi, Appl. Phys. Lett. 82 (2003) 4352–4354.
[8] M. Mizuno, Y. Sasaki, M. Inoue, C.N. Chinnasamy, B. Jeyadevan, D. Hasegawa, T. Ogawa, M. Takahashi, K. Tohji, K. Sato, S. Hisano, J. Appl. Phys. 97 (2005) 10J301.