Chapter 3

Fabrication of Magnetic Nanostructures of Nickel and Cobalt and Elucidation of Mechanism of Growth

Magnetic nanowires and nanotubes are ideal materials for the fabrication of various multifunctional nanostructures which can be manipulated by means of an external magnetic field. This chapter discusses the fabrication, structural, morphological and magnetic properties of Nickel and Cobalt nanowires and nanotubes. A plausible growth mechanism, mobility assisted growth mechanism, has been suggested for the growth of one-dimensional nanostructures during potentiostatic electrodeposition inside porous alumina membrane. The veracity of the mobility assisted growth mechanism has been tested using various precursors. The template assisted synthesis has been extended to synthesize hybrid structures of Ni and Co, a new system called Ni @ Co nanorods. The interesting magnetic features observed in these one dimensional nanostructures are elaborately discussed in this chapter.

*A part of the work discussed in this chapter has been reported in
3.1 Introduction

Design and control of nanowire and nanotube growth with limited degree of complexity will surely impact the development of nanotechnology.\textsuperscript{[1]} Soon after the discovery of carbon nanotubes by Iijima,\textsuperscript{[2]} nanotube based materials received sufficient attention from the scientific community because of their extensive application potential in nanodevices and sensors.\textsuperscript{[3]} Nanohole arrays having uniform size and shape have been identified as potential materials for fabricating various functional nanodevices.\textsuperscript{[4-7]} Tubular structures offer multitudes of opportunities because they can be used as pipes, microcavities, or microcapsules. Nanoholes, for example, with large surface area, can successfully replace the low purity nanoparticles that are prepared using more sophisticated techniques for various applications such as catalysis, sensor technology, high density magnetic storage, and delivery vehicles.\textsuperscript{[8-9]}

Inorganic nanotubes have also attained considerable attention during the last few years due to their diverse utilities in racemic mixtures, sensors, selective separation or selective ion transportation.\textsuperscript{8} However, literature on non-carbon nanotubes is limited as compared to their carbon counterparts.\textsuperscript{[10-14]} Among the non carbon cousins, much interest has been devoted to metal nanotubes and nanowires. Several techniques are reported for the synthesis of metal nanotubes. This include chemical routes such as chemical reduction of metallic complexes and chemical vapour infiltration within porous templates such as AAO or polymer nanochannels.\textsuperscript{[14,9,10,15]} There are also reports where in nanotubes and nanowires have been synthesized using highly sophisticated techniques like pulsed laser deposition or molecular beam epitaxy.\textsuperscript{[16-17]}

Magnetism is a cooperative phenomenon and is dictated by size, dimension, shape, structure and morphology of the constituent phases along with the type and strength of the magnetic coupling that exists among the
constituent phases. [18-20] Nanoscaled magnetic materials have been receiving much attention, due to their unique magnetic properties that are different from their bulk counterparts and are promising candidates for various applications. One-dimensional structures—nanowires, nanotubes, and nanorods provide an ideal platform for exploring properties like magnetisation reversal and shape anisotropy. [21] Ferromagnetic nanowires and nanotubes of Fe, Co, and Ni are candidate materials for studying fundamental phenomena like micromagnetic reversal process and quantum size effects. [22-23] Ferromagnetic nanowires and nanotubes have innumerable applications in areas such as ultrahigh density recording, GMR sensors, [24-25] supermolecular architectures [27] and nanoscale electronic and optoelectronic devices. [28-29] Moreover, control of morphology in nanostructures is very vital in tailoring their properties. [30]

Deposition of metals inside nanometric pores of membranes is the most inexpensive technique to produce nanosized patterned structures. The template-assisted synthesis is developing into an elegant chemical approach for the fabrication of nanoscale structures, as an alternative to sophisticated lithographical methods, especially for larger areas. Here, the template-assisted electrodeposition is receiving much attention for the fabrication of magnetic nanostructures because of its low cost, simplicity of operation, and the ability to tailor magnetic properties by tuning the length and diameter of the porous material. Aligned wires obtained via electrodeposition are likely to replace today’s unstructured magnetic media with tera bit per square inch capacity. These nanowires are promising candidates for nanoscopic electrodes in applied electrochemistry [32-33] and for various other fundamental studies. [34-36]

The high ordering and the magnetic nature of the wires will induce outstanding cooperative phenomenon that differ from the bulk and even from their thin film counterparts. Among these ordered magnetic wires, the
interwire interactions play an important role and have been the subject of extensive investigations.\textsuperscript{[37-40]} It has been reported that these interwire interactions are so strong that they can even change the easy axis of magnetisation and control the magnetisation reversal depending upon the strength of the interaction.\textsuperscript{[21-23]} A complete understanding of the mechanism of magnetisation reversal in such systems remains elusive and is a challenge to researchers. Rivas et al.\textsuperscript{[38]} reported the change of easy axis of Cobalt nanowires depending upon the magnetostatic interaction among them and Escrig et al.\textsuperscript{[37]} studied the geometry dependence of coercivity in nickel nanowires. These studies indicate that the modes of magnetisation reversal and other magnetic properties in such systems are strongly influenced by the microstructure and the interwire separation between nanowires. A complete understanding of the mechanism of magnetisation reversal in such systems remains elusive and it is persisting as a challenge for researchers.

Ferromagnetic nanotubes based on Ni, Fe and Co are being investigated in great detail due to their application potential in diverse fields such as perpendicular magnetic recording, cell separation, diagnosis, therapeutics and magnetic resonance imaging for detection. The ease with which they can be functionalized using specific group is an added advantage of these nanostructures and can be used for drug targeting and other applications in biotechnology.\textsuperscript{[41-42]} However, not much literature exists as regard the utilization of magnetic nanotubes in medicine. A survey of literature reveals that a systematic method of preparation of nanotubes and elucidation of growth mechanism is largely elusive.\textsuperscript{[3,43]}

Electrodeposition over nanoporous membrane is a simple, low cost and an ingenious technique for the preparation of one dimensional structure with high purity. The ability of this technique to tune the material properties by controlling the length and diameter makes it promising for nanoscale
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material fabrication as an alternative to more expensive techniques such as Molecular Beam Epitaxy and micro lithography.\textsuperscript{[44]}

Most of the reports on the synthesis of magnetic nanotubes are by chemical modification of inner surface of the porous template prior to the deposition.\textsuperscript{[4,9,10,15,17]} However, these techniques result in low yield and impure structures. Moreover, the mechanism leading to the formation of nanostructures from nanoporous template is seldom elucidated which is very essential for tailoring the properties of these nanostructures.\textsuperscript{[3]}

Hybrid magnetic nanostructures with high coercivity have immense application potential in various fields. Metallic magnetic nanotubes/wires of Ni, Co and Fe and also their alloys such as FePt, CoPt, NiFe, NiZn, CoCu and FeB were investigated in great detail due to their application potential in diverse fields such as perpendicular recording, cell separation, diagnosis, therapeutics, and magnetic resonance imaging.\textsuperscript{[45-49]} Controlled synthesis of smart nanostructures based on magnetic materials assumes important due to their potential applications in various fields and the possibility for manipulating these structures using an external magnetic field.\textsuperscript{[50]} The Co-Ni system is special due to the capability of tuning the magnetic properties such as coercivity, by varying the Co content.\textsuperscript{[46]} Several groups have reported the synthesis of various magnetic alloys using template assisted electrodeposition\textsuperscript{[45-48]} and they have achieved this by mixing the electrolyte precursors in different compositional ratio. The lacuna of such techniques is the unpredictability in the magnetic properties such as coercivity of the resultant one dimensional structures after electrodeposition. Co-axial hybrid magnetic structures synthesized via two step electrodeposition technique can surpass this problem by controlling the deposition of one of the components. Preparation and characterisation of such hybrid structures is the main motive of this study presented through this chapter.
3.2. Experimental

Alumina membranes (AAO template, Whatman) of high purity (99.9%) and uniform pore density, with average pore diameter ~ 150 nm and thickness ~ 60 μm, were employed for electrodeposition. Figure 3.1 shows the FESEM and AFM image (top view) of AAO template employed for electrodeposition.

![Figure 3.1: (a) FESEM image, (b) AFM image of AAO template used for electrodeposition.](image)

The FESEM and AFM images are well correlated and both confirm the uniform distribution of pores and average pore size is found to be ~ 150 nm. The three electrode potentiostatic electrodeposition (as explained in Chapter 2) was carried out by employing metal coated AAO template as working electrode. Initially, a layer of Ag (about 200 nm thickness) was thermally evaporated onto one side of the AAO template which acted as the working electrode for the electrochemical deposition. The electrodeposition was carried out on the nanopores, using a standard three electrode potentiostat system (Princeton EG & G 273 A). Ag/AgCl was the reference electrode and platinum was used as the counter electrode. It is noteworthy
that using this process the length of the metal nanotube can be controlled by varying the time of deposition.

Various metal salt solutions were employed as precursors for electrodeposition. The electrodeposition was standardised at a constant voltage of -1V. Different precursors like Cobalt acetate, Cobalt acetate tetrahydrate, Cobalt sulphate heptahydrate were used for the electrodeposition of Cobalt where as Nickel Sulphate and Nickel sulphate hexahydrate were employed for the electrodeposition of Nickel. The resultant nanostructures were found to highly depend on the precursor solutions employed. 0.2 M Cobalt acetate was used as the precursor for electrodeposition of Co nanotubes (Co NTs) and Cobalt acetate tetrahydrate was employed for the synthesis of thick walled Co nanotubes. For Ni nanowires (Ni NWs), the aqueous solution of 0.2M nickel sulphate hexahydrate (NiSO₄.6H₂O) in 0.1M Boric acid (H₃BO₃) was used as the precursor. The latter works as a buffer. Co nanowires (Co NWs) were fabricated using aqueous solution of 0.2M CoSO₄.7H₂O in 0.1M Boric acid (H₃BO₃). Once the electrodeposition was over, AAO was dissolved using 3M Sodium hydroxide (NaOH) [alkaline treatment].

X-ray powder diffraction pattern of nanotubes was recorded using Cu Kα radiation, λ = 1.5418Å (Rigaku Dmax-C). The morphology of the nanotubes after removing the template was studied by Field Emission Scanning Electron Microscope (SEM), JSM-6335 FESEM. Room temperature and low temperature magnetic properties of these nanotubes were investigated using a SQUID magnetometer (MPMS-5S XL Quantum Design). Surface morphology and the magnetic phases were identified using an Atomic Force Microscopy/Magnetic Force Microscopy (AFM/MFM) (Nanoscope Digital Instruments). Transmission Electron Microscopy (TEM) experiments were performed using JEM 2010 Transmission Electron Microscope.
3.3. Results and Discussion

3.3.1 Nickel Nanowires and Tubes

The growth rate of Ni NWs synthesised using Nickel sulphate hexahydrate was studied at each hour and it was found that a 5 hour electrodeposition was results in high aspect ratio Ni NWs of average length 50 µm and diameter ~150 nm.

Figure 3.2: Electrodeposition curve of Ni NWs.

Figure 3.2 shows a typical electrodeposition curve exhibiting the time dependence of electrical current during electrodeposition for Ni NWs. The horizontal part of the current transient indicates the production of nanowires in the pores of the alumina membrane. Current variation also shows that there is no over-deposition and the nanowire is in the growth state.\[^{51}\]
Figure 3.3: XRD pattern of Ni NWs inside AAO template.

XRD pattern of Ni NWs (Figure 3.3) indicates that the wires are highly crystalline (polycrystalline) in nature and they crystallize in the face centred cubic phase. Preferential growth along (220) can also be noticed from the XRD pattern. It must be noted here that the broad diffraction occurring around 15-35° is due to amorphous alumina.\textsuperscript{52}

The high relative intensity ratio of 220 and 111 diffraction lines in the case of Ni NWs is an evidence for strong texturing along $<110>$ direction.\textsuperscript{53}
Figure 3.4: (a), (b), (c) FESEM images of Ni NWs, (d) EDS of Ni NWs.

FESEM images (Figure 3.4. a, b and c) indicate the formation of good quality nanowires with a maximum length of 50μm and diameter of 150 nm. Figure 3a and Figure 3b depict the bundles of Ni NWs after the separation of AAO template by alkaline treatment. Figure 3c shows individual Ni NWs on a silicon substrate. Figure 3d is the EDS of Ni NWs after removing the AAO template. The purity of Ni NWs is verified using EDS and it is to be noted that there is no other elemental impurities. The peak corresponding to Cu (~15% of Ni) arises from the Cu tape used for EDS measurements.

TEM and SAED images of Ni NWs are shown in Figure 3.5.a. It must be noted here that the samples were subjected to TEM studies after removing the template (alumina) using 3M NaOH and the residue was
magnetically separated. The residue was dissolved in ethanol and drop casted over copper grid. The quality of the nanowire is evident from the micrograph.

Figure 3.5: (a) TEM and SAED (inset) images of Ni NWs, (b) TEM image of Ni NTs.

The SAED patterns (Figure 3.5.a, inset) indicate that the nanowires are crystalline in nature. The marked (200) and (311) planes are corresponds to that of Ni.

Nickel nanotubes (Ni NTs) have been obtained after electrodeposition by replacing the precursor with Nickel sulphate (NiSO₄). Figure 3.5.b depicts the TEM image of Ni NTs. A Y-junction formed in the Ni NTs may be due to the defect already present in the AAO template (voltage variation during the synthesis of AAO template leads to various hierarchical branched structures).¹,⁵⁴

The nanowires within the alumina template were subjected to morphological studies using AFM/MFM. Figure 3.6 shows the AFM and MFM images of bulk Ni NWs.
Figure 3.6: AFM-MFM images of Ni NWs along with the AAO template.

The average diameter of Ni NWs inferred from the MFM is ~ 160 nm and is correlated with that of FESEM and TEM results. It is also to be noted from the MFM image that the electrodeposited Ni NWs exhibit the “sky scraper” phenomenon associated with the lack of length uniformity and control. This can be removed by selective etching of the surface using concentrated acids.\textsuperscript{[271]}

3.3.2.1 Magnetisation studies on Ni Nanowires
Magnetisation measurements (M-H measurements) were carried out using a SQUID magnetometer. SQUID measurements were carried out by keeping the nanowires inside AAO template so as to keep their alignment intact. Magnetisation studies of Ni NWs show features similar to that of Nickel nanotubes \textsuperscript{[54]}, but the length of the nanowire for the present study is much higher and hence exhibit a high shape anisotropy. The M-H curves at 300K and 6K are shown in Figure 3.7 (7a and 7b) and Figure 8 respectively.
Figure 3.7: M-H curves of Ni NWs at 300K, (a) low resolution, (b) high resolution.

Figure 3.7.b represents the rescaled and expanded view of Figure 3.7.a, representing the in- and out-of-plane coercivity differences.

Figure 3.8: M-H curve of Ni NWs at 6K.

The loop parameters are evaluated and are exhibited in Table 1.
Table 3.1: Hysteresis loop parameters for Ni NWs at two different geometries and two different temperatures.

Coercivity values of Ni nanowires ($H_c$ parallel and $H_c$ perpendicular) exhibit an enhanced value compared to the bulk Ni (around 0.7 Oe for Ni\textsuperscript{55-56}). The coercivity values reported for Nickel nanowires of similar diameters is ~220Oe for longitudinal fields with a squareness value of 0.8.\textsuperscript{57} The squareness obtained for parallel field is much less than the reported values for Nickel nanowire. It has long been known that aligning nanoparticles gives rise to magnetic anisotropy, that is, a squarer hysteresis loop for a magnetic field applied parallel to the direction of the alignment than for a magnetic field applied perpendicular to this direction. This behavior is predicted by the Stoner-Wohlfarth model or more recent calculations and verified experimentally by a large number of studies.\textsuperscript{58-63}

The Crystal anisotropy $K_1$ of Ni NW is ~ $4 \times 10^4$ erg/cm$^3$ and shape anisotropy is $\pi M_r^2 = 7 \times 10^5$ erg/cm$^3$. Due to this large shape anisotropy and high aspect ratio (~330), the easy magnetisation direction always lies along the wire axis. Moreover, for an fcc lattice the anisotropy orientation is pointing along the (110) direction. Therefore, from XRD and magnetisation measurements it is to be concluded that anisotropy axis is aligned along the wire axis and it adds up to the shape anisotropy. So the easy axis is parallel to the wire axis. Reported measurements on isoradial Ni NWs are on polycarbonate membranes or single crystal mica films where the typical pore
density is $10^{-2}\,\mu\text{m}^2$. In the case of alumina template (used for the present study) the pore density lies in the range of $10^2-10^3\,\mu\text{m}^2$.

Figure 3.9 indicates that the inter-pore distance in the alumina template is $\sim 100\,\text{nm}$.

![Figure 3.9: FESEM image of AAO template indicating the inter-pore distance.](image)

The high pore density in the case of alumina results in high interwire interaction which induces a dipolar field due to the adjacent wire interaction. This dipolar field will act as the demagnetization field, which is given by $\Delta H = -\Delta N M$, where $\Delta N$ is the demagnetization factor and $M$ is the magnetisation. The low $M_r/M$, observed in the case of parallel field, where it is expected to be $\sim 1$, is due to this high interwire interaction. Both the magnetisation curves are highly sheared due to this demagnetization field indicating strong interwire interaction, which is expected because the average separation between the nanowires is $\sim 100\,\text{nm}$. The alumina template is unable to mediate exchange interactions over more than a few interatomic distances, so the interaction between the wires is realized only through magnetostatic dipolar interactions.\textsuperscript{[64]}

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The effect of high dipolar interaction for perpendicular fields is to reduce the saturating field. Saturating field for perpendicular field is $H_{Ls}=7\text{KOe}$ whereas that of parallel field is $H_{Ls}=10\text{KOe}$. M-H curve recorded at 6K exhibits an increase in coercivity and decrease in remanence parallel to the nanowire axis, consistent with an enhanced contribution of cubic magnetocrystalline anisotropy which is in competition with the uniaxial shape anisotropy.\textsuperscript{[65]} Shape anisotropy is identical at low and high temperature measurements, because of the large length to diameter ratio ($\sim 330$).\textsuperscript{[66]} Figure 3.10 shows the $M(T)$ measurement at 20KOe parallel to the nanowire. In this measurement the sample is cooled in zero field to low temperature (5K). Then a field of 20KOe is applied parallel to the wire and the $M(T)$ curve has been measured by warming up the sample in this field.

![Figure 3.10: M-T curve of Ni NWs at 20KOe.](image)

Such a study enables one to compare the thermal demagnetization process with field induced reversal process at low temperatures. M(T) curves show a switching of magnetisation from a high magnetisation value to a lower one ($\sim$ one order change in magnetisation value) at a temperature $\sim$
20K during warming. Since the sample is ferromagnetic both at low and room temperatures as inferred from M-H curves, this cooperative switching can only result because of surface spin disorder. Since there are no indications of any oxide layer formation as evident from the XRD (Figure 3.3), the chance of surface spin disorder resulting from antiferromagnetic interaction of nickel oxide is ruled out. The only possibility for such a switching of magnetisation in the parallel field measurement can be because of the dipolar interaction between adjacent nanowires. This helps to align the spin antiferromagnetically between adjacent wires. Magnetisation switching in terms of shape anisotropy is questionable and will not be complete in the case of wires where an interwire magnetostatic interaction exists. In the case of strong interwire interaction, the individual wires switches cooperatively and it is more or like the magnetisation switching happens in a thin film.\textsuperscript{[67]} M-T curve in Figure 3.10 depicts such a cooperative switching and hence this type of unusual M-T curve also proclaims the presence of strong interwire magnetostatic interactions in Ni.

### 3.3.2 Cobalt Nanowires and Tubes

X ray Diffraction (Rigaku Dmax-C) pattern (Figure 3.11.a) of cobalt nanotubes (Co NTs, synthesized using Cobalt acetate) indicate the formation of polycrystalline pure cobalt hexagonal close packed phase (space group:p63/mmc). Broad features appearing in the 15-35\(^0\) 2\(\theta\) range arise from the amorphous alumina. This is in agreement with the earlier reports.\textsuperscript{[52]}
Figure 3.11: XRD Pattern of (a) Cobalt NTs and, (b) Co NWs, with alumina template.

Figure 3.11.b. shows the XRD pattern of Cobalt nanowires (Co NWs, synthesized using cobalt sulphate heptahydrate). The formation of highly crystalline (polycrystalline) and textured Co hcp phase is evident from the XRD. The FESEM images of Cobalt nanotubes, after removal of supporting alumina template by alkaline treatment, are depicted in Figure 3.12. Figure 3.13 shows the TEM image of Cobalt nanotubes and Figure 3.14, the Energy Dispersive Spectrum (EDS) of Co NTs which confirms the presence of Cobalt in cobalt nanotubes and also establishes the absence of other elemental impurities.

Figure 3.12: FESEM images of Cobalt nanotubes, (a) 1hr electrodeposition (b) Top view of 5hr deposited nanotube.
Figure 3.13: TEM image of Co NT.

Figure 3.14: EDS of Cobalt nanotube.

The absence of other impurities in the nanotubes is further confirmed by FT-IR (Figure 3.15.a) and Micro Raman analysis (at an excitation wavelength of 514.5nm, Figure 3.15.b). The FT-IR and Raman analysis were carried out after etching the AAO template using NaOH (alkaline treatment). The FT-IR peaks corresponding to 630 and 1385 cm$^{-1}$ can be assigned to Metal-Hydroxide bond and –OH in plane bending.
vibration.\textsuperscript{64} The metal hydroxide group may arouses during the alkaline treatment and subsequent rinsing using deionised water.

Figure 3.15: (a) FT-IR, (b) Microraman analysis of Co nanotube (After etching out the alumina template with NaOH).

Moreover, the peak corresponding to \( \sim 550 \text{ cm}^{-1} \) in the Raman spectrum (Figure 3.15.b) can also assigned to that of Cobalt hydroxide, formed during the etching process. The FESEM image of Co NWs (synthesized using Cobalt sulphate heptahydrate) is shown in Figure 3.16.a.

Figure 3.16: (a) FESEM image, (b) EDS of Co NWs.
The electrodeposition was carried out for a time period of 5 hours and the resultant nanowires have found to be having an average length of 50 µm. The EDS of Co NWs is shown in Figure 3.16.b. This confirms the purity of Co NWs. The morphology of the synthesized Co NWs is mapped using and AFM/MFM and is shown in Figure 3.17. AFM/MFM studies were carried out on a single Co NW taken over a silicon substrate.

The sample has been prepared as follows; the AAO template is etched out using alkaline treatment and the residue was magnetically separated and dispersed in ethanol. A high magnetic field (~1T) was then applied to the solution and the resultant solution was drop casted over a silicon substrate. The Co NW can magnetised along the axis of the wire and that may be reason for the absence of a higher contrast in the MFM image. This is further confirmed by magnetisation studies using a SQUID magnetometer.

3.3.2.2 Magnetisation studies on Co nanotubes
Magnetic hysteresis loops, which display the magnetic response of a magnetic sample to an external applied magnetic field, have been used to
characterize the nanostructured materials. SQUID measurements are carried out by keeping the nanotubes inside AAO template so as to keep their alignment intact. Room temperature M (H) behaviours for both fields parallel and perpendicular to the tube, is studied using a SQUID magnetometer is shown in Figure 3.18. Figure 3.18.b. shows that for a field parallel to tube the coercivity $H_c = 824$ Oe and for field perpendicular $H_c$ is $\sim 123$ Oe.

![Figure 3.18: Room Temperature M-H curve of Co NTs.](image)

This very high coercivity observed for field parallel to the tube (highest reported value for Cobalt wire system of the similar diameter $\sim 150$ nm)\(^{10,42,64,69}\) indicates that easy axis of magnetisation is parallel to the tube axis. Perfect ordering and defect free end surfaces may be one of the reasons for the exhibition of high coercivity in these one dimensional structures. Recent studies indicate that parameters like shape, wire ends and diameter fluctuations will lead to localized magnetisation reversal, resulting in reduction of coercivity.\(^{170}\) Eventhough the magnetisation is parallel to the tube, squareness ($M_r/M_s$) is less compared to the $M_r/M_s$ value obtained with field perpendicular to the tube and hence a higher anisotropy results along the tube. This is due to the high inter-tubular interaction where the inter-tubular separation is $\sim 100$nm. Since alumina template is not able to mediate
exchange interactions over more than a few inter-atomic distances, the interaction between the tubes are predominantly magnetostatic dipole interactions. The magnetic field produced by a dipole at a distance, \( x \) in a direction perpendicular to the dipole is given by the relation,

\[
H_x = \frac{m}{(x^2 - \frac{l^2}{4})^{3/2}}
\]

where \( m \) is the magnetic moment and \( l \) is the length of the dipole. So this field, effectively acts as the demagnetizing field and will become an important factor when the intertubular distance is of the same order of tubular diameter. The magnetostatic interaction between larger nanometer tubes or wires, which are closely packed in an alumina template, is more important than smaller ones. The main effect of wire or tube interaction is to decrease the saturation field for perpendicular fields, and this effectively reduces the anisotropy. Figure 3.19 shows the M-H behaviour of Co NTs for the field perpendicular to the nanotube.

![Figure 3.19: M-H curve of Co NTs at 6K.](image)

The enhancement of \( H_c \) at low temperature (\( H_c \sim 345\text{Oe} \)) is consistent with the monotonic increase of uniaxial anisotropy constant with
decreasing temperature, with the basic assumption that the shape anisotropy is independent of temperature for high aspect ratio tubes.\textsuperscript{22}

3.3.2.3 Magnetisation studies on Co nanowires

The SQUID magnetisation studies were carried out on Co NWs and are shown in Figure 3.20.

![M-H curves of Co NWs](image)

**Figure 3.20:** M-H curves of Co NWs, (a) at 300 K, (b) at 6K.

Room temperature (300K) and low temperature (6K) magnetic properties of Co NWs are depicted in Figure 3.20.a and 3.20.b respectively. The loops (parallel and perpendicular) are highly sheared and both exhibit a very low $M_r/M_s$ ($\sim 0.1$). This is perhaps due to the high interwire interaction. Room temperature coercivity values of Ni NWs and Co NWs are by and large comparable. As in the case of Ni NWs, low temperature coercivity of Co NWs exhibit an enhanced value ($H_{c||} \sim 290$ Oe) because of higher magnetocrystalline anisotropy by these materials at low temperatures. A high field $M(T)$ measurement were also performed on Co NWs in the same way as done for Ni NWs and is depicted in Figure 3.21.
A high interwire dipolar interaction can be inferred from the cooperative switching of the magnetisation as explained for Ni NWs.

3.3.2.4 Thick-walled Co nanotubes

Thick-walled nanotubes (some of them are completely filled as wires) of Cobalt were obtained when the precursor was replaced by an aqueous solution of Cobalt acetate tetrahydrate. Parameters like pH, molarity and field gradient are kept constant for both depositions (cobalt acetate and cobalt acetate tetrahydrate). Figure 3.22.a. and 22.b. show the FESEM images (side view and top view) of thick-walled cobalt nanotubes.

Figure 3.21: M(T) curve of Co NWs at 20kOe.

Figure 3.22: FESEM images of thick walled Co NTs (a) side view, (b) top view.
Figure 3.23 shows the EDS and TEM pictures of thick walled Co NT. No other elemental peak is observed in EDS other than that of Co (a small peak after Co is that of Cu from copper tape used for EDS measurements). TEM also confirms the quality of nanotubes and the patches came at the surface may be due to the organic solvents used for TEM measurements.

3.3.3 Mobility assisted Growth mechanism

Understanding the growth mechanism plays an important role in controlling and designing of nanostructures. Yao et al. [24] have explained a possible growth mechanism for the formation of metal nanostructures over alumina based on a current assisted growth mechanism. However, the role of metal ion mobility was not forthcoming in their investigations. It must be noted here that Yao et al. have carried out the electrodeposition at constant current density while the present set of experiments was carried out by keeping the voltage constant.

A possible mechanism based on the mobility assisted formation of nanotubes and wires in the case of constant voltage (Potentiostatic) deposition is discussed below. It is an already established fact that growth
mechanism in a porous material originates from the cathode surface at the bottom edge of the pore. Because of their reduced coordination number and high surface area, porous parts of the template (alumina) serve as energetically favourable sites for initiating metal atom adsorption.\textsuperscript{[75-76]}

![Figure 3.24: Schematic of mobility assisted growth mechanism. (a) nanotube growth, (b) nanowire growth.](image)

When a negative potential is applied to the working electrode, divalent metal ions of Co\(^{2+}\) (Ni\(^{2+}\) ion in the case of Nickel sulphate) surrounded by hydration layer move towards the cathode and reduces to metal. This is a three stage process and are as follows.

1. The hydration number of metal ions decreases and the metal ions (Co\(^{2+}\)) are rearranged in solution near the cathode surface which can be written as follows,

\[
\text{Co}^{2+} \cdot m \text{H}_2\text{O} \rightarrow \text{Co}^{2+} \cdot (m-n) \text{H}_2\text{O} + n \text{H}_2\text{O}
\]  \hspace{1cm} (3.2)

2. Co\(^{2+}\) ions, surrounded by water molecules are then reduced. This is a step by step process as observed in 3.3 and 3.4,
3. Eqn. 3.5 is an adsorption process and the adsorbed metal cobalt discards the hydration layer and enters into the crystal lattice.

\[
\text{Co}^{(m-n)}\text{H}_2\text{O} \rightarrow \text{Co}^{+}(m-n)\text{H}_2\text{O}
\]

The movement rate of ions in a given electric field \( E \) is depends on two factors, mobility of ions and the potential gradient across the working and counter electrode.

\[
V_+ = \mu_+ \frac{dE}{dx}, \quad V_- = \mu_- \frac{dE}{dx}
\]

where \( V_+ \), \( V_- \) are the movement rates of cobalt ion and acetate ion and \( \mu_+ \), \( \mu_- \) are the mobility of cobalt ion and acetate ion respectively. The components of the metal ion movement rate \( V_\parallel \) and \( V_\perp \) and their competitions are the key parameters determining the resultant geometry after electrodeposition. Cao \textit{et al.}\(^3\) reported the formation of nanowires under low applied current density, where in \( V_\parallel = V_\perp \). At high applied current densities, this will lead to high values of \( \frac{dE}{dx} \), and nanotubes are the resultant geometries because in this case \( V_\parallel > V_\perp \). In our investigation a constant potential is maintained (Potentiostatically) for electrodeposition instead of keeping the current density constant (Galvanostatically).

A schematic representation of the mobility assisted growth of nanotubes and wires are depicted in Figure 3.24.a. and Figure 3.24.b.
respectively. The mobility of cobalt ions in cobalt acetate and cobalt acetate tetrahydrate can be different. The presence of other inorganic ions and organic additives in the double layer or adsorbed on to the surface can greatly modify the electro-crystallisation and growth process. The three factors affecting the mobility of the ions during electrodeposition are the asymmetry effect, electrophoretic effect and the viscous effect. Each of these can be different from precursor to precursor and the electrophoretic effect, which is due to the radicals of water of hydration, can be prominent in hydrated salt solutions. Based on these considerations, several deposition mechanisms have been proposed.\textsuperscript{[77-79]} So the extra hydration in tetrahydrate will act as a dead layer and shield the metal ions from the external potential. This case is similar to that of low current density deposition in Current Directed Tubular Growth Mechanism (CDTG) as discussed by Yao et al., where $V_i$ is similar to $V_i$. Here, as the time increases, metal atoms will fill most of the template pores until they are completely filled. But in the case of Cobalt acetate, Cobalt ion mobility will be much higher and also have an enhanced parallel velocity component. So a Co nanotube is the resultant one.

The key factors determining the morphology of the one dimensional objects (nanowires or tubes) in an electrodeposition are the mobility of metal ions and number of hydrated ions attached. Similarly, in the case of Nickel ions, the mobility can be different in Nickel sulphate and Nickel sulphate hexahydrate. It is also inferred that the presence of hydration layer will act as a shield for external applied potential and thereby ion mobility can be reduced. This mechanism is validated and generalised by other precursors like cobalt sulphate too. This can be treated as a general growth mechanism in the constant voltage deposition process for all types of metal nanowires, and open the possibility for controlling the formation of one dimensional structures. Optimization and standardization of process parameters will help
to control the thickness of nanotubes and thereby pave the way for tailoring the properties.

3.3.4 Ni @ Co core-shell nanostructures

The expertise gained during the synthesis of Ni and Co nanowires and nanotubes using various precursors extended to the synthesis of their hybrid structures. Nickel (Ni) electrodeposited inside Cobalt (Co) nanotubes (a new system named Ni @ Co nanorods) are fabricated using a two-step potentiostatic electrodeposition method. Testing the veracity of the growth mechanism in other porous membranes such as metal nanotubes will help to design multisegmented nanostructures; they can find enormous applications in various fields such as energy storage, controlled transport, and magnetic memory elements. (80)

3.3.4.1 Fabrication of Ni @ Co nanorods

0.2 M Cobalt acetate was used as the precursor for electrodeposition for making cobalt nanotubes and the deposition was carried out for a time period of 1 hour. Ni NWs have been electrodeposited into these Co NTs using 0.2M nickel sulphate hexahydrate (NiSO₄·6H₂O) in 0.1M Boric acid (H₃BO₃) as electrolyte for 1 hour.
The formation of Co NT and subsequent formation of Ni NW inside Co NT are consistent with the mobility assisted growth mechanism as discussed above for nanoporous alumina. In generalizing this mobility assisted growth mechanism, it is to be concluded that mobility of the cation and the hydration layer over the cation are the important parameters determining the morphology of one dimensional structure after electrodeposition.

Figure 3.25: Schematic diagram showing the synthesis of Ni @ Co nanorods.

Figure 3.26: (a) FESEM image of Ni @ Co nanorods, and (b) TEM image of Ni @ Co nanorod.
Figure 3.26.a depicts the FESEM image of Ni @ Co nanorods. It indicates that the Ni @ Co nanorods have an average length of 15μm and diameter of ~150 nm. The formation of core-shell nanostructure with Co NT as shell and Ni NW as core is clear from the TEM image (Figure 3.26.b). The compositional analysis of these nanorods has been carried out using Energy Dispersive Spectrum (EDS), and is shown in Figure 3.27.

![EDS of Ni @ Co nanorods.](image)

The presence of Co and Ni is evident from the EDS. The presence of small amount of silver (Ag) is coming from the back coating, which served as working electrode during electrodeposition. The phase formation in Ni @ Co nanorods is verified using XRD pattern. Figure 3.28 shows the XRD pattern of Ni @ Co nanorods and it indicates the presence of two separate phases, face centred cubic (fcc) Ni and hexagonally closed packed (hcp) Co. It also indicates that the Ni @ Co nanorods are crystalline.
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![XRD pattern of Ni @ Co nanorods](image)

Figure 3.28: XRD pattern of Ni @ Co nanorods.

Broad features appearing in the 15-35° 2θ range arise from the amorphous alumina. The phase formation is consistent with that of Co NTs and Ni NWs as presented earlier in this chapter.

3.3.4.2 Magnetisation studies on Ni @ Co nanorods

In order to investigate the magnetic properties of crystalline Ni @ Co nanorods, room temperature and low temperature (6K) magnetic properties of the Ni @ Co nanorods were evaluated using SQUID magnetometer. Figure 3.29.a and 3.29.b depict the room temperature and low temperature (6K) M(H) curves of Ni @ Co nanorods measured parallel to the nanorods respectively.
Figure 3.29: M(H) curves of Ni @ Co nanorods; (a) at room temperature (b) at 6K.

The Ni @ Co nanorods exhibit a very good magnetic response with room temperature coercivity of 200 Oe. This coercivity is much higher than the bulk coercivity values of both the Ni (Hc=0.7 Oe) and Co (Hc=10 Oe). The enhanced coercivity in Ni @ Co nanorods arises from the enhanced shape anisotropy. Li et al. reported a similar coercivity value for Co nanotubes synthesized via template assisted synthesis, but it is much smaller than of Co NTs discussed earlier having very high aspect ratio. This is due to the fact that the shape anisotropy in the earlier report is much higher (aspect ratio of Co NTs is ~330) than that of the present (aspect ratio of Ni @ Co nanorods is ~100). The coercivity value for Ni @ Co nanorods is higher than that reported for Ni NWs having very high aspect ratio and it is due to the presence of cobalt. This indicates that one can tailor the coercivity of these heterostructures by controlling the aspect ratio as well as cobalt content. M(H) curve at 6K exhibit an enhanced coercivity of ~380 Oe. This is much higher than the other reported values of Co based alloy nanowires. The enhancement in coercivity at low temperatures is consistent with the monotonic increase of uniaxial anisotropy constant with decreasing temperature, with the basic assumption that the shape anisotropy is independent of temperature for high aspect ratio tubes. Similar to Co
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NTs, Co NWs and Ni NWs, squareness ratio \((M_r/M_s)\) of the Ni @ Co nanorods is also very small. This may be due to the very high magnetic dipolar interrod interaction between each rod. This type of hybrid magnetic system with higher aspect ratio and much higher coercivity can find applications in fields such as data storage where a high coercivity is required.

**Conclusion**

Magnetic nanowires and nanotubes of Ni and Co are synthesised using template assisted electrodeposition technique. Highly crystalline and textured Ni NWs and Ni NTs are synthesised using Nickel sulphate as precursor for electrodeposition in a potentiostatic electrodeposition of -1V. Co NTs of highly ordered with hexagonal close packed structure are formed by the electrodeposition of cobalt acetate (for the first time) in a constant potential of -1V. The nanotubes and nanowires of 5 hour electrodeposited have a maximum outer diameter of \(\sim 150\) nm and length of \(\sim 50\)\(\mu\)m. Co NTs exhibit the highest reported longitudinal coercivity \(\sim 820\) Oe at room temperature. Co NWs with high aspect ratio (\(\sim 330\)) and high coercivity are synthesized by electrodeposition using and cobalt sulphate heptahydrate (\(\text{CoSO}_4\cdot 7\text{H}_2\text{O}\)) precursor and constant potential of -1V. They exhibit a preferential growth along \(<110>\). Cobalt acetate tetrahydrate is employed to fabricate thick-walled nanotubes. A very high interwire interaction resulting from magnetostatic dipolar interaction was observed between nanowires and nanotubes. An unusual low temperature magnetisation switching due to this dipolar interaction for field parallel to the wire axis is evident from the peculiar high field \(M(T)\) curve.

A plausible mechanism for the formation of nanotubes and nanowires during template assisted electrodeposition based on mobility assisted growth mechanism is elucidated. Such tunability and control over
the formation of magnetic nanotubes or wire opens a unique opportunity to systematically approach these one dimensional structures for exploring their possible applications in areas such as magnetic recording, sensors, catalysis, and so forth. The role of hydration layer on the resulting one dimensional geometry in the case of potentiostatic electrodeposition is verified. These highly crystalline textured Ni and Co NWs and NTs are possible candidates for perpendicular recording and various other multifunctional devices. Moreover, understanding the growth mechanism of one dimensional structures will help design different coaxial multifunctional nanostructures which can find enormous applications in various fields.

A novel magnetic nanostructure called Ni @ Co nanorods with Ni NW as core and Co NT as shell was synthesized using a two step electrodeposition method. Mobility assisted growth mechanism for the formation of one dimensional nanostructures in potentiostatic electrodeposition is verified in the case of other nanoporous membrane such as Co NTs too. Structural studies indicate the formation of Ni and Co in two phases. Magnetic studies exhibited a high coercivity for the Ni @ Co NTs and they can find enormous applications in various fields where high coercivity is required.
References

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