Synthesis of magnetic CoPt/SiO₂ core-shell nanoparticles

Takafumi Seto¹², Kenji Koga¹², Fumiyoshi Takano¹³, Hiroyuki Akinaga¹³, Takaaki Orii¹², and Makoto Hirasawa¹², Mitsuhiro Murayama⁴

¹Research Consortium for Synthetic Nano-Function Materials Project (SYNAF), National Institute of Advanced Industrial Science and Technology (AIST), Central 2, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan
²Also at: Advanced Manufacturing Research Institute, AIST, 1-2-1 Namiki, Tsukuba 305-8564, Japan
³Also at: Nanotechnology Research Institute, AIST, 1-1-1 Higashi, Tsukuba 305-8565, Japan
⁴National Institute for Material Science, 1-2-1 Sengen, Tsukuba 305-0047, Japan

E-mail: t.seto@aist.go.jp

Abstract. Core-shell nanoparticles composed of ferromagnetic cobalt platinum cores covered by non-magnetic silica shells were synthesized by laser ablating a composite target in a helium background gas. The average diameter of the CoPt core was controlled by adjusting the CoPt/SiO₂ ratio of the ablation target. The particles were also classified in the gas phase using an electrical mobility classifier. The present method successfully synthesized nearly monodispersed nanoparticles with an average core diameter of 2.5nm. This article describes the synthesis of the core-shell nanoparticles and investigates their magnetic properties.

1. Introduction

A nanoscale composite (Nano-composite) composed of ferromagnetic domains dispersed in a non-magnetic matrix possesses unique magnetic and transport properties which make it suitable for use as a magnetic recording medium [1] or as a giant magnetoresistance (GMR) material [2]. In view of their ability to compete with the thermal fluctuation of the electron spin, highly anisotropic materials such as ordered fcc phase CoPt and FePt make good candidates as ferromagnetic domains. Nano-composites 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 dependence of the generation mechanism on the surface nucleation and growth makes it rather difficult to control the size and inter-domain distance without changing the crystal structure. As one alternative, Sun and colleagues 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) \[5, 6\]. Our earlier papers describe the use of this method to fabricate surface-oxidized metal nanoparticles such as Ni/NiO and CoPt/CoO, and investigate the magnetic properties of the nanoparticles 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 ferromagnetic CoPt nanoparticles 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\(_2\). Two target compositions were used to control the morphologies of the generated particles (atomic ratio, Co:Pt:SiO\(_2\) = 75:25:10 and 75:25:30, respectively). The target materials were simultaneously vaporized and condensed into nanoparticles when the target was irradiated by a high-energy laser beam (Nd:YAG, wave length 532nm, frequency 20Hz, pulse energy 23 to 60mJ) in a helium background gas (pressure, 1000Pa), as shown in Fig. 1. The disk target of 50mm in diameter was rotated at a rate of 20rpm. 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 1273K. During the APA process, the nano-agglomerates were restructured and the cores of CoPt alloy were formed. SiO\(_2\) was separated out to the surface and formed a shell structure which protected the cores from further agglomeration and growth. The APA temperature of 1273K was sufficiently high 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. 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 is nearly proportional to the square of surface area of particles, the diameter of the primary particles obtained from the electron micrographs, \(d_{\text{TEM}}\), differed from the mobility-equivalent diameter, \(d_m\), in the case of the fractal agglomerates. The mobility size distribution was measured by scanning the voltage applied to the LP-DMA and counting the number concentration using an electrometer. We also measured the core and shell diameters of at least 350 primary particles from TEM images in order to determine the size distribution and average diameters of the cores and shells, \(d_{\text{core}}\) and \(d_{\text{shell}}\). Lastly, we evaluated the magnetic properties of these core-shell nanoparticles using a SQUID magnetometer.

![Figure 1 Experimental setup used for generating CoPt:SiO\(_2\) core-shell nanoparticles.](image)
3. Results and discussions

The size distribution of the generated polydisperse nanoparticles was measured by LP-DMA and an electrometer. The average mobility-equivalent diameter near the lowest threshold intensity of laser ablation (23mJ) was about 7nm. As this almost coincided with the outer diameter of the core-shell nanoparticles (Fig. 2 (b)), it appeared that most of the generated particles existed as single spheres in the gas phase. The distributions were well-fitted by a log-normal size distribution function (dotted lined in Fig. 2 (a)), and both the average mobility diameter and current increased with the laser intensity. Particles larger than 15nm were measured by LP-DMA when the laser intensity was increased. The average diameters of the cores measure by TEM increased slightly in parallel with the laser intensity; but they remained in the range from 1 to 10nm even at the highest laser intensities applied. This may have been due the action of SiO₂ in protecting against grain growth during the APA process.

![Graphs](image)

Figure 2 (a) Size distributions of nanoparticles measured by LP-DMA and electrometer at variable laser intensities. (b) Size distributions of primary core-shell particles measured by TEM.

Figures 3 (a) and (b) show typical TEM images of mobility-classified CoPt:SiO₂ core-shell nanoparticles. The single crystal cores of CoPt alloy (1 to 18nm in diameter, depending on the experimental condition) were covered by SiO₂ shells (1 to 2nm in thickness).

![Images](image)

Figure 3 Typical TEM image of core-shell nanoparticles generated by a laser ablation of a Co:Pt:SiO₂ target with atomic ratios of (a) 75:25:30 and (b) 75:25:10. The particle mobility-equivalent diameters were classified at (a) 8nm and (b) 15nm.
The particles generated from the target containing 30 atomic percent silica had thicker surface layers than the particles generated from the 10%-$\text{SiO}_2$ target. The core diameter was therefore much smaller than the mobility diameter (8nm), given that most of the particles were agglomerates and the primary particles were protected from grain growth by the $\text{SiO}_2$ shells, as shown in Fig. 3 (a). The core-shell particles with larger diameters, on the other hand, were generated from the 10%-$\text{SiO}_2$ target. The surface-area-equivalent diameters of the agglomerates for both images (Figs. 3 (a) and (b)) were close to the mobility diameters (8 and 15nm, respectively).

Figure 4 shows the hysteresis curve of the CoPt:SiO$_2$ core-shell nanoparticles measured by a SQUID magnetometer. The particles were generated from a 30 at%-$\text{SiO}_2$ target and the core diameter was about 2.5nm (similar to that in Fig. 3 (a)). The particles exhibited ferromagnetism at 5K with a coercive force of 2kOe.

![Hysteresis curve of CoPt:SiO$_2$ core-shell nanoparticles with an average core diameter of 2.5nm. The curve was measured at 5K.](image)

4. Summary
Core-shell nanoparticles were synthesized by laser ablating a multi-component disk target composed of Co, Pt, and SiO$_2$. The diameters of the CoPt core and SiO$_2$ shells were controlled by adjusting the target composition and performing electrical mobility classification. The core-shell nanoparticles with a core diameter of 2.5nm exhibited ferromagnetism at 5K.

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