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Ag assisted evolution of ordered $L1_0$ CoPt alloy nanoparticles

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ABSTRACT

CoPt–Ag nanoparticles were successfully prepared by the simultaneous polyol reduction of the corresponding metal precursors in the presence of poly(*N*-vinyl-2-pyrrolidone) (PVP). This study details the influence of Ag additive on the structural and magnetic properties of CoPt as a function of Ag concentration. Despite a slight tetragonal distortion, the XRD studies reveal the maximum degree of transformation from fcc to $L1_0$ phase, for CoPt–Ag nanoparticles containing the highest Ag percent (i.e. 70%) on annealing at 700 °C for 2 h. The Ag particles are clearly observed to be in contact with the surface of the annealed CoPt thus imparting surface strain to these nanoparticles. A magnetic phase transformation is observed after heat treatment showing an evolution of a hard magnetic material from the initially synthesized soft CoPt–Ag nanoparticles. The measure of magnetic hardness increases with increasing Ag content. Consistent with XRD, magnetic measurements show the most remarkable increase in coercivity for the maximum Ag content attaining a value of 1.5 T. The interesting feature of tunability between chemical ordering and coercivity may be useful for data storage devices.

1. Introduction

Magnetic nano-materials have drawn a lot of attention because of their wide range of technological applications in permanent magnets, high density data storage [1–5], biomedicine [6,7], etc. The interest to further improve the storage density has been a primary focus of research these days. The key point while making progress toward this direction is the processing of nano-magnetic materials with high magnetocrystalline anisotropy and a well oriented growth [8]. The $L1_0$ materials, e.g. FePt and CoPt, etc., which possess a natural multilayered structure, are being recently investigated for this application. Their high magnetocrystalline anisotropy value ($4–7 \times 10^7$ ergs cm^{-3}) permits stability of magnetization against thermal fluctuations. However, the necessary heat treatment required for its formation leads to unavoidable effects like grain growth, etc. hence limiting its practical utility. A significant reduction in the temperature required for $L1_0$ phase formation of CoPt and FePt can be obtained by the addition of a third element (e.g. Ag, Au, Cu, etc.) [9–14]. Besides this assistance, a complementary enhancement in the magnetic properties has also been observed in such systems [15–19] thereby promoting its applicative approach. Encouraged by the results obtained in our previous communication on the stabilization of $L1_0$ CoPt in the presence of Ag [20], lead us to examine the possible mechanism of this effect.

In the present communication we report a systematic study on the effect of Ag on the magnetic behavior of CoPt nanoparticles with varying Ag content.

2. Experimental

2.1. Synthesis of CoPt–Ag nanoparticles

CoPt–Ag nanoparticles with varying concentration of Ag were synthesized by the simultaneous polyol reduction of platinum(II)acetylacetonate (Pt(acac)$_2$), cobalt(II)acetylacetonate (Co(acac)$_2$) and silver nitrate ($AgNO_3$) using PVP as a capping agent and ethylene glycol as the solvent and reducing agent. Detailed synthesis process for the preparation of CoPt–Ag nanoparticles has been described in our previous report [20]. The concentration of Ag in CoPt could easily be varied by varying the mole ratio of CoPt to $AgNO_3$ salt precursors added during the particle synthesis. To study the role of Ag additive in the structural and magnetic ordering of $L1_0$ CoPt phase, CoPt–Ag nanoparticles with mole ratio ranging from 2:0.5 to 2:4 were prepared. These nanoparticles are further referred according to their mole percentage of Ag, i.e. 20%, 40% and 70% Ag content.

The as synthesized powders of CoPt–Ag with different concentrations of Ag were subjected to a heat treatment in Ar + 5%H_2 atmosphere at 700 °C for 2 h using a microprocessor controlled temperature furnace. Heat treatment at 700 °C was chosen as the temperature of interest due to preliminary studies that showed a formation of $L1_0$ phase at 600 °C and a significant enhancement in the magnetic properties on further annealing [20].

2.2. Characterizations

The crystalline structure was studied by the XRD patterns recorded using a Rigaku Miniflex II diffractometer with Cu Kα radiation (λ = 1.54056 Å), operated at 30 kV and 15 mA. TEM analysis was performed on the powders using a 300 keV FEI Tecnai G^2 30 Model. Room temperature magnetic measurements were performed using a Vibrating Sample Magnetometer, Micro Sense EV9 with a maximum magnetic field of 2.2 T.

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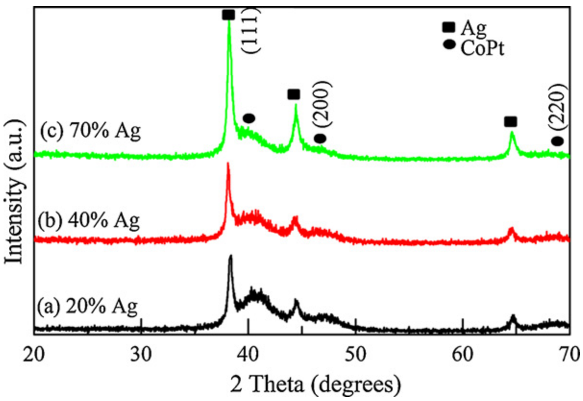

Fig. 1. X-ray diffraction pattern for the as synthesized CoPt–Ag nanoparticles with (a) 20%, (b) 40% and (c) 70% Ag content.

3. Results and discussion

The effect on the structural ordering of CoPt induced by the presence of Ag was investigated using X-ray diffraction (XRD). Fig. 1 compares the XRD patterns corresponding to the as synthesized CoPt–Ag nanoparticles containing different percentages of Ag.

The sharp peaks (solid squares) observed are signatures of the presence of Ag and the broad humps correspond to the disordered fcc CoPt phase (solid circles) with *hkl* planes (1 1 1), (2 0 0) and (2 2 0), respectively. The relatively high percentage of Ag compared to CoPt leads to a suppression of the humps as clearly observed for 70% concentration (curve 1c). The width of the humps corresponding to CoPt is considerably broad indicating the formation of small size particles. An average particle size of 2–3 nm was estimated from the full width at half maxima for the (1 1 1) peak of CoPt for each Ag concentration using Scherrer's formula. A shift in the most intense peak of CoPt (1 1 1) is observed suggesting a lattice expansion [9,21]. This expansion maybe due to the strain induced in the system on account of the difference in the lattice parameters of CoPt and Ag. The increasing amount of Ag atoms substituted in the lattice, causes a corresponding increase in the $d_{1\,1\,1}$-spacing's [18] ranging from 2.22 Å to 2.27 Å for 0% to 70% Ag, respectively. Fig. 2 shows the change in the CoPt unit cell dimensions, i.e. the variation in the *d*-spacing (calculated from the position of CoPt (1 1 1) peak) with increasing content of Ag. The plot includes a data point corresponding to 0% and 50% Ag content which is in accordance to the previously reported results [20].

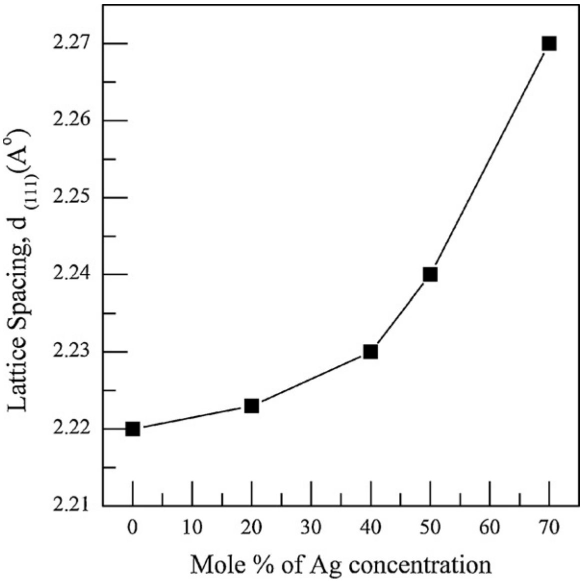

Fig. 2. Variation of *d*-spacing with increasing content of Ag.

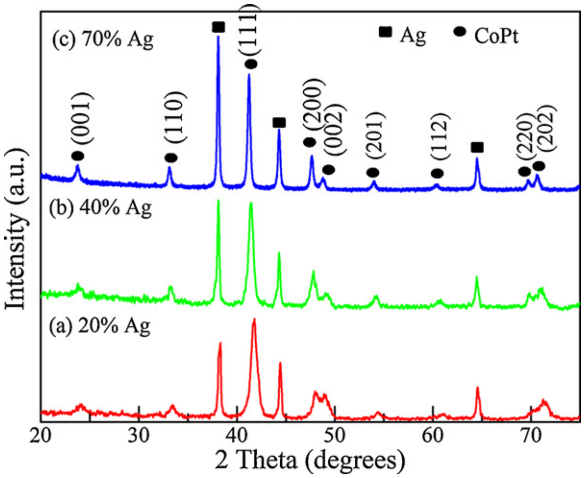

Fig. 3. X-ray diffraction pattern for CoPt–Ag nanoparticles annealed at 700 °C with (a) 20%, (b) 40% and (c) 70% Ag content.

In order to obtain the chemically ordered $L1_0$ phase, CoPt–Ag nanoparticles with different Ag contents were annealed at 700 °C for 2 h under the same annealing conditions. The CoPt broad humps evolved as relatively sharp peaks at 700 °C as observed in Fig. 3. Evidence of the formation of an ordered $L1_0$ phase at this temperature was indicated by the presence of the superlattice peaks (0 0 1) and (1 1 0) at low 2θ values (24° and 33°, respectively) and the splitting of the (2 0 0) hump into two distinguishable peaks, i.e. (2 0 0) and (0 0 2) for each concentration of Ag [22]. Strain in the annealed samples was analyzed using Williamsons–Hall plot [23]. A continuous increase in the strain ranging from 0.3% to 3% has been observed with increasing Ag content.

Since Ag has a low surface energy [24], after annealing, the Ag atoms tend to segregate from CoPt hence assisting CoPt to achieve the ordered phase. The CoPt–Ag sample with 70% additive attains a value, $d = 2.19$ Å which is close to that of bulk $L1_0$ CoPt ($d = 2.17$ Å). In all concentrations, as clearly observed, the greatest degree of transformation from fcc to $L1_0$ phase, is seen in the diffraction pattern corresponding to the highest percentage of Ag, i.e. 70% (curve 3c) with a tetragonality ratio, $c/a = 0.976$ and ordering parameter, $S = 0.89$. For 50% Ag content we had however obtained a c/a ratio of value = 0.973 and a better ordering of $S = 0.96$ [20]. From these analyses it is clear that there may be an optimum percentage of Ag which helps in the chemical ordering, beyond which, there is a possible tetragonal distortion in the unit cell due to the excessive strain in the system.

An attempt to determine the location of the Ag additive, pre and post heat treatment was made by HRTEM analysis. Fig. 4a shows the TEM image of as synthesized CoPt–Ag nanoparticles with 20% Ag additive.

The TEM micrograph shows a spherical morphology for the nanoparticles. The corresponding particle size histogram (inset) follows a Gaussian distribution with an average particle size of 2.6 nm. Inset shows the HRTEM image of an individual nanosphere with a *d*-spacing of 0.133 nm which closely matches the (2 2 0) plane of fcc CoPt hence confirming its formation. The formation of a disordered fcc CoPt phase is further confirmed by the indexed selected area diffraction (SAD) pattern given in Fig. 4b. The diffused nature of the diffraction rings is consistent with the formation of particles with small size. The existence of Ag was however remains unnoticed in the TEM image and the SAD pattern as well showed no plane corresponding to Ag.

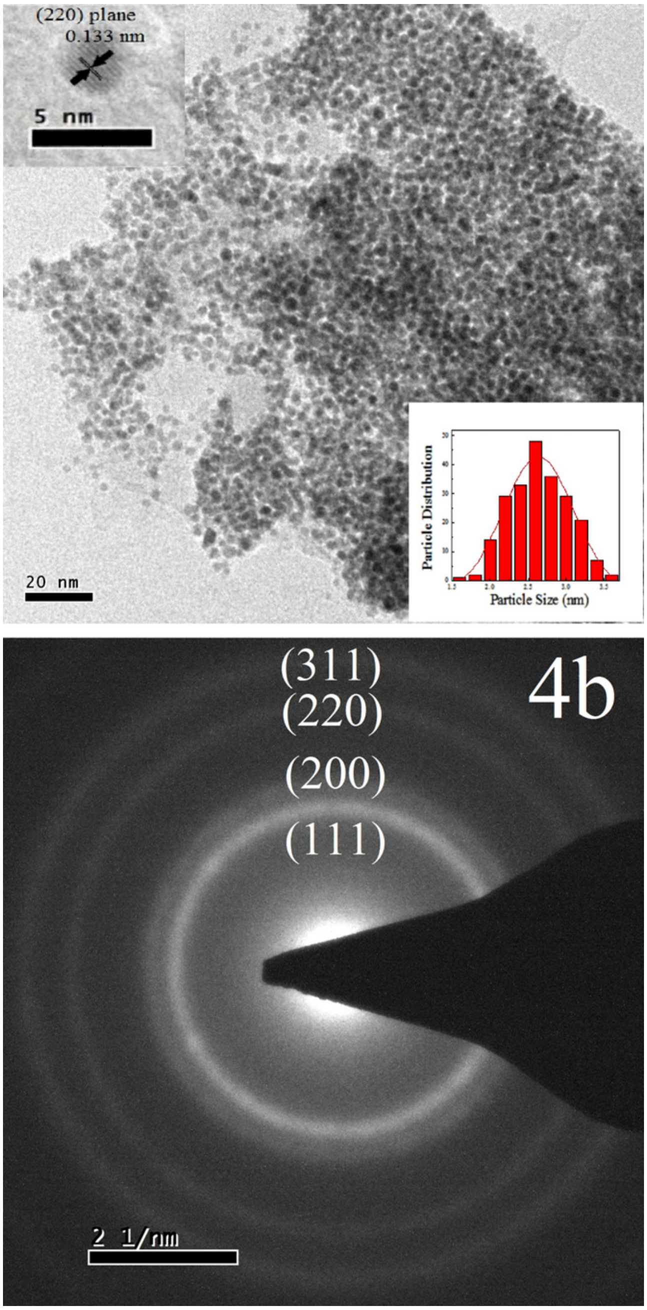

Fig. 4. (a) TEM image of as synthesized CoPt–Ag nanoparticles with 20% Ag additive and (b) the corresponding SAD pattern.

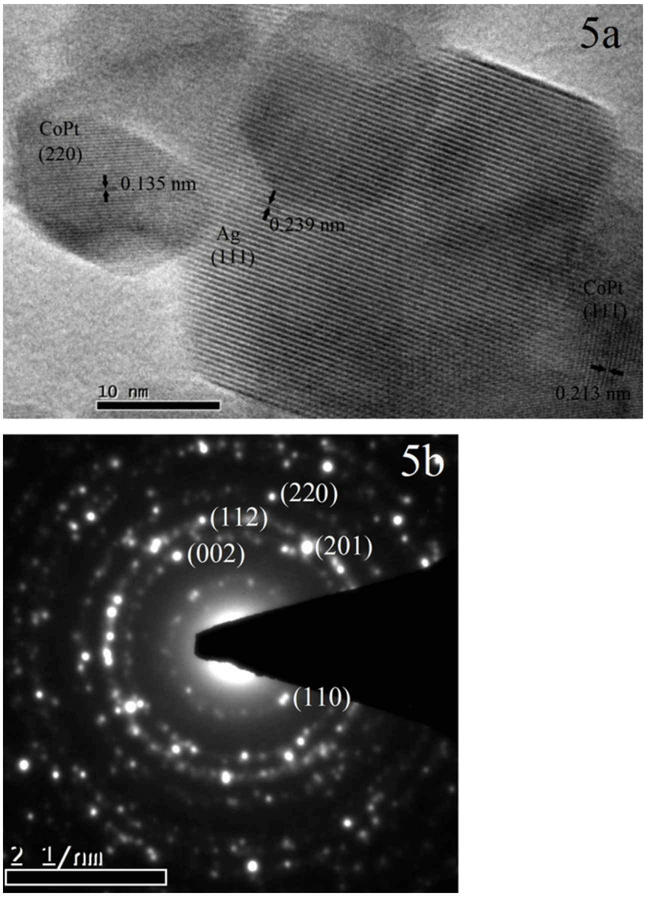

Fig. 5. (a) HRTEM image of CoPt–Ag nanoparticles with 20% additive annealed at 700 °C and (b) the corresponding SAD pattern.

The HRTEM image of these nanoparticles, subsequent to annealing, has been shown in Fig. 5a. The presence of two distinct planes with different *d*-spacing values are observed. The distance between the lattice fringes 0.213 nm and 0.135 nm closely match to the $L1_0$ CoPt planes (1 1 1) and (2 2 0), respectively, while the *d*-spacing 0.239 nm corresponds to (1 1 1) plane of Ag [25]. The arrangement of Ag atoms in the $L1_0$ CoPt–Ag nanoparticles was found to be in contact with the surface region surrounding and overlapping the CoPt nanoparticles.

Using ESCA technique, Iskandar et al. [26] also reported an arrangement of Ag atoms on the surface region of annealed FePt nanoparticles. The corresponding SAD pattern (Fig. 5b) show rings indexed to planes prominently matching with $L1_0$ CoPt phase. The suppression of any ring related to Ag planes may be due to the relatively less percent of Ag in the sample. Interestingly, the annealed sample containing 70% Ag content shows a distribution of two particles (Fig. 6a).

It is observed that small size particles are overlapped by particles of comparatively large size. These big particles may correspond to Ag atoms which overlap the small CoPt nanoparticles. This statement is supported by the corresponding SAD pattern (Fig. 6b) which shows Ag planes, i.e. (1 1 1), (2 0 0) and (2 2 0) dominate over CoPt whose presence is justified by the appearance of a minor reflection of (1 1 0) superlattice plane.

The hysteresis measurements, recorded up to a field of 2.2 T at 300 K, have been performed on the CoPt–Ag nanoparticles with varying concentration of Ag, both pre and post annealed. The as synthesized nanoparticles exhibit a magnetically soft behavior with a low coercivity, H_c as shown in Fig. 7. The relative value of saturation magnetization, M_s for the different Ag percent nanoparticles match well according to the concentration of Ag.

The effect of Ag additive as a function of increasing concentration on the magnetic behavior of CoPt–Ag nanoparticles subsequent to heat treatment at 700 °C is shown in Fig. 8. According to these results, there is a strong increase in the magnetic anisotropy with increasing Ag concentration. The most prominent increase was observed in the sample with 70% of Ag giving a maximum coercivity of 1.5 T.

As clearly observed, the hysteresis loop corresponding to each sample has a shoulder close to the zero field. Such a curvature suggests a mixture of nanoparticles with different magnetic phases, i.e. soft and hard phase [27,28]. The shoulder in these nanoparticles reduces with increase in the Ag content thus indicating an improvement in the $L1_0$ phase formation. These results are

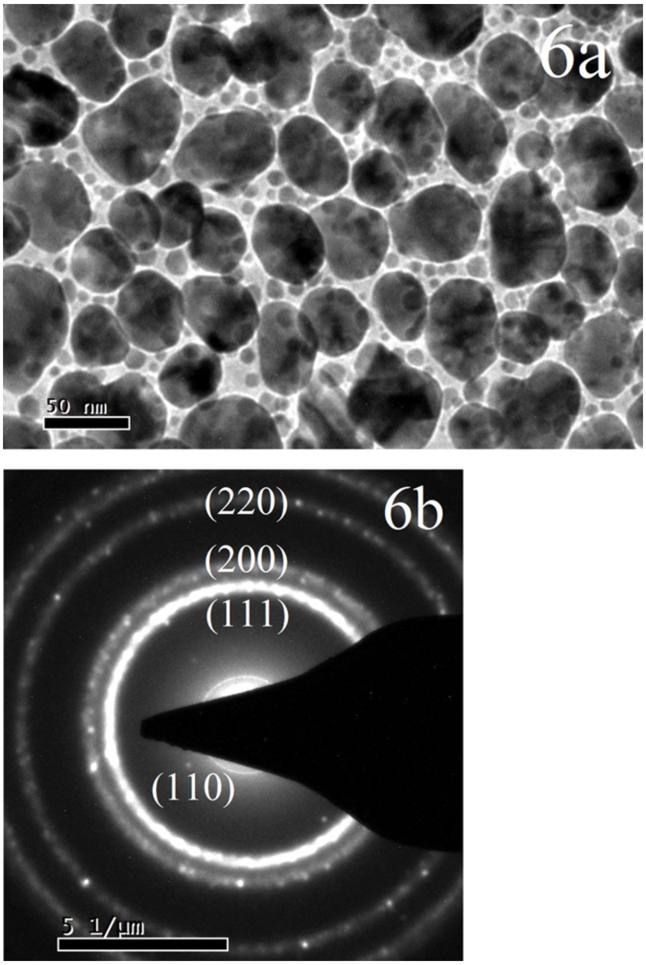

Fig. 6. (a) TEM image of CoPt–Ag nanoparticles with 70% additive annealed at 700 °C and (b) the corresponding SAD pattern.

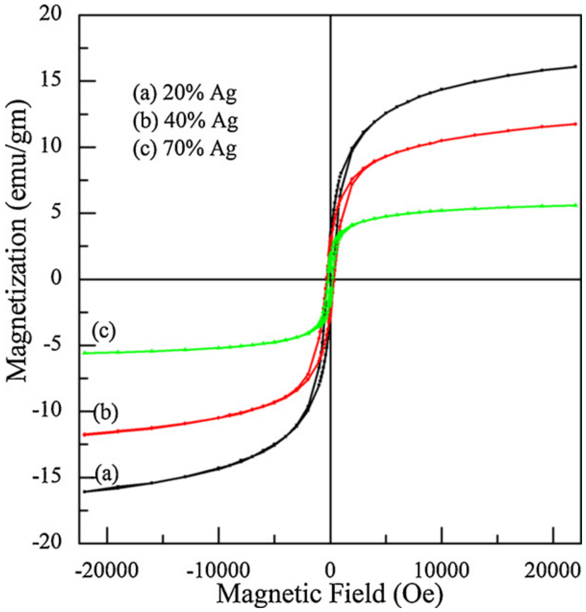

Fig. 7. Hysteresis loop for the as synthesized CoPt–Ag nanoparticles with (a) 20%, (b) 40% and (c) 70% Ag content.

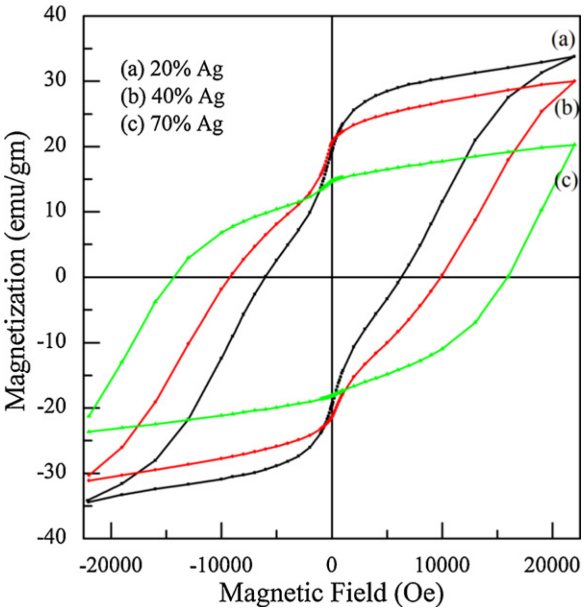

Fig. 8. Hysteresis loop for the 700 °C annealed CoPt–Ag nanoparticles with (a) 20%, (b) 40% and (c) 70% Ag content.

consistent with XRD where the highest degree of transformation to the $L1_0$ phase was observed for 70% Ag content.

4. Conclusions

The role of Ag additive in influencing the $L1_0$ ordering and in magnetic anisotropy enhancement, as a function of varying Ag content, can hence be understood by the correlating the XRD, TEM and VSM results. The XRD studies reveal that on annealing the CoPt–Ag nanoparticles, due to maximum lattice expansion, the sample with highest Ag content will create more vacant sites on segregation. Therefore the relative percent of Co and Pt atoms able to arrange themselves in an ordered manner will be more, resulting in a relatively higher volume fraction of $L1_0$ grains than the disordered fcc phase. This is supported by the VSM analysis which shows an improved coercivity and better degree of transformation (less shoulder) for the sample with maximum Ag. Despite the improved coercivity, the c/a ratio for the 70% Ag is less with respect to that of 50% Ag [20] implying a tetragonal distortion. Thus, it is clear that merely the concept of chemical ordering is not the only reason for the enhancement in the magnetic properties. The enhancement in coercivity may quite possibly be related to the contribution of strain to the magnetic anisotropy. As observed by the TEM images it is clear that Ag particles are in contact around the surface of CoPt nanoparticles. This pinning of Ag to the surface may perhaps introduce a strain in the surface and hence impart an additional contribution to the magnetic anisotropy reflected by the improved coercivity value. In addition to magnetocrystalline anisotropy of the $L1_0$ CoPt phase, the strain anisotropy contributed due to the presence of Ag results in an appreciable enhancement of magnetic anisotropy. This enhanced coercivity is effective in stabilizing magnetization, a main property required for magnetic data storage devices. Thus the interesting feature of tunability between chemical ordering and coercivity may be useful for practical applications.

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