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TAILORING MORPHOLOGY AND MAGNETIC PROPERTIES OF $CoPt_3$ NANOPARTICLES PREPARED VIA REVERSE MICELLES

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ABSTRACT

Magnetic nanoparticles with an average size of 11 nm have been prepared by using reverse micelle solutions. The effect of gold coating on the morphology and magnetic properties of cobalt-platinum nanoparticles were investigated by X-ray powder diffraction, energy dispersive x-ray, transmission electron microscopy and vibrating sample magnetometry. Nanoparticles that had useful magnetic properties needed to be protected from oxidation to avoid degrading the favorable magnetic properties. $CoPt_3$ nanoparticles showed a blocking temperature of 40K and coercivity of 261.6Oe. Gold coating of $CoPt_3$ cores with a shell thickness of 5nm further enhanced blocking temperature and coercivity to 45K and 421.1Oe respectively.

Keywords: core-shell; magnetic nanoparticles; coercivity; reverse micelle; superparamagnetism

INTRODUCTION

Cobalt-platinum nanoparticles are potential candidates for the next generation of ultra-high density magnetic recording media due to their high anisotropy. In these materials the coercivity must be sufficiently high in order to resist the effect of demagnetization resulting from the particle size sensitive magnetic transitions. The issue is that reduction in grain size below the critical size causes thermal instability in single domain particles and particles behave like a superparamagnet [1]. Furthermore the synthesis method has a direct influence on the magnetic properties of nanoparticles. Nanoparticles with a narrow size distribution (high uniformity) are synthesized in aqueous cores of reverse micelles as nano-reactor allowing nucleation and growth within a confined space and gaining the advantage of size restriction. Precipitation occurs in tiny droplets of water in oil (reverse micelle). The size of water droplets are adjusted by the molar ratio of water to surfactant [2].

METHOD

$CoCl_2$, $PtCl_2$, $AuCl_3$ and $NaBH_4$ were used as starting raw materials for preparing nanoparticles. $CoPt_3$ and $CoPt_3$/Au binary alloy and core/shell structure nanoparticles were prepared in one and two steps reverse micelle solutions respectively. The nanometer size particles were synthesized using reverse micelles of cetyltrimethylammonium bromide (CTAB) as the surfactant, 1-butanol as the co-surfactant and n-octane as the oil phase. To this solution, an aqueous solution containing the metal ions was added. Initially Co^{2+} and Pt^{4+} ions were reduced under argon atmosphere by sodium borohydride as the reducing agent.

In preparing $CoPt_3$/Au core/shell structure nanoparticles, micelles of gold ions (Au^{3+}) were injected to the previous solution in the second step. Gold ions were further reduced via sodium borohydride and resulted core/shell as $CoPt_3$/Au. The particles were then separated from the solution by centrifuge (with 3500rpm) and dried at room temperature. The particles were further annealed at 800°C under argon gas.

RESULTS AND DISCUSSIONS

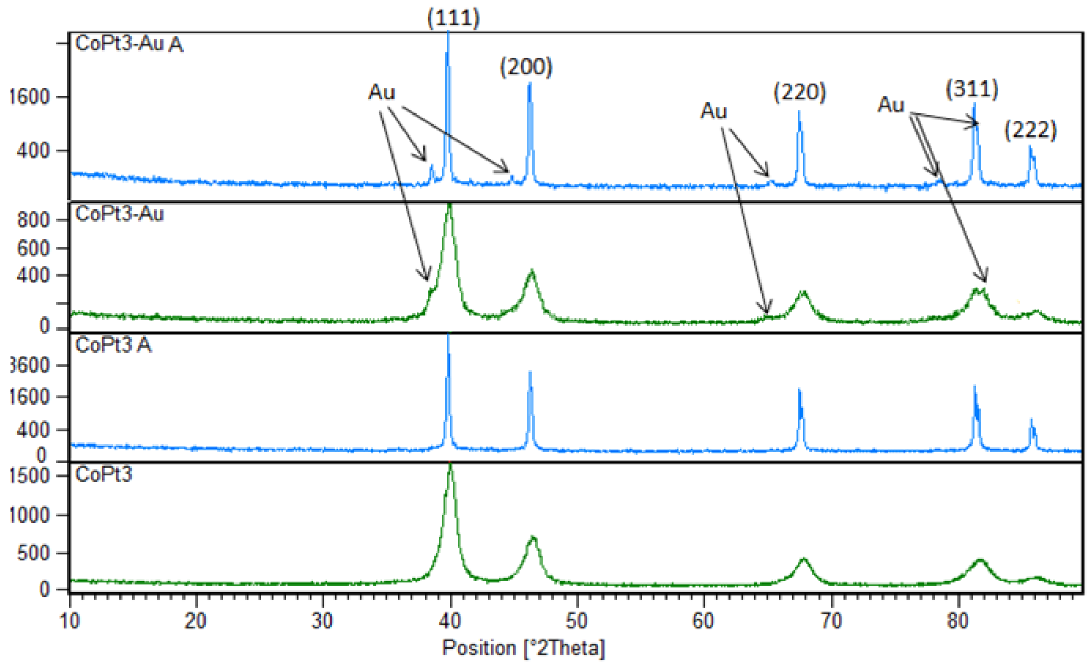

Figure 1: X-ray patterns of $CoPt_3$ and $CoPt_3$-Au before and after annealing at 800°C under argon atmosphere for 1 hour

Figure 1 shows XRD patterns of $CoPt_3$ and $CoPt_3$ nanoparticles coated with gold before and after annealing. The crystal planes were indexed to cubic $CoPt_3$. After the gold coating the peaks of Au were observed due to the formation of a shell around the $CoPt_3$ cores. The narrower peak width after the annealing indicates growth of the particles and

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increase in grain size. Figure 2 shows TEM results for $CoPt_3$ before and after the gold coating. A formation of a gold shell with mean size of 5nm was observed around the cores. The aim of the coating was to prevent oxidation of particles which were exposed to air. Figure 2 shows that samples were spherical in shape and had a narrow size distribution as well.

In addition EDX results (figure 3 a, and b), show the peaks of Co, Pt and O. After the gold coating the peaks of Au become more significant. The FESEM image confirms that the particles are spherical agglomerated nanoparticles with small shiny Au dots covering the surface of cores.

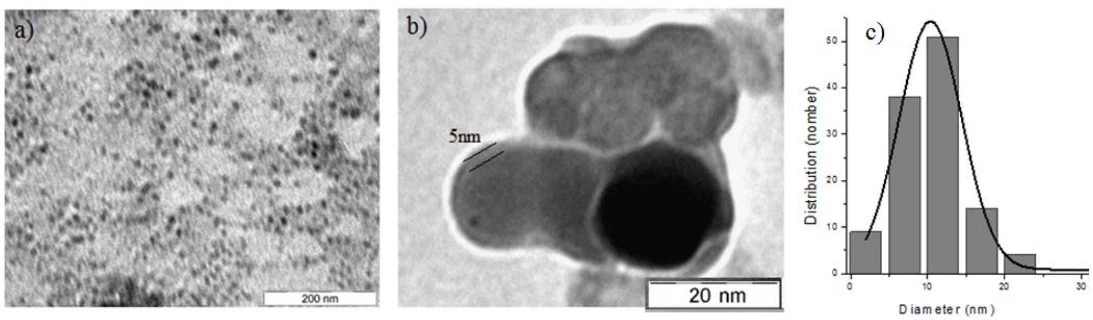

Figure 2: a and c) TEM result of $CoPt_3$ and related size distribution. b) $CoPt_3$/Au after gold coating

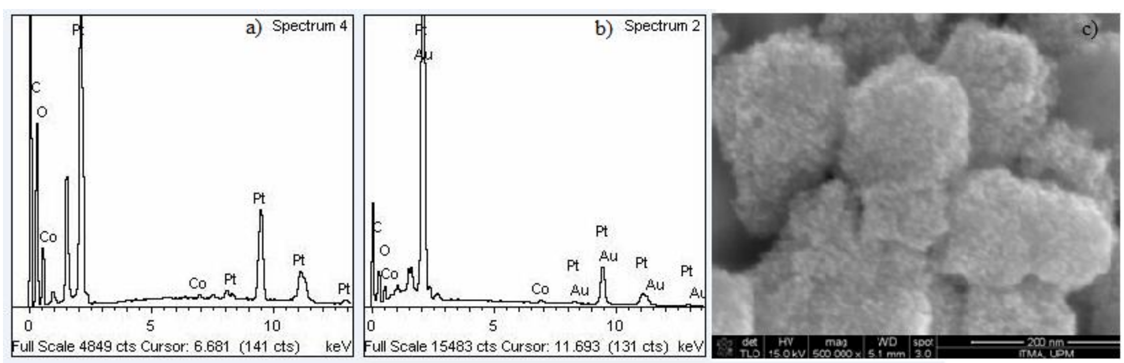

Figure 3: EDX pattern of a) $CoPt_3$, b) $CoPt_3$/Au and c: FESEM image for $CoPt_3$/Au after annealing in 800^{o}C for 1 hour

Magnetic measurements were performed on powdered samples. Figure 4 reveals an open loop hysteresis and non-zero coercivity for as-prepared $CoPt_3$ and $CoPt_3$-Au nanoparticles. After annealing the particles at 800^{o}C the coercivity increased from 83.3 and 192.2 to 261.6 and 421.1Oe in the case of $CoPt_3$ and $CoPt_3$-Au nanoparticles respectively. The increase in coercivity after annealing was due to grain growth [3] from 11.5 and 13.5 to 14.4 and 16.1 correspondingly. After the gold coating an increase in coercivity and decrease in saturation magnetization was observed (TABLE 1). This is because of the spin configuration at the interface between the core and shell [4]. Interparticle interaction between the spins at the interface causes an existence of disordered phase so the difficulty for the spins to rotate, thus causing the decrease in saturation magnetization.

Blocking temperature measurement was carried out by a simple method. Figure 4 b illustrates the measured magnetization vs temperature curve. A cusp in zero-field-cooled (ZFC) magnetization indicates the blocking temperature (T_B). At temperatures near T_B all the moments are aligned caused by a strong interaction between Co moments within a small grain size. $CoPt_3$-Au nanoparticles showed a blocking temperature at 45K higher than $CoPt_3$ (40K). In the literature, it is mostly reported that superparamagnetic (or paramagnetic) behaviour occurs above the blocking temperature and ferromagnetic behaviour below T_B. However in the results obtained from the VSM the non-zero coercivity in open sigma shape hysteresis loops, indicate that the samples have a behaviour in between the above two behaviours.

TABLE 1: Summary of magnetic measurements

sample	H_C (Oe)	M_S (emu/g) (K)	T_B	Grain size (nm)
$CoPt_3$	83.3		0.14	11.5
			-	
$CoPt_3$/Au	192.2		0.11	13.5
			-	
$CoPt_3$ annealed	261.6		0.041	14.4
$CoPt_3$/Au annealed	421.1		40	16.1
			0.023	
			45	

After the heat treatment on the particles, the coercivity increases and the saturation magnetization decreases in both $CoPt_3$ and cobalt-platinum nanoparticles coated with gold. This is mainly due to thermal fluctuations of surface moments which happen at room temperature in superparamagnetic region. Magnetic properties of ultrafine particles are controlled by two prime factors: interparticle coupling between the particles and interparticle interactions. In nm size ranges, surface atoms have a significant percentage of the total number of atoms in the particle which influence the magnetic anisotropy. The atoms near the surface are in a less symmetric environment than those in the core [5]. The anisotropy constant value (K_u) of cobalt-platinum nanoparticles can be estimate from equation 1.

$$K_u = \frac{25kT_B}{V_p} \qquad (1)$$

where k is Boltzman constant, T_B is the blocking temperature and V_p is the volume of particles. $CoPt_3$-Au with the average size of 16.1nm has an anisotropy constant of

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$1.2x10^7 emu/cm^3$ which is lower than that of bulk ($2x10^7 emu/cm^3$). The lower value of anisotropy arises from the decrease in the particle size to nano-range [6].

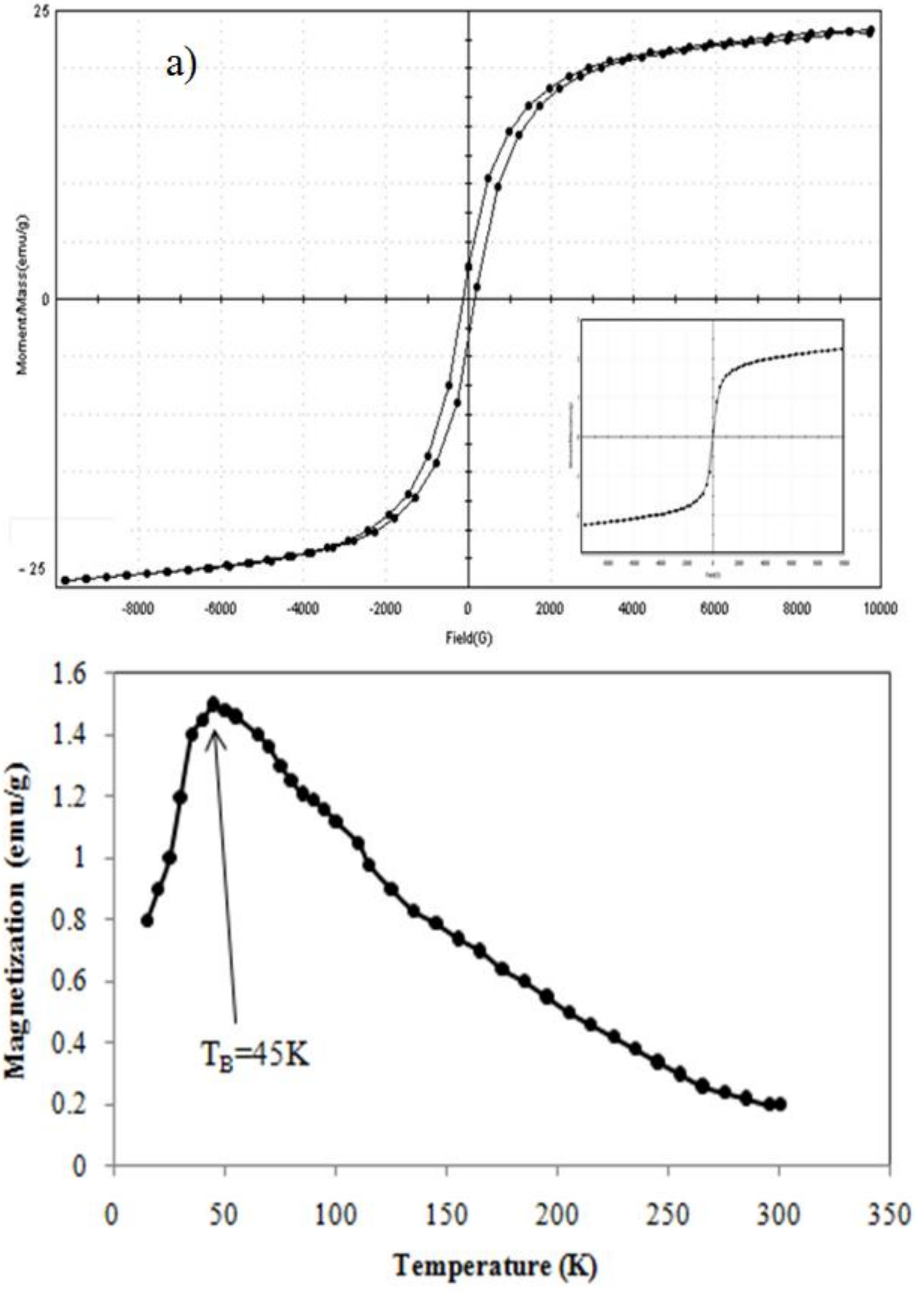

Figure 4: Summary of a) magnetization vs. field plot of as-prepared and the annealed sample of gold coated $CoPt_3$ nanoparticles at 300K. b) magnetization vs. temperature plot of gold-coated $CoPt_3$ performed with no applied field

CONCLUSION

CoPt3 and CoPt3/Au nanoparticles were prepared successfully via reverse micelles with average sizes of 11.5 and 13.5nm and show very high coercivity at room temperature (421.1Oe) which makes them good candidates for magnetic recording media. The samples were a single-domain ferromagnet below the blocking temperature at 45K with the anisotropy constant value of $1.2x10^7$emu/cm^3.

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