Effect of chemical composition and Co-core size on the magnetic and magneto-transport properties of Co$_y$Ag$_{100-y}$ core–shell nanocrystallites

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ABSTRACT

This paper describes the applicability of a modified polyol process in conjunction with a transmetallation reaction in synthesis of Co$_y$Ag$_{100-y}$ nanocrystallites of a core–shell structure. The substitution Co $\rightarrow$ Ag is varied as $20 \leq y \leq 95$ by tuning the microstructure with functional magnetic and giant magneto resistance properties. The existence of core–shell structures was confirmed through transmission electron microscope and the size of Co-core increased from 8 to 50 nm with decrease in Ag-content of the sample. The magnetic behaviour of the sample changed from a pseudo-superparamagnetic nature to ferromagnetic with increase in Co-core size. Normalised saturation magnetisation values increased from 89.5 to 128.6 emu/g with increase in size of Co-core; however, none of the ferromagnetic samples exhibited any magneto resistance (MR). A value of 2.0% MR was observed in case of Co$_{20.6}$Ag$_{79.4}$ which increased to a maximum of 3.6% MR for Co$_{36.6}$Ag$_{63.4}$ sample when measured at 5 K.

KEYWORDS

core–shell nanocrystallites; Co$_y$Ag$_{100-y}$; magneto resistance

1. Introduction

Synthesis and characterisation of magnetic core–shell nanocrystallites (CSNCs) has gained prominence due to their potential applications in diverging fields such as magnetic recording, magnetic sensing, catalysis, diagnosis, drug delivery and bio-separations [1–5]. The physical, chemical and magnetic properties of CSNCs can be tuned by controlling the core and shell thicknesses as well as their chemical composition [6]. The 3$d$-block elements Fe(3$d^6$), Co(3$d^7$) and Ni(3$d^8$) form the most prominent and fascinating group of ferromagnetic materials. These three elements exhibit huge ferromagnetism in the elemental forms useful to derive a variety of tailor made magnetic materials with functional properties in the form of core–shell structures [2,6–8]. Fe has the highest saturation magnetisation, 220 emu/g, amongst them, with 170 emu/g in cobalt and 55 emu/g in nickel at room temperature. Though iron has superior magnetisation value, it tends to get oxidised rather readily in air in comparison to the other two elements due to its higher negative
reduction potential \( (E^0) \). Co and Ni are less prone to oxidation with significantly lower \( E^0 \) values. This oxidation process manifests many folds as the surface area enlarges in small particles. Compared to Ni, Co reserves superior technological significance because of its higher magnetisation and larger magnetocrystalline anisotropy with pretty large Curie point \( T_C = 1131 \) °C. It yields tunable properties with proper microstructuring and surface modification, and hence is an ideal choice as core material. A very important factor to form core–shell structures is that the core and shell materials should not form an alloy during synthesis. Au, Ag and Cu are the three elements that are non-ferromagnetic and highly insoluble at atomic scale with Co under equilibrium conditions. Therefore, these three elements are largely chosen as shell constituents \([1,2,6,8,9]\).

The giant magneto resistance (GMR) effect is a unique phenomenon exhibited by \( \text{Co}_y \text{Ag}_{100-y} \) CSNCs, and it leads to potential applications in many areas such as magnetic field sensors and recording media \([4,5]\). Various physical methods such as sputtering and mechanical alloying have thus far been reported for the preparation of \( \text{Co}_y \text{Ag}_{100-y} \) nanometric thin films or nanocomposites \([5,10]\). However, true core–shell structures are envisaged as better alternative over thin films or composites as the particle size could be effectively controlled to near ideal situation of two ferromagnetic single domains separated by a non-ferromagnetic layer. A plethora of chemical routes such as co-precipitation, thermal decomposition, reverse micelle route and transmetallation have been reported thus far to synthesise such CoAg CSNCs \([11–16]\). In comparison to the physical methods, the chemical methods provide an additional advantage of precisely controlling the chemical composition, size and shape (also surface topology) in CSNCs. Most of the chemical routes reported thus far for the synthesis of \( \text{Co}_y \text{Ag}_{100-y} \) crystallites have been restricted to selective alloy compositions for developing GMR for pertinent applications. This leads to create a gap in the proper understanding of the effect of cobalt core size on the net GMR effect in small \( \text{Co}_y \text{Ag}_{100-y} \) crystallites. Considering all these technicalities, in this work, an emphasis is laid on the synthesis and characterisation of \( \text{Co}_y \text{Ag}_{100-y} \) crystallites of varied compositions \( (y = 20, 35, 50, 60, 70, 85 \text{ and } 95) \) in optimising the functional magnetic and GMR properties. The onus has been taken-up on (1) optimising the reaction parameters, (2) to study the role of the initial \( \text{Ag}^+ \) ions concentration on the size of the core in small crystallites and (3) to characterise the magnetic and magneto-transport properties in the various \( \text{Co}_y \text{Ag}_{100-y} \) alloys.

2. Experimental

Analytical grade chemicals (purchased from Alfa Aesar laboratories, Germany) of cobalt acetate tetrahydrate, silver acetate, ethylene glycol (EG), hydrazine hydrate, poly-(vinyl-pyrrolidone) (PVP) and ethanol were used as the starting materials to synthesise \( \text{Co}_y \text{Ag}_{100-y} \) (20 \( \leq y \leq 95) \) in the form of nanocrystallites (NCs) with a core–shell structure. In order to carry out the modified polyol reaction, a cobalt hydrazine precursor complex was prepared by dissolving 0.3 g of cobalt acetate tetrahydrate (0.18 M) in 25 mL of EG, followed by the addition of 25 mL EG containing 0.4 mL hydrazine hydrate (0.36 M) solution in a drop-wise manner under constant magnetic stirring at room temperature. A polymer solution of PVP was prepared separately by dissolving 0.5 g of PVP in 50 mL of EG. The cobalt hydrazine complex and polymer solutions were mixed together by mechanical stirring for 15 min at room temperature in a 250 mL three-necked round
bottom flask fitted with a reflux condenser. This step allows a proper dispersion of PVP molecules into a precursor solution. After thoroughly mixing, the solution so obtained was subjected to heating to its refluxing temperature (~195 °C) for 30 min. Throughout the reaction process, the mechanical stirring was applied at a rate of 100 rotations per minute. Under these specified conditions, the pink coloured cobalt precursor turns into a blackish solution due to a Co$^{2+}$ → Co reduction reaction.

Upon the formation of a black coloured colloidal solution, heating was turned off and the solution so obtained was allowed to cool down to room temperature, with the stirring kept on. Once the room temperature was attained, a silver acetate powder was added and stirred for 15 min before the heating was turned on. Then, the solution temperature was raised to a predetermined temperature 120 °C and allowed to hold thereon for another 15 min. During this time period of the mixing in a hot condition, the Ag$^+$ ions dissolve into the solution and start reacting with the surrounding medium to result in a colour change of the reaction contents from a blackish to greyish silver. The heating was turned off at this stage and the final product was stirred for another 15 min before decanting the colloidal solution to separate out the Co$_{1-y}$Ag$_{100-y}$ NCs. Finally, 50 mL of ethanol was added to the colloidal dispersion so that it helps extract the Co$_{1-y}$Ag$_{100-y}$ crystallites from the solution. Collection of the product was carried out by centrifugation. The final product Co$_{1-y}$Ag$_{100-y}$ so obtained was thoroughly washed with 15 mL of ethanol for three times to remove traces of any unreacted species present therein. The composition and shell thickness could be varied in the Co$_{1-y}$Ag$_{100-y}$ NCs by using a 0.18 M concentration of the cobalt complex with different silver salt precursor contents in all the experiments. The various alloy compositions Co$_{1-y}$Ag$_{100-y}$ prepared in this simple method are given in Table 1. The collected magnetic Co$_{1-y}$Ag$_{100-y}$ powders of predetermined compositions were then dried in a vacuum desiccator at room temperature before carrying out further characterisations.

A combination of three analytical techniques including JY-ULTIMA inductively coupled plasma optical emission spectrometer (ICP-OES), LECO TC-600 oxygen and nitrogen determinator and LECO CS-444 carbon and sulphur analyser were used to obtain the chemical compositions of the various Co$_{1-y}$Ag$_{100-y}$ powders shown in Table 1. The Co- and Ag-contents were analysed in ICP-OES at their respective characteristic wavelengths of 228.616 and 328.066 nm. Absorption spectra of the solution samples were recorded at various stages of the reaction using a PG instruments T90+ UV-vis spectrometer. All the samples were uniformly diluted five times using EG as a solvent before recording the spectra under identical experimental conditions. A Bruker instrument TENSOR 27 model

### Table 1. Chemical compositions of the Co$_{1-y}$Ag$_{100-y}$ core–shell crystallites obtained at various preparation conditions.

| Expt | Wt taken (g) | Co (II) acetate | Ag (I) acetate | Chemical composition in (wt%) | Composition in (at%) |
|------|-------------|-----------------|----------------|-----------------------------|---------------------|
| a    | 0.3         | 0.20            |                | 12.3 (0.1) 86.6 (0.6) 1.09 (0.06) 0.15 (0.02) 0.11 (0.01) Co$_{20.6}$Ag$_{79.4}$ |
| b    | 0.3         | 0.16            |                | 23.7 (0.2) 75.1 (0.5) 1.22 (0.05) 0.14 (0.03) 0.11 (0.01) Co$_{36.6}$Ag$_{63.4}$ |
| c    | 0.3         | 0.12            |                | 33.6 (0.2) 65.2 (0.4) 1.15 (0.04) 0.15 (0.02) 0.12 (0.02) Co$_{48.5}$Ag$_{51.5}$ |
| d    | 0.3         | 0.08            |                | 45.4 (0.3) 53.4 (0.4) 1.20 (0.03) 0.14 (0.02) 0.13 (0.01) Co$_{60.9}$Ag$_{39.1}$ |
| e    | 0.3         | 0.04            |                | 57.6 (0.3) 40.5 (0.4) 1.19 (0.05) 0.15 (0.01) 0.13 (0.03) Co$_{72.2}$Ag$_{27.8}$ |
| f    | 0.3         | 0.02            |                | 73.9 (0.5) 24.6 (0.4) 1.17 (0.05) 0.14 (0.03) 0.12 (0.01) Co$_{84.6}$Ag$_{15.4}$ |
| g    | 0.3         | 0.01            |                | 89.6 (0.5) 9.2 (0.2) 1.28 (0.1) 0.16 (0.02) 0.13 (0.02) Co$_{94.7}$Ag$_{5.3}$ |
Fourier transform infra-red (FTIR) spectrometer was used to study the transmission spectra of the Co\textsubscript{y}Ag\textsubscript{100−y} powders dispersed in KBr in comparison with a virgin PVP polymer.

A Philips-PW3020 X-ray diffractometer (XRD) consisting of an X-ray source of CuK\textalpha of 0.15405 nm wavelength was used to obtain the diffraction patterns from different Co\textsubscript{y}Ag\textsubscript{100−y} powders. Crystallite size, shape and core–shell structure in the different as-prepared Co\textsubscript{y}Ag\textsubscript{100−y} powders were analysed using a FEI TECNAI G2 transmission electron microscope (TEM) at an accelerating voltage of 120 kV. To obtain the TEM images and selected area electron diffraction (SAED) patterns, a re-dispersed sample solution in acetone was drop-coated onto a 3 mm carbon coated copper grid and analysed in a bright field mode. An ADE EV9 model vibrating sample magnetometer (VSM) was used for magnetic characterisation of the as-prepared Co\textsubscript{y}Ag\textsubscript{100−y} powders at room temperature. In order to obtain the hysteresis loop, a powder of known mass was put into a quartz cup and fixed onto a quartz rod and then mounted into the VSM prior to applying the magnetic field (max 20 kOe). Low temperature magnetic measurements were carried out with the help of a magnetic property measurement system (MPMS) superconducting quantum interference device (SQUID) VSM. In order to record the zero-field cooled (ZFC) curve, the sample was first cooled down to 4 K in a zero field and then a field of 100 Oe was applied to record its magnetisation as a function of increasing temperature up to 300 K in a SQUID magnetometer. After attaining the temperature of 300 K, the sample was progressively cooled and its magnetisation was recorded in the presence of the applied magnetic field, which resulted in a field cooled (FC) curve. To study the magneto-transport properties of the samples, the powder Co\textsubscript{y}Ag\textsubscript{100−y} samples were pressed into a pellet of 1.5–2 mm thickness using a hydraulic press. The green compact was heat treated at 300 °C for 2 h, which was used to investigate the magneto-transport properties at room temperature 300 K and at low temperature of 5 K, i.e. just below the \( T_b \) point. The GMR measurements were performed on the pellets at two representative temperatures 300 and 5 K using a four probe standard technique in the applied magnetic fields between −10 kOe and 10. All the different samples given in Table 1 were measured under identical conditions in order to make a comparison of the magnetic and GMR properties of the Co\textsubscript{y}Ag\textsubscript{100−y} NCs as composition is varied.

3. Results and discussion

The formation of Co-NCs from a cobalt hydrazine complex and a transformation of them into Co\textsubscript{y}Ag\textsubscript{100−y} NCs are analysed in terms of the electronic absorption spectra after the reactions in the solutions. For illustration, Figure 1(a–c) shows a typical set of three absorption spectra obtained from the samples of (a) a cobalt hydrazine complex, (b) a colloidal solution of Co-NCs and (c) a colloidal solution of Co\textsubscript{94.7}Ag\textsubscript{5.3} NCs. In the synthesis of Co-NCs through a polyol process, the cobalt hydrazine complex prepared from a cobalt acetate precursor is characterised by two distinct absorption bands which appear at 468 and 527 nm in the visible region of the spectrum in Figure 1(a). These bands arise from the 3d–3d Co\textsuperscript{2+} (3d\textsuperscript{6}) transitions 4\( T_{1g} \) → 4\( T_{1g} \) (P), and 4\( T_{1g} \) → 4\( A_{2g} \) respectively, which unambiguously indicates that the Co\textsuperscript{2+} state retains even after the addition of hydrazine. Heating the above complex to the refluxing temperature of EG (~195 °C) for 30 min period results in a drastic change of the solution colour from pink to blackish. It is also reflected in the absorption spectrum of a black coloured colloidal sample as shown in
Figure 1(b), wherein the Co$^{2+}$ bands completely disappear leading to a flat profile. This leads to a conclusion that the Co$^{2+}$ ions have reduced presumably to Co atoms. Upon the addition of silver acetate powder to the blackish colloidal solution, a slow but distinct change in its colour was observed. The blackish tinge slowly transformed into a greyish silver colour which resulted in a new band with an absorption maxima ($\lambda_{\text{max}}$) at 432 nm as shown in the spectrum in Figure 1(c). The 432 nm band could be attributed to the typical signature of the surface plasmon resonance (SPR) absorption from Ag-NCs [17].

The role of surface stabiliser PVP polymer molecules during the reaction in forming surface stabilised Co$_y$Ag$_{100-y}$ NCs was analysed using FTIR spectra. Figure 2(a–g) shows the FTIR spectra collected from the samples after completion of the reaction from

Figure 2. FTIR spectra of Co$_y$Ag$_{100-y}$ core–shell nanocrystallites obtained from various experiments, (a) Co$_{20.6}$Ag$_{79.4}$, (b) Co$_{36.6}$Ag$_{63.4}$, (c) Co$_{48.5}$Ag$_{51.5}$, (d) Co$_{60.9}$Ag$_{39.1}$, (e) Co$_{72.2}$Ag$_{27.8}$, (f) Co$_{84.6}$Ag$_{15.4}$ and (g) Co$_{94.7}$Ag$_{5.3}$, with (h) a virgin PVP sample.
successive experiments. A comparison with a spectrum of virgin PVP is shown in Figure 2 (h), which comprises of a broad band at 1655 cm\(^{-1}\) arising from the C = O stretching. Modified IR spectra with two bands in this region support the fact that the PVP molecules are present on the Co\(_y\)Ag\(_{100-y}\) NCs. A red shift by 25–30 cm\(^{-1}\) in the C = O stretching frequency is observed in all the spectra in Figure 2(a–g) in comparison to the virgin PVP molecules. The red shift envisages a weak coordination between the lone pair of the electrons on the O atoms of the carbonyl groups in the polymer and the surface of the Co\(_y\)Ag\(_{100-y}\) NCs [18]. The peak at 1655 cm\(^{-1}\) which corresponds to the C = O stretching frequency of PVP molecules that are not directly bound to the Co-NCs as shown in a schematic in Figure 3.

In Table 1, a close observation of the chemical compositions of the different Co\(_y\)Ag\(_{100-y}\) (20 ≤ y ≤ 95) NCs, prepared as a fine powder, gives a marked variation in the minor ingredients of C, O and N from a by-product phase which arises from the PVP polymer molecules added during the synthesis as a surface stabiliser. All the values of the elements reported in Table 1 are an average of three different measurements with their standard deviation mentioned in the parenthesis. Apparently, the values of the minor components vary from the sample to sample as 1.1–1.3 wt% carbon, 0.14–0.17 wt% oxygen and 0.11–0.13 wt% nitrogen because of a variation in the shell thickness and its relative fraction. Further, keeping a cobalt precursor content constant (0.3 g) and decreasing a silver acetate precursor from 0.20 to 0.01 g from experiments (a–g) in the synthesis process, a gradual increase in the ultimate Co-content in the final product so obtained from the different batches (a–g) is clearly observed. However, the ratio of Co:Ag, when
compared from reactant side to product side in the individual reactions, show considerable decrease in the Co-content in the final samples.

The depletion of Co in the final product could be attributed to the *in situ* reactions taking place during the formation of the core–shell structure. As the Co-NCs are present in the solution prior to the addition of the silver acetate, the Ag⁺ ions displace Co atoms due to the favourable transmetallation reactions as depicted in Equations (1)–(3). The half cell reactions thus suggest that the reduction of Ag⁺ → Ag is facilitated by the Co-NCs, which act as an electrode during the reaction process and ultimately get oxidised to Co²⁺ ions. Thus, a reduction of the Ag⁺ ions in this experiment can be attributed to the consorted effect of polyol and Co-NCs. Further, the Co-NCs also act as favourable sites for nucleation and growth of the silver-NCs resulting in a heterogeneous nucleation mechanism during the formation of Co_yAg_100−y core–shell NCs. As the Co and Ag are immiscible in solid solution under an equilibrium condition, they do not form an alloy of the predetermined composition but rather result in the attainment of a core–shell structure. This follows a very simple way of forming a core–shell structure of Co_yAg_100−y (20 ≤ y ≤ 95) NCs with promptly surface tailored magnetic and other properties. A displacement reaction involved in this example can be expressed as follows:

\[
\begin{align*}
E^0 \quad V \\
(\text{Ag}^+ + e^- & \rightleftharpoons \text{Ag} + 0.80) \\
(\text{Co}^{2+} + 2e^- & \rightleftharpoons \text{Co} - 0.28) \\
\text{Co} + 2\text{Ag}^+ & \rightleftharpoons 2\text{Ag} + \text{Co}^{2+} + 1.08
\end{align*}
\]

These half cell reactions suggest that during a reduction reaction Ag⁺ → Ag by adding a silver salt to a cobalt precursor solution, part of the Co atoms are displaced back into the reaction medium as Co²⁺ ions, showing a decrease in the net Co-content in the final product of Co_yAg_100−y NCs. In order to ascertain the material balance of the Co-content, the supernatant solutions at two stages of the reaction were collected (i) after a reduction of a cobalt hydrazine complex to Co-NCs and (ii) after the formation of the Co_yAg_100−y core–shell NCs. Both these solutions were centrifuged thoroughly to remove any suspended particles before the analysis. In the solution (i), a very negligible amount of <0.2 wt% Co had been observed, whereas the solution (ii) contains a substantial amount of Co, which was in good agreement to the displaced Co-content as estimated with a back calculation. A schematic of a complete reaction process involved in the formation of Co_yAg_100−y core–shell NCs is depicted with a model diagram in Figure 3.

The powder XRD patterns of the various Co_yAg_100−y NCs prepared from the above experiments (a–g) are presented in Figure 4 in order to examine how the pattern changes with the average composition. From a comparison of these results, it could be observed that the pattern comprises of four characteristic peaks at 2θ values of 38.19°, 44.36°, 64.52° and 77.44° which are common in all the seven samples in Figure 4. These four peaks could be discerned to the lattice reflections of (111), (200), (220) and (311) of the face centred cubic (fcc) Ag as per the reported Joint Committee on Powder Diffraction Standards (JCPDS) file 87–0720. In the samples (a–c), no peaks other than the fcc-Ag are observed giving an impression that the total sample content is only silver and apparently there is no cobalt. Further, the XRD pattern obtained from experiment (g) exhibits a
larger intensity for the fcc-Co (220) peak when compared to the hexagonal closed packed (hcp-Co) (100) peak. This result indicates that the cobalt of small crystallites appears predominantly in the fcc crystal structure. In all these XRD patterns, the major peak of fcc-Co (111) conspicuously merges with the Ag (200) peak as both these peaks fall in a close proximity to each other and, therefore, a precise distribution of the Co phases could not be determined with the present data in this investigation. However, an indicative picture could be deduced from the observed patterns by comparing the fcc-Ag (111) and (200) peaks. A sharp and intense Ag (111) peak found in the sample (a) is shown to be decreasing gradually in its intensity and it also broadens with a decrease in the predetermined Ag-content in the XRD patterns in the samples in Figure 4(b–g).

The peak broadening in the characteristic XRD peaks clearly signifies that the average crystallite size of the fcc-Ag is decreasing with a decrease in the Ag-content in the precursor Co$_y$Ag$_{100-y}$ compositions. Further, the intensity of the fcc-Ag (200) peak does not decrease with a decrease in the Ag-content, but it contrarily increases in case of the sample (g) where the Co-content is pretty large 89.6 wt%. This observation implies a fact that the XRD peak located at 44.36°C does not solely arise from the fcc-Ag (200) reflection but is a combination of the two overlapping fcc-Ag (200) and fcc-Co (111) lattice reflections. Hence, it is discerned to both the fcc-Co and fcc-Ag in the XRD patterns in these samples. Further, the intensities of the fcc-Ag peaks are much higher when compared to those of the fcc-Co in a given Co$_y$Ag$_{100-y}$ composition, as it can be seen very clearly from the XRD in the samples (a) and (f), where the contents of Co and Ag are ~20 at% respectively. This peculiar phenomenon of the absence, or diminishing of the fcc-Co peak intensities, could be attributed primarily to two main factors, (1) a difference in the mass absorption coefficient of CuKα radiation for Co (354 cm$^2$/g), which is significantly higher than the value of 223 cm$^2$/g for Ag, and (2) the Ag-NCs are present as a stable surface
coating over the Co-core, which ultimately leads to further diminishing its apparent XRD intensity.

Bright field TEM images along with the SAED patterns were studied from selective regions from the various Co$_y$Ag$_{100-y}$ NCs samples as given in Table 1. For example, Figure 5(a–c) compares the TEM images obtained on three typical compositions of (a) Co$_{20.6}$Ag$_{79.4}$, (b) Co$_{60.9}$Ag$_{39.1}$ and (c) Co$_{84.6}$Ag$_{15.4}$. The images in the first two samples in

![Figure 5](image-url)
Figure 5(a,b) that have a higher Ag-content of 39.1 at%, or still larger, represent a markedly different microstructure of a kind of a reinforced hybrid composite structure. Distinctly well-separated images (dark contrasts) are seen in Figure 5(c) in the sample which has a rather small Ag-content of 15.4 at%. The dark central region refers to a Co-rich phase, which is encapsulated by a shell of an Ag-rich phase of a less darkish contrast. As expected, the shell fraction is decreased progressively from sample (a), which contains 79.4 at% Ag, to the sample (b) with 39.1 at% Ag or sample (c) with 15.4 at% Ag in Figure 5(a–c). These results confer the conjuncture that part of the silver bounds and embeds a Co-rich phase in a core–shell nanostructure.

The average size of Co-core varies with average composition of the sample over the series of Co$_{y}$Ag$_{100-y}$ core–shell NCs studied in this investigation. In the TEM microstructure in Figure 5(a), the sample Co$_{20.6}$Ag$_{79.4}$ measures an average size 8.5 nm of the Co-core, which is increased to 20–25 nm in the images in Figure 5(b) in the sample Co$_{60.9}$Ag$_{39.1}$ or to a still larger value of 45 nm in those in the sample Co$_{84.6}$Ag$_{15.4}$ Figure 5(c). Qualitatively, a magnified TEM image reproduced in the inset in Figure 5(b) represents a distinct core structure of cobalt of an average 30 nm diameter with a demarcated Ag-shell binding it and bridging of a gap between adjacent Co$_{y}$Ag$_{100-y}$ features around, wherein the tiny Ag-NCs start accumulating on the cobalt surfaces that ultimately grow into a continuous phase resulting in a composite structure.

A general implication is that the average size of an fcc-Co-core is growing up progressively when the Co-content is increasing in the above three samples. This is consistent with a fact that the Ag$^+$ ions induce a transmetallation reaction while preparing the sample from a liquid precursor, so as it leads to the decrease in the final core size upon the Ag-content increases over the composition series. It has also been observed that at comparatively lower Ag-contents, mostly individual core–shell crystallites persist throughout the sample with an Ag-shell of 7 nm thickness under the observation, whereas only a few NCs last barred without a shell structure at pretty high Ag-contents. The number density of such Ag-NCs is very small and is below 5% of the total value in the TEM images in Figure 5. The SAED pattern obtained from the Co$_{60.9}$Ag$_{39.1}$ sample in Figure 5(d) contains six well-separated concentric rings of which four could be discerned to the (111), (200), (220) and (311) lattice reflections of the fcc-Ag of 0.2350, 0.2029, 0.1439 and 0.1226 nm of the $d_{hkl}$ values (according to an average $a = 0.4069$ nm) in agreement with the corresponding values shown in the XRD pattern in Figure 4. Both the fcc-Co (111) and fcc-Ag (200) share a common lattice reflection as the spots over the concentric rings in Figure 5(d). Further, the remaining two diffraction rings could be assigned to the (200) and (222) lattice reflections of the fcc-Co (following the JCPDS file 15–0806). The prominent reflections which arise from an fcc-Ag illustrate unambiguously that the boundary phase is definitely an fcc-Ag rich phase and it exists in the form of a shell in a core–shell structure. It can be further confirmed from the energy dispersive X-ray spectra (EDS) that the core region comprises predominantly of Co with a little Ag-content as shown in Figure 5(e). The little Ag peaks observed arise from the coating of Ag over the Co-core. In Figure 5(f), the EDS spectra obtained from the shell region show predominantly Ag. This leads to a conclusion that the Co forms the core, and Ag engulfs it in the form of a shell.

Another interesting observation in this work is that the samples prepared with effectively low Ag-contents, as evident from the TEM images in Figure 5(c), exist in well-separated structures, whereas those prepared with an effectively large Ag-content (as evident
from the TEM images in Figure 5(a,b)) exhibit a rather composite structure in which the fcc-Ag forms a continuous matrix phase encompassing the Co-NCs in small assemblies. This phenomenon could be explained by invoking a fact that Co-NCs upon formation tend to stay independently rather than a cluster. Upon an effectively higher loading of the Ag-content, the Ag-NCs not only encapsulate the Co-NCs, but also tend to adjoin themselves with the surrounding shells and therefore render a matrix like appearance. An agglomeration of Ag-NCs at around higher concentrations could not be controlled as the PVP molecules in the basic reaction were not used much, and that may not have been sufficient enough to control and regulate the particle size distribution at high metallic loading during the reaction process with a liquid precursor.

The magnetisation vs magnetic field (M–H) loops for various Co$_y$Ag$_{100-y}$ samples at room temperature were used in analysing how the Ag-content when varied from 5 to 80 at% can ultimately lead to tune the functional magnetic properties out of a tailor made core–shell structure of small ferromagnetic crystallites. The M–H loops so obtained from

![Magnetic hysteresis loops of Co$_y$Ag$_{100-y}$ core–shell nanocrystallites obtained from (A) experiments (a) Co$_{20.6}$Ag$_{79.4}$, (b) Co$_{36.6}$Ag$_{63.4}$ and (c) Co$_{48.5}$Ag$_{51.5}$ (inset showing the magnified portion of second quadrant) and (B) experiments (d) Co$_{60.9}$Ag$_{39.1}$, (e) Co$_{72.2}$Ag$_{27.8}$, (f) Co$_{84.6}$Ag$_{15.4}$ and (g) Co$_{94.7}$Ag$_{5.3}$.](image-url)
as-synthesised samples (a–g) are shown in Figure 6(A,B). From these results, it could be observed that the first two samples (a) and (b) exhibit a pseudo-superparamagnetic behaviour with a small coercivity \(H_c\) as shown in the inset, which indicates that most of the Co-NCs are below the ideal single domain size (17 nm). As expected, the magnetisation does not saturate before 20 kOe of a maximum applied field over here in the present measurements. These results of the surface tailored magnetism and magnetic properties are in good agreement with the TEM images which show a core of cobalt of 8.5 nm average diameter for the \(\text{Co}_{20.6}\text{Ag}_{79.4}\) sample obtained from the experiment (b). A wider ferromagnetic hysteresis loop develops in Figure 6(c) in a sample \(\text{Co}_{48.5}\text{Ag}_{51.5}\) in which the magnetisation still does not saturate before 20 kOe of a maximum applied field in this investigation. This indicates that a significant fraction of the ferromagnetic Co-NCs are co-present in the sample along with some superparamagnetic particles, which do not saturate in magnetisation over such low fields. The ferromagnetic character is grown up in this sample at the expense of the superparamagnetic character prominent in the first two samples, (a) and (b).

A comparison of the hysteresis loops of the other \(\text{Co}_y\text{Ag}_{100-y}\) samples in Figure 6(B) implies that the \(M_s\) value is increased regularly from a minimum of 40.6 emu/g observed in the sample (d), which contains 39.1 at% Ag, to as large as 115.2 emu/g upon decreasing the Ag-content to as low level as 5.3% in sample (g). The values observed in the individual samples are given in Table 2. An increase in the \(M_s\) value is concomitant with the decrease of the Ag-content which contributes no effective value assuming it to be nonmagnetic in nature. In general, the \(M_s\) value stands lower in all the samples when compared to a bulk value, 170 emu/g, known in the hcp-Co at room temperature. In order to make a closer observation on \(M_s\) value arising primarily from the cobalt, we estimated the magnetisation by normalising the Co-content to 100% in the \(\text{Co}_y\text{Ag}_{100-y}\) \((20 \leq y \leq 95)\) samples. The effective \(M_s\) value so obtained is shown to be still varying over a wide range 89.5–128.6 emu/g, but it is comparable to earlier reported values in Co-NCs prepared via different routes [18–20]. The normalised values of the magnetisation measured at 20 kOe field thus suggest that the magnetisation of Co-NCs is affected significantly by an Ag-shell thickness and it no longer remains an inherent property of the Co-core alone in a kind of surface modified small magnets. As it is expected, this could be attributed to a fact that most of the variations in the magnetic properties arise in small crystallites below the ideal single domain size.

Furthermore, the \(H_c\) value, which is an extrinsic magnetic property in a ferromagnetic or a ferrimagnetic material of randomly dispersed ideal single domains, varies differently with Ag-content over a wide window from 93 to 599 Oe in the \(\text{Co}_y\text{Ag}_{100-y}\) samples, primarily according to a core–shell nanostructure. A maximum \(H_c\) value of 599 Oe is shown in a specific sample \(\text{Co}_{72.2}\text{Ag}_{27.8}\) which comprises a critical composition with three times content of Co than the Ag. It seems a result of forming and anchoring a sufficiently rigid

| Sample | Average formula | \(M_s\) (emu/g) | \(H_c\) (Oe) | Co (wt%) | Normalised \(M_s\) (emu/g) | Co-core size (nm) |
|--------|----------------|----------------|-------------|--------|---------------------------|------------------|
| a      | \(\text{Co}_{20.6}\text{Ag}_{79.4}\) | – 130          | 12.3        | –      | –                         | 8.5              |
| b      | \(\text{Co}_{36.6}\text{Ag}_{63.4}\) | – 160          | 23.7        | –      | –                         | 9.3              |
| c      | \(\text{Co}_{48.5}\text{Ag}_{51.5}\) | – 154          | 33.6        | –      | –                         | 14.5             |
| d      | \(\text{Co}_{64.8}\text{Ag}_{35.2}\) | – 40.6         | 500         | 45.4   | 89.5                      | 21               |
| e      | \(\text{Co}_{72.2}\text{Ag}_{27.8}\) | – 62.7         | 599         | 57.6   | 108.9                     | 32               |
| f      | \(\text{Co}_{84.6}\text{Ag}_{15.4}\) | – 93.9         | 112         | 73.9   | 127.1                     | 45               |
| g      | \(\text{Co}_{94.7}\text{Ag}_{5.3}\) | – 115.2        | 93          | 89.6   | 128.6                     | 50               |
shell (nonmagnetic) on a ferromagnetic core of cobalt so that it behaves as an ideal single magnetic domain. A kind of a nonmagnetic shell serves as a strong pinning barrier which supports devising an effectively large $H_c$ in the ideal single magnetic domains of small fcc-Co crystallites bounded in an Ag-shell [12,16]. These results are in good agreement with the earlier reported work of Co@Au core–shell NPs, wherein with an increase in shell thickness the $H_c$ values increased due to enhanced interfacial pinning effect [9]. Eventually, in an Ag-rich, as well in a Co-rich Co$_y$Ag$_{100-y}$ ($20 \leq y \leq 95$) sample, the two magnetic and nonmagnetic components grow in support of each other in independent phases, forming not so rigid core–shell structure with the ideal single magnetic domains. The $H_c$ also exhibits a percolation effect attaining a maximum value 599 Oe in sample (e) of a composition Co$_{72.2}$Ag$_{27.8}$ and it tends to decrease on either side of the Ag-content. This leads to an inference that an optimal size of Co-core and Ag-shell is required to obtain a maximum coercivity value in such an intimate core–shell structure.

Since the two samples in Figure 6(a,b) showed a pseudo-superparamagnetic behaviour with some coercivity, further measurements were carried out to obtain a detailed information about their magnetic behaviour at low temperature. Figure 7(A,B) shows the ZFC and FC curves obtained from two representative samples of (a) Co$_{20.6}$Ag$_{79.4}$ and (b) Co$_{36.6}$Ag$_{63.4}$ respectively. These curves display a blocking temperature ($T_b$) of 6.3 K for sample (a), while a marginally modified value of 6.9 K for sample (b), as marked by a distinct peak in the ZFC curves as usual in a pseudo-superparamagnetic state of such materials. The close proximity in the $T_b$ values in the two compositions leads to an inference that the crystallite size of the Co-cores does not differ much in these two samples, although a relative concentration of the Co-content has increased by 16 at% in sample (b) when compared to the sample (a).

A maximum value of the spontaneous magnetisation in a pseudo-superparamagnetic sample, such as Co$_{20.6}$Ag$_{79.4}$ and Co$_{36.6}$Ag$_{63.4}$ as described in Figure 7, is observed at a temperature below its $T_b$ value. At $T \leq T_b$, the Co-core exhibits an irreversible magnetisation and exists in a ferromagnetic state in preponderance of the magnetocrystalline energy over the thermal energy. This could be clearly observed from Figure 8(A,B), where Figure 8 (A) shows the M–H curves obtained from Co$_{20.6}$Ag$_{79.4}$ sample at (a) 300 and (b) 5 K. The M–H curve recorded at 300 K shows paramagnetic behaviour and that recorded at 5 K

![Figure 7](image)

**Figure 7.** Zero-field cooled (ZFC) and field cooled (FC) curves obtained from (A) Co$_{20.6}$Ag$_{79.4}$ and (B) Co$_{36.6}$Ag$_{63.4}$ core–shell nanocrystallites prepared from a liquid precursor.
shows a ferromagnetic behaviour with a markedly enhanced magnetisation, 4.6 emu/g. Another sample of Co$_{36.6}$Ag$_{63.4}$ studied with ZFC–FC curves in Figure 7, which comprises a relatively smaller nonmagnetic 63.4 at% Ag-content, exhibits a similar behaviour of the temperature dependence magnetism. This is clearly demonstrated with the two curves measured in Figure 8(B) at room temperature and at 5 K. As expected, the magnetisation is increased more effectively in this specific sample, showing a value as much as 14.9 emu/g at 5 K, i.e. a roughly 3.2 times the value shown in the above sample Co$_{20.6}$Ag$_{79.4}$. Obviously, this much large value cannot be accounted for the higher Co-content present in this sample by 1.8 times alone. The difference reveals that part of the cobalt forms an alloy with the silver and that is relatively less magnetic in nature. As a result, the net magnetisation value does not increase in a proportion to the total cobalt content present in the sample but rather than in a proportion to merely the magnetic part confined primarily to the core.

At room temperature, none of the samples (a–g) exhibits any change in its electrical resistance with applied magnetic field up to 10 kOe. However, when the measurements were carried out at 5 K, two out of a total of seven samples studied in this investigation exhibit a considerable MR effect. For illustration, Figure 9(A) shows the variation of the electrical resistance with an applied field at 5 K in the samples of three representative compositions (a) Co$_{20.6}$Ag$_{79.4}$, (b) Co$_{36.6}$Ag$_{63.4}$ and (c) Co$_{48.5}$Ag$_{51.5}$, which all consist of a core–shell structure of small fcc-Co crystallites with primarily an fcc-Ag in part the shell on the individual crystallites. It could be observed that the first two samples (a) and (b) in Figure 9(A) exhibit a significant change in their electrical resistance within an applied field swept from (−)10 to (+)10 kOe, whereas the sample (c) which consists of an average Ag-content of 51.5 at% does not show any significant change in its electrical resistance under similar conditions of the field and temperature. A variation of the electrical resistance with applied field in the various Co$_{y}$Ag$_{100−y}$ samples (d–g) exhibit similar results as found in sample (c) and those are not discussed in detail over here. Further, the GMR values were estimated from the electrical resistance values in the different samples by using the
below equation.

\[ \text{GMR}(H) = 100 \times \left[ \frac{R(H) - R(H_0)}{R(H_0)} \right] \]

where \( R(H) \) is the electrical resistance observed at an applied magnetic field \( H \) and \( R(H_0) \) is the electrical resistance at \( H = 0 \).

Figure 9(B) shows the MR plots obtained at 5 K temperature from the representative samples of a core–shell structure of small crystallites (a) \( \text{Co}_{20.6}\text{Ag}_{79.4} \), (b) \( \text{Co}_{36.6}\text{Ag}_{63.4} \) and (c) \( \text{Co}_{48.5}\text{Ag}_{51.5} \). It could be observed that a reasonable value of 2.0% MR is obtained in case of the first sample \( \text{Co}_{20.6}\text{Ag}_{79.4} \), and that is enhanced to 3.6% in the second sample \( \text{Co}_{36.6}\text{Ag}_{63.4} \) while vanished completely in the third sample \( \text{Co}_{48.5}\text{Ag}_{51.5} \). From these results, it could be observed that a strong dependence exists between the chemical composition and Co-core size in a core–shell structure and the MR properties. The first two samples whose core sizes are well below the ideal single domain size of Co-NCs exhibit a substantial MR value; at these compositions, the inter particle distance of Co-cores is favourably placed to exhibit MR properties. Whereas, the rest of the samples (c–g) do not show any MR value because the core size is grown above the ideal single domain value and the inter particle distance of Co-cores has also increased.

Nevertheless, a large difference in MR (80%) persists between the first two samples in spite of small variation in the core sizes as evidenced from the close \( T_b \) values of them in the FC–ZFC curves in Figure 7. That attributes undoubtedly to a difference in the basic core–shell structure. The present experimental results show that the MR properties of the materials \( \text{Co}_y\text{Ag}_{100-y} \) studied in this investigation in correlation to the microstructure are not solely governed by a ferromagnetic Co-core but also by its effective size, shape, surface topology and the shell structure. The GMR of a material is believed to be a spin dependent scattering phenomenon occurring at the interface in a core–shell structure. These observations lead to a vital conclusion that along with the chemical composition, Co-core size and the number density of the ferromagnetic Co-cores also play a crucial role in the MR properties with the spin-scattering from the pinning surfaces of the core–shell interfaces. A sample \( \text{Co}_{36.6}\text{Ag}_{63.4} \) exhibits an enhanced MR over that of \( \text{Co}_{20.6}\text{Ag}_{79.4} \) in an optimised
The TEM images in Figure 10 show that (a) Co$_{20.6}$Ag$_{79.4}$ has a large particle size variation with average size of 8.5 ± 4 nm, whereas image (b) Co$_{36.6}$Ag$_{63.4}$ shows uniform Co-cores of 10 ± 1 nm. This clearly indicates that the substantial decrease in both the magnetic property as well as MR property is due to the large variation in Co-core size in Co$_{20.6}$Ag$_{79.4}$, when compared to Co$_{36.6}$Ag$_{63.4}$ crystallites. Consistent with the results reported in the literature by Garcia-Torres et al. on similar Co-Ag alloys [12], another key factor which controls the MR properties in such materials is the thickness of the shell, and as the shell thickness increases, the MR properties deteriorate significantly. It supports a lower MR value observed in the sample Co$_{20.6}$Ag$_{79.4}$ over an increased number of magnetic centres in the sample Co$_{36.6}$Ag$_{63.4}$ which has a larger Co-content.

4. Conclusions

In this work, we report a facile and fast wet chemical route employing a modified polyol process in conjunction with a transmetallation reaction for the synthesis of Co$_y$Ag$_{100-y}$ core–shell NCs of varying compositions and different Co-core sizes. In this process, Co-NCs act as sacrificial seeds, wherein the displacement of Co by Ag$^+$ ions leads to the decrease in Co-core size. This gives a distinct advantage to precisely control the chemical composition and core–shell structure by simply varying one of its constituents. TEM results show that all the samples exist in the form of core–shell structures. The size of Co-core in Co$_{20.6}$Ag$_{79.4}$ sample is 8.5 nm, which gradually increases with decrease of Ag-content in the samples (a–g). Out of the seven different compositions prepared in this work, two of them showed pseudo-superparamagnetic behaviour, whereas the rest of them showed ferromagnetic behaviour with gradual increase in $M_s$ value with decrease in Ag-content. The two pseudo-superparamagnetic samples exhibited very close blocking temperature (∼6 K) indicating that their Co-core sizes are close to each other. A value of 3.6% MR was observed in case of sample (b) at 5 K, which is higher by 20% when compared to earlier reported values. It is experimentally demonstrated in this report the
effective role of chemical composition on controlling the Co-core size and in turn the MR property by carrying a systematic study on seven different samples.

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Disclosure statement

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