Directed self assembly of patterned magnetic nanostructures

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**DIRECTED SELF ASSEMBLY OF PATTERNED
MAGNETIC NANOSTRUCTURES**

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SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

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DIRECTED SELF ASSEMBLY OF PATTERNED MAGNETIC NANOSTRUCTURES

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Abstract

There is tremendous interest in magnetic nanostructured arrays of various shapes, driven by the urgent need for novel high density data storage media. This thesis presents the directed self assembly of curved and high aspect ratio chemically synthesized periodic magnetic nanostructures and their characterization and property evaluation. Chemical synthesis of magnetic structures was used since the shapes studied in this work, e.g., bowl, wire and chain of spheres are difficult to create using conventional physical methods. Chemical methods also offer enhanced homogeneity from the “bottom up” processing of the material, high throughput, low cost, facile surface modification and control of size, shape and size distribution of the nanoparticles. Morphological, structural, surface and magnetic characterization of these nanostructures was carried out using SEM, TEM, XRD, XPS and VSM.

Chemical synthesis of cobalt nanobowl arrays with minimal volume shrinkage was carried out by the template directed assembly technique. Borohydride reduction within the interstitials of colloidal templates of polystyrene (PS) spheres followed by annealing resulted in long range periodic metallic Co nanobowl arrays. Surface and structural analysis was carried out to investigate the boron removal and the two phase (h. c. p. and f. c. c.) microstructure of the cobalt nanobowls. The coercivity values of cobalt nanobowl arrays increase with decreasing bowl diameter and are larger than their nanoparticle and thin film counterparts due to shape effects. Cobalt ferrite nanobowl arrays were also synthesized using the colloidal crystal templating methodology, a single phase cubic structure was observed with coercivity values which were enhanced compared to the nanoparticle and thin film counterparts.

Cobalt nanoparticles with an average size of 4.3 nm and unusually high saturation

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magnetization were synthesized by borohydride reduction technique and subsequently directed by an external magnetic field assembly to produce nanowires, the coercivity of such nanowires was found to be greater than that of nanoparticles due to shape anisotropy. The difference between the experimental values of coercivity and the predictions of Jacobs and Bean model was ascribed to the thermal fluctuations that occur for small particle size. Chemical synthesis of cobalt within the pores of an AAO template was also carried out to create periodic arrays of Co nanowires, textured growth of Co nanowires within the pores was observed and the magnetic properties exhibited interesting magnetization cross over behavior.

Two phase cobalt chains of spheres and chains of ellipsoids were synthesized by thermal decomposition of cobalt oxalate nanorods. This morphological transition was driven by Rayleigh instability effects. The fragmentation process and decomposition kinetics were found to be in reasonable agreement with the theoretical predictions of Nichols and Mullins. The magnetization reversal of these chains could be explained by the fanning mechanism as predicted by Jacobs and Bean.

These results show that directed self assembly can be used in conjunction with chemical synthesis to form patterned magnetic nanostructures with interesting magnetic properties.

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List of Abbreviations

3-D:	Three Dimensional
AAO:	Anodized Aluminum Oxide
AFM:	Atomic Force Microscope/Atomic Force Microscopy
BF/DF:	Bright Field /Dark Field
CASAXPS:	Computer added surface analysis XPS
f.c.c.:	Face Centered Cubic
h.c.p.:	Hexagonal Close Packed
JCPDS:	Joint Committee on Powder Diffraction Standards
PS :	Polystyrene
NIST:	National Institute of Standards and Technology
SEM:	Scanning Electron Microscope/ Scanning Electron Microscopy
TEM:	Transmission Electron Microscope/ Transmission Electron Microscopy
VSM:	Vibrating Sample Magnetometer/ Vibrating Sample Magnetometry
XRD:	X-ray Diffraction
XPS:	X-Ray Photoelectron Spectroscopy

Chapter 1

Introduction

The hard disk which stores data in magnetic elements plays a key role player in the storage hierarchy of modern computers. Storage requirements are increasing everyday, hence the study of magnetic materials for information storage is of considerable scientific interest^[1-4]. Currently, commercially available magnetic disks utilize a continuous magnetic film and a longitudinal or perpendicular bit format in which one bit is stored in hundreds of grains. Smaller grain size is required to increase the areal storage density of the disks, but below a certain size these grains cannot store data since the integrity of the data is affected by thermal fluctuations. Fig 1.1 presents the magnetic disk storage area density vs. year of production. It can be seen that the superparamagnetic effect caused by thermal fluctuations is serious obstacle to further increase in storage density.

Figure 1.1: Magnetic disk storage area density vs. year of IBM product introduction [1].

Extensive analysis by researchers predicts that the superparamagnetic limit will impose a barrier on the growth of areal density at about 16 Gb/cm² for longitudinal recording and 150 Gb/cm² for perpendicular recording ^[1, 2], hence avoiding superparamagnetism has become a serious challenge. There are many companies e.g., Toshiba, Hitachi, Fujitsu using perpendicular recording format in commercially available hard disk devices, the maximum data density achieved so far in an actual demonstration is ~80 Gb/cm² by Western Digital ^[4]. Patterned magnetic media which consists of arrays of individual nanomagnets is seen as a potential solution for ultrahigh density magnetic recording in order to achieve recording densities of multi Tb/inch² ^[1, 2].

1.1 Conventional Media: The Motivation

Conventional recording media consists of a thin film of magnetic alloy, independent magnetic elements are formed by a mosaic consisting of hundreds of nanometer-scale grains (Fig 1.2) which store one bit of data.

Figure 1.2: Schematic of (a) a thin film medium, bits are represented by the transition between oppositely magnetized regions [2].

Since one bit of data is stored in hundreds of grains, reducing the grain size is an option to increase the areal storage density of hard disks however, due to the onset of superparamagnetism this reduction cannot be carried out below a certain minimum size ^[2]. In modern hard disk media, the polycrystalline alloy of Co, Cr and Pt with additional elements such as B and Ta is deposited by sputtering. In such systems, ~10 nm grains with an easy axis parallel to the Co c-axis (usually parallel to film plane in longitudinal media) behave as single domain particles ^[2]. The recording process is carried out by magnetizing the bits either in parallel or antiparallel direction to the track direction. The readback process is carried out by detecting the fringing field from the magnetization transitions of the bits by the read head ^[2]. A coercivity typically in the range of 500-3000 Oe and saturation magnetization of atleast 500 G (typically up to 1000 G) is required for recording medium ^[5].

1.1.1 Superparamagnetic limit: The problem

A decrease in the size of grains to increase the areal density of hard disk drives has been tried by researchers, but the superparamagnetic limit remains a cause of worry. Small grains undergo random, thermally activated switching called the superparamagnetic effect ^[2, 3]. If each grain is considered as a magnetically bistable single domain, the energy barrier between two stable states of a grain is given by KV (Fig 1.3), where K is the magnetic anisotropy energy density and V is the volume of the grain. As the grain size becomes smaller, the thermal energy $k_B T$ becomes a significant fraction of the energy barrier between the two stable states.

The average magnetization reversal time for a grain is given by,

$$\tau^{-1} = f_0 e^{(-KV/k_B T)} \quad (1.1)$$

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where, f_0 is an attempt frequency, typically taken as 10^9 sec^{-1} . For the grains to retain their magnetization, on an average, for 100 sec, $KV = 25 \text{ k}_B T$, whereas for data storage over $t = 10$ years, $KV = 40 \text{ k}_B T$.

When the energy barrier between the two stable states of a single domain ferromagnetic grain is $\sim 25 \text{ k}_B T$, superparamagnetism is observed. Since there is little opportunity to decrease grain volume, increasing the anisotropy constant, K , is an option. But very large values of K render the data more difficult to write^[2].

Figure 1.3: The energy barrier, in zero applied field, between two stable states of a single domain particle [3].

1.1.2 Patterned magnetic media: Overcoming the problem

Patterned magnetic media with discrete magnetic elements have shown great promise to overcome this problem of the superparamagnetic limit. In patterned magnetic media,

particles are small enough to be single domain and since one bit of data can be stored in this single domain particle [Fig 1.4 (a) and (b)], we can utilize particles with larger volume which overcomes the problem of superparamagnetism and make the particles thermally stable. Media noise is absent in such media because the boundaries of a bit are physically defined [2-4, 6-8].

Figure 1.4: Schematic of (a) a patterned medium with perpendicular magnetization (b) a patterned medium with in-plane magnetization [2].

1.2 Objectives:

A literature survey on the synthesis and characterization of patterned magnetic media suggested several advantages to the chemical synthesis [8-10] of magnetic structures. These advantages include low cost, high throughput, control of size, shape and size distribution, facile surface modification and enhanced homogeneity. However, synthesis of long range periodic assemblies by chemical synthesis techniques is still a challenge because patterned magnetic media is targeted to achieve storage densities of multi Tbit/inch². Since 1 bit is

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stored in one magnetic element, it is a difficult task to produce periodic arrays of such a large number of magnetic elements by chemical synthesis techniques such as borohydride reduction, reverse micelle technique and decomposition of organometallic precursors [9, 10]. Still, the research of chemical synthesis techniques is worthwhile because it is very unlikely that the currently used sputtering technique in hard disk industries can create the required nanostructures at affordable prices. The sputtering technique is also not useful in forming high aspect ratio nanostructures.

Noise associated with storage determines the linear density limits; the number of grains constituting a single bit determines the signal to noise ratio (SNR). The performance of isolated magnetic bits with small size can be limited by the thermal stability of the magnetization transitions; magnetic nanoelements with appropriate magnetization reversal behavior are thus potentially useful for patterned media. It has also been found that the magnetization reversal behavior of curved nanostructure offer considerable potential for patterned nanomagnetic media. Elongated magnetic nanostructures in the form of wire and rod shapes are also important because such anisotropic nanostructures exhibit shape anisotropy which alters the magnetization reversal process and enhances the coercivity. Enhancement in the coercivity implies that a higher magnetic field is needed to reverse magnetization for elongated nanostructures compared to randomly dispersed nanoparticles. High coercivity is needed to avoid bits being unintentionally “flipped” by stray fields within the magnetic media, hence the study of magnetic structures with anisotropic shapes is relevant to data storage media.

The overall objective of this work is the chemical synthesis, characterization and property evolution of magnetic nanostructures in curved and elongated morphologies for data storage applications. Template directed assembly combined with chemical synthesis as well as

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template free chemical synthesis was performed followed by characterization to investigate the morphology as well as structural, surface and magnetic evaluation. In this project, Co is selected (rather than Fe and Ni) due to the wide use of Co based materials (such as Co-Cr-Pt alloy) in the data storage media, the lower exchange length (~ 7 nm) of cobalt is advantageous in achieving high storage density ^[3].

In order to synthesize nanostructures with the desired morphology, we have undertaken both template assisted and template free synthesis techniques. Arrays of curved and elongated nanostructures have been synthesized by colloidal crystal templating ^[11, 12] and AAO template assisted assembly ^[13], respectively. Elongated nanostructures were synthesized by thermal decomposition leading to rod to chain morphological transformation partially driven by the Rayleigh instability effect ^[14]. The magnetic field induced assembly ^[15] of nanoparticles to produce elongated nanostructures was also examined. The chemical reactions involved in the formation of desired material such as cobalt or cobalt ferrite leads to byproducts ^[16], the removal of these byproducts was studied. Size, shape anisotropy and crystal structure had a significant effect on the magnetic properties of these structures. The unusually high magnetic moment (151.3 emu/g) of 4.3 nm Co nanoparticles was examined.

1.3 Scope:

Patterned magnetic media requires discrete magnetic elements with magnetization high enough to be sensed by a suitable magnetic sensor. Patterned magnetic media also requires low magnetostatic interactions so that bits do not “flip” due to stray fields present in the magnetic media ^[2, 3]. The synthesis of magnetic nanostructures can be classified as:

(1) Achieving data density of 30 Gb/cm^2 and beyond for longitudinal media requires a

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periodicity of 50 nm or smaller (25 nm elements with 25 nm separation) ^[2], a density of 40 gigaparticles can be achieved using a 50 nm period ^[2]. Nanostructures in this size range can be fabricated using physical techniques such as conventional lithography, in which a lithographically patterned template is used to create periodic nanostructures ^[1]. Such lithographic patterns can be fabricated using e-beam lithography which has the disadvantage of low throughput. Large area patterns can also be fabricated by X-ray lithography, using a mask fabricated by e-beam lithography, but this technique is limited by its high cost.

(2) Chemical synthesis techniques have been widely used for synthesis of nanoparticles. These nanoparticles are arranged in a periodic order by controlling their mutual interactions. Achieving long range order of the assembly is a difficult task by this method.

Further, the use of various surfactants in chemical synthesis process can also affect the magnetic properties. This work uses a combination of both techniques; the template assisted self assembly was combined with the chemical synthesis route to create periodic nanostructures. Chemical synthesis of materials was carried out in the interstitials of a template. The templates used, i.e., colloidal crystal templates of polystyrene (PS) ^[11, 12] spheres and anodized aluminum oxide (AAO) template ^[13], have relatively long range periodic structures hence the resulting pattern of magnetic material also exhibits an ordered arrangement. These templates are much cheaper compared to those made by conventional lithography e.g. e-beam lithography. Template assisted fabrication of magnetic nanostructures is superior to template free chemical synthesis in terms of achieving long range order. Colloidal crystal assisted assembly can be considered to be superior to AAO template assisted assembly because in the former process, ordering and size distribution of magnetic elements is typically better than in AAO templated assembly. Though these techniques are very useful in creating nanoarrays, there are still many challenges; colloidal

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crystal templates are fragile and exhibit ordering in distinct domains. In order to eliminate these domains from the templates, gravitational sedimentation is required which is an extremely slow process. The AAO templates are brittle and handling of such templates in industrial applications is a limiting factor.

The techniques developed in this work provide a facile approach to synthesize magnetic nanostructures in a range of sizes and shapes. Such nanostructures are potentially useful in data storage devices. These nanostructures are also seen as promising candidate for drug delivery (hollow magnetic spheres can be loaded with drugs and targeted to a tumor site by applying an external magnetic field), cell separation and biosensors ^[8].

1.4 Methodology:

The methodology was based on chemical synthesis techniques. Colloidal crystal assisted assembly was used to synthesize curved magnetic nanostructures (nanobowl arrays). The anodized aluminum oxide (AAO) template assisted technique was used to create elongated nanostructures (nanowire arrays). Elongated magnetic nanostructures were synthesized by template-free chemical synthesis techniques: cobalt nanochains were also produced by thermal decomposition of cobalt nanorods and magnetic field directed synthesis was used to synthesize cobalt nanowires. The morphology, crystal structure, surface chemistry and magnetic property evolution were examined. The dependence of magnetic properties on the morphology and structure were compared with models such as those of Jacobs and Bean ^[15]. Table 1.1 summarizes the synthesis and characterization techniques employed.

Table 1.1: Synthesis, characterization and property evaluation techniques

Nanostructure	Synthesis Technique	Characterization
Co nanobowl	Colloidal crystal (PS spheres) templated assembly. Chemical synthesis of nanoparticles: borohydride reduction of cobalt salt.	SEM, TEM, XRD, VSM, Fourier Transform, Rietveld Refinement.
Co ferrite nanobowl	Colloidal crystal (PS spheres) templated assembly. Chemical synthesis of nanoparticles: borohydride reduction of a mixture of cobalt and iron salts.	SEM, TEM, XRD, VSM.
Co nanoparticles and nanowires	Magnetic field induced assembly of cobalt nanoparticles. Chemical synthesis of nanoparticles: borohydride reduction of cobalt salt.	SEM, TEM, XRD, XPS, VSM.
Co nanowire arrays	AAO template directed assembly. Chemical synthesis of nanoparticles: borohydride reduction of cobalt salt.	SEM/TEM, XRD, VSM, AFM.
Co chain of spheres and chain of ellipsoids.	Thermal decomposition of cobalt oxalate nanorods.	SEM, TEM, XRD, VSM.

1.5 Significant Findings:

(a) A novel approach to synthesize ordered arrays of magnetic nanobowls, with minimum volume shrinkage and enhanced coercivity compared to the thin film counterpart has been investigated. Yan et al ^[11] reported the formation of 3-dimensionally ordered macroporous alloys of $\text{Ni}_x\text{Co}_{1-x}$ (solid solution) and Mn_3Co_7 (an intermetallic compound) produced by the

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precipitation of mixed metal salts within the interstitials of a colloidal template of poly(methyl methacrylate) spheres. The precursor metal salts occupy a greater volume than the final alloy, hence volume shrinkage was observed. Large volume shrinkage (up to 30%) and cracking of the material are disadvantages in Yan's process^[11]. Bartlett et al^[12] instead used electrochemical deposition to fabricate macroporous structures of cobalt and nickel-iron alloy without volume shrinkage; however the electrochemical method greatly restricts the choice of materials and processing conditions. Hence in this work a simple and versatile modified infiltration approach involving minimal volume shrinkage for the fabrication of 3-D cobalt nanobowl arrays of 1 μm , 200 nm and 100 nm diameters is presented. This technique was also used to synthesize cobalt ferrite nanobowl arrays. The size and shape effects on magnetic properties of these nanobowl arrays were identified.

(b) Nanostructures in the sub-10 nm size range exhibit interesting magnetic properties such as high magnetic moment^[17]. Hence the synthesis of nanostructures in this size range is of considerable interest. Two phase Co nanoparticles with an average size of 4.3 nm were synthesized by the borohydride reduction. Such a two phase system could be beneficial for the development of multifunctional devices since the h.c.p. phase of cobalt is useful for data storage applications while the low coercivity f.c.c. phase is useful for power electronics. The surface chemistry studies of such nanoparticles have not been previously reported, in this work, surface chemistry of these nanoparticles was performed by the XPS technique. Magnetic field induced assembly of these nanoparticles into nanowires was performed. These nanoparticles and nanowires were found to exhibit unusually high magnetic moment compared to the corresponding values for bulk Co. The effect of shape anisotropy on these nanowires was also investigated; the shape was found to significantly affect the magnetization reversal process and enhances coercivity compared to the counterpart

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nanoparticles.

(c) Synthesis of ferromagnetic nanowire arrays has been extensively reported in literature ^[13]. Most of the previous reports were based on the sputtering, pulsed laser deposition (PLD) and electrodeposition. On the other hand, in our approach materials are formed by in-situ chemical reactions within the pores of an anodized aluminum oxide (AAO) template. Such a chemical synthesis technique has advantages compared to physical techniques. The physical methods suffer from “shadowing effects” which drastically limit the aspect ratio of nanowires, in the electrodeposition process an additional coating of conducting layer is required which can adversely affect the magnetic properties. Infiltration of aqueous solution of precursors within the pores of a template is more versatile and can be extended to a wide range of materials and alloy compositions.

(d) Chains of spheres and chain of ellipsoids were produced by a facile chemical synthesis method in which cobalt oxalate rods were converted to cobalt chains of spheres and chains of ellipsoids, in part driven by Rayleigh instability effects ^[14]. Lian et al ^[14] have earlier studied the Rayleigh instability driven synthesis of chains but no magnetic property results were reported. The chains were produced by thermal decomposition of cobalt oxalate nanorods in a controlled annealing process. The kinetics of rod to chain fragmentation process was found to be in good agreement with the Rayleigh criterion. Coercivity values of these chains were in closest match with the fanning mechanism of magnetization reversal ^[15].

1.6 Organization of the Thesis:

(a) Chapter 1 is the **Introduction** of the thesis, presenting an overview and the importance of nanomagnetic structures for data storage media applications. This chapter also describes our

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methodology and the findings.

(b) Chapter 2 describes the **Background and Motivation**, relevant concepts of magnetization as well as previous work and the state of the art in patterned magnetic media is described. This chapter also describes the suitability of the techniques used in this work and why they were chosen over other available techniques.

(d) Chapter 3 consists of results and discussion related to **Synthesis and Characterization of Curved Magnetic Nanostructures**.

(e) Chapter 4 presents results and discussion related to **Synthesis and Characterization of High Aspect Ratio Cobalt Nanostructures**. This chapter is divided into two parts: the synthesis of elongated nanostructures by magnetic field induced assembly and the AAO template assisted assembly of cobalt nanowire arrays.

(f) Chapter 5 describes the work on **Synthesis and Characterization of Chains of Co Nanoparticles**.

(g) Chapter 6 presents the **Conclusions** of the thesis.

(h) Appendix A provides the details of various instruments and software used for characterization and analysis in this work.

In the next chapter, the concepts of ferromagnetism and magnetometry are given. The Background and Motivation on the synthesis and characterization of patterned nanomagnetic media is also provided.

Chapter 2

Background and Motivation

Magnetic nanostructures are interesting both from the fundamental and technological point of view, hence an understanding of the physics of magnetism as well as synthesis techniques of magnetic nanostructures is of great interest. This chapter presents an overview of magnetization fundamentals such as magnetic anisotropies, magnetic reversal processes and energy concepts of nanoscale magnets. A literature review of the synthesis and characterization of magnetic nanostructures e.g., nanowires ^[13], nanodots ^[2, 7], nanobowls ^[16, 18], nanobelts ^[19], nanorings ^[20] etc. is presented. Template assisted techniques such as anodized aluminium oxide template assisted synthesis ^[21], nanosphere lithography ^[18] and template-free chemical synthesis techniques e.g., borohydride reduction ^[22], decomposition of organometallic precursor ^[23], polyol method ^[24], sol-gel method ^[25] and micelle route ^[26] were examined. This chapter also describes the characteristics of the synthesis techniques used in this work. The state of the art, advantages and disadvantages of the synthesis techniques has been provided. The justification for the use of particular techniques in this work is also described. Details of various instruments and software used for characterization and analysis in this work are presented in appendix A. First, we present an introduction to magnetic materials and magnetometry.

2.1 Classes of Magnetic Materials:

Magnetism arises from the orbital and spin motion of electrons in the material. The classification of magnetic materials can be performed on the basis of their response to an

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external magnetic field. Magnetic materials can be classified into the following five groups [27].

(a) Diamagnetism: Diamagnetism arises from orbiting electrons when they are exposed to an applied magnetic field. Diamagnetism is found in all matter but it is usually very weak. Diamagnetic materials have atoms in which all the orbital shells are filled, which have no unpaired electrons (no net magnetic moment). A negative magnetization is produced when these materials are exposed to an applied field, hence susceptibility is negative.

(b) Paramagnetism: In this class of materials, atoms having unpaired electrons in their half filled orbital exhibit a net magnetic moment. In an applied magnetic field, partial alignment of the atomic magnetic moment in the direction of the field takes place which leads to positive susceptibility. The magnetization is zero when the field is removed since the magnetic moments associated with individual atoms do not interact magnetically in paramagnetic materials.

(c) Ferromagnetism: In this class of materials, the atomic moments exhibit very strong interaction. These interactions are produced by large exchange forces which results alignment of atomic moments. A detailed description of ferromagnetism and ferromagnetic materials is provided in this chapter.

(d) Antiferromagnetism: In an antiferromagnet, the exchange coupling between neighboring moments causes moments to align in antiparallel fashion.

(e) Ferrimagnetism: In a ferrimagnet, two sublattices couple through a super exchange mechanism to create an antiparallel alignment.

2.2 An Introduction to Ferromagnetism and Magnetometry:

This section provides an introduction to ferromagnetism and magnetometry. Ferromagnetism

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is discussed in terms of magnetic domains. Properties exhibited by ferromagnetic materials and their role in data storage applications are subsequently provided. A long range cooperative ordering phenomenon at the atomic scale is responsible for the parallel alignment of unpaired electron spins, resulting in ferromagnetic material. There is a high degree of magnetization within individual domains in ferromagnetic materials. Iron, nickel, cobalt are the most common examples of ferromagnetic materials ^[27, 28]. Section 2.2.1 presents a description of magnetic domains in a ferromagnetic material.

2.2.1 Magnetic domains:

The formation of regions of magnetic alignment, called domains, arises due to the microscopic ordering of electron spins. In the absence of external magnetic fields these domains are randomly oriented [Fig 2.1 (a)]. In the presence of an applied magnetic field, the magnetic moments align in the direction of the external field [Fig 2.1(b)]. In a ferromagnetic specimen an increase in the magnetic moment occurs by the following two independent processes: in weak applied fields, the volume of domains favorably orientated with respect to the field increases at the cost of unfavorably oriented domains, in strong applied fields, the domain magnetization rotates towards the direction of the field ^[27-29].

Figure 2.1: (a) Without any external applied field, domains cancel each other and leave the material unmagnetized (b). In an externally applied magnetic field, domains are aligned.

2.2.2 Hysteresis:

Ferromagnetic materials have found applications in data storage applications due to their magnetic hysteresis. Hysteresis can be understood as the lack of retracability. A ferromagnetic material, magnetized in one direction, does not relax back to zero magnetization upon the removal of the applied magnetizing field. A field in the opposite direction is required to drive it back to zero magnetization. A loop traced out by the magnetization (M) due to the application of an external magnetic field (H) is known as hysteresis loop ^[27-29]. A schematic of a magnetization hysteresis loop in a ferromagnetic material is presented in fig 2.2, in which M_s , H_c and M_r are the saturation magnetization, coercivity and remanent magnetization.

Figure 2.2: Schematic of a magnetization hysteresis loop in a ferromagnetic material.

2.2.3 Magnetic recording in terms of the hysteresis loop:

We now describe magnetic recording in terms of the hysteresis loop. An input signal at the

level indicated by dashed line in Fig 2.3 could, because of hysteresis, yield magnetization anywhere between c and d, depending upon the immediate previous history of the tape (i.e., the signal which preceded it). This clearly unacceptable situation is remedied by the bias signal which cycles the grains around their hysteresis loops so quickly that the magnetization averages to zero when no signal is applied. The result of the bias signal is like a magnetic eddy which settles down to zero if there is no signal superimposed upon it. If there is a signal, it offsets the bias signal so that it leaves a remnant magnetization proportional to the signal offset^[30].

Figure 2.3: Hysteresis in magnetic recording [30].

2.3 Magnetic Variables and Units:

Magnetic field strength (or intensity), magnetization (or polarization) and magnetic flux density are usually represented by H , M and B , respectively. Magnetic field strength is

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reserved for the fields that result solely from free current. The magnetization is a measure of the magnetic moment of a material per unit volume, mainly due to the orbital and spin motion of electrons. This motion is often viewed macroscopically as an equivalent or effective current. The magnetic flux density (B) can be described as a general case of a field due to both free and equivalent currents. B is related to H and M by the permeability $\mu = \mu_r \mu_0$. μ_0 ($=4 \pi \times 10^{-7}$ Henry/m) is the permeability of free space and μ_r is the relative permeability. The relationship between B , H and M is given by $B = \mu_0 (H + M) = \mu_0 (H + \chi_m H) = \mu_0 (1 + \chi_m) H = \mu H$ in the MKS system and $B = H + 4 \pi M = H + 4 \pi \chi_m H = (1 + 4 \pi \chi_m) H$ in the CGS system. χ_m is the magnetic susceptibility. Table 2.1 describes the units of the various quantities in MKS and CGS units.

Table 2.1: Magnetization Units

Quantity	MKS	CGS
Magnetic Field Strength	1 A/m	$4\pi/10^3$ Oe
Magnetic Flux Density	1 T	10^4 G
Magnetic Moment	1 Am^2	1000 emu
Energy	1 J	10^7 ergs

After this introduction to ferromagnetic materials and magnetometry, in the next section we describe the dependence of magnetic properties on particle size. This section also describes the importance of single domain particles in data storage.

2.4 Magnetism in Small Particles:

The magnetism of small scale ferromagnetic systems is governed by the following two

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features. First, the magnetostatic energy of bulk ferromagnetic materials can be minimized by restructuring the materials into domains. Below a certain size, however, it is energetically unfavorable to break up into domains because formation of domains costs energy, and it remains as a single domain material ^[5].

For a particle with size D , the magnetostatic energy is proportional to $M_s^2 D^3$ since the energy density in the field varies as B^2 (hence we obtain the M_s^2 term), the total energy is the energy density times a volume term, hence a D^3 term is introduced. If γ is the domain wall energy per unit area, domain wall energy is proportional to γD^2 . For large values of D , the D^3 term of magnetostatic energy is larger. In order to reduce this energy, the smaller D^2 term of wall formation is favorable and domain wall formation takes place. For small values of D , the D^2 term dominates and domain wall formation becomes energetically too expensive and the particle does not break into domains. The critical size for a particle to be single domain is when these two energies are equal. Ignoring the proportionality constants,

$$\gamma D_s^2 = M_s^2 D_s^3 \quad (2.1)$$

which gives,
$$D_s = \gamma / M_s^2 \quad (2.2)$$

The typical values of D_s range from 10-100 nm. The single domain size for spherical particles of Fe, Co and Ni are 14 nm, 70 nm and 55 nm, respectively ^[28].

The second important characteristic is that thermal fluctuations can dominate the anisotropy energy for small particles and give rise to superparamagnetism (discussed earlier in chapter 1). Fig 2.4 provides an overview of the size dependence on coercivity for ferromagnetic particles, r_0 and r_c denote the superparamagnetic and single domain size limits, respectively. Particles with size (r) between r_0 and r_c exhibit single domain behavior while the particles

with size (r) greater than r_c show multidomain configuration. For an assembly of identical, noninteracting single domain particles, the coercivity is given by $H_c \approx \frac{a}{r^2} - b$. For exchange coupled single domain particles the expression for coercivity is $H_c \approx r^{-6}$ ^[5]. The coercivity (H_c) is zero below the superparamagnetic particle size^[5].

Figure 2.4: Dependence of coercivity on particle size^[5].

2.5 Demagnetization:

The magnetic field inside a magnetic material is generally not equal to zero, even in the absence of an external magnetic field. This internal ("demagnetizing") field (H_D) depends on the shape of the sample and the direction of magnetization M . In matrix notation^[31],

$$H_D = \begin{pmatrix} H_{D_x} \\ H_{D_y} \\ H_{D_z} \end{pmatrix} = - \begin{pmatrix} N_{D_x} & 0 & 0 \\ 0 & N_{D_y} & 0 \\ 0 & 0 & N_{D_z} \end{pmatrix} \begin{pmatrix} M_x \\ M_y \\ M_z \end{pmatrix}$$

where, N_D matrix is the proportionality or demagnetizing factor. The values of N_{D_x} , N_{D_y} and N_{D_z} are constrained by the condition, $\sum N_D = 1$.

Consider the case of an ellipsoid of revolution (Fig 2.5 with $b = c$), with M parallel to the long axis, (a prolate spheroid).

$$N_a = \frac{1}{q^2 - 1} \left[\frac{q}{q^2 - 1} \ln(q + \sqrt{q^2 - 1}) - 1 \right] \rightarrow \frac{1}{q^2 - 1} (\ln 2q - 1) \quad (2.3)$$

where $q = a/b$, the second expression holds for $q \gg 1$.

Figure 2.5: A general ellipsoid with Cartesian axes taken to coincide with the principal axes.

For flat ellipsoids with two long axes and b nearly equal and much greater than the short axis c ,

$$N_a = \frac{\pi c}{4 a} \left[1 - \frac{1}{4} \frac{a-b}{a} - \frac{3}{16} \left(\frac{a-b}{a} \right)^2 \right] \quad (2.4)$$

$$N_b = \frac{\pi c}{4 a} \left[1 + \frac{5}{4} \frac{a-b}{a} + \frac{21}{16} \left(\frac{a-b}{a} \right)^2 \right] \quad (2.5)$$

Since the shape rather than the size of the particles gives rise to a demagnetization field, demagnetization factors are a function of the aspect ratio of the particle. The demagnetization field of a particle contributes to the particle's anisotropy. Certain directions become

unfavorable for magnetization due to the large demagnetization field. In the case of an oblate ellipsoid, the axis of symmetry supports a large demagnetization field and that is why magnetization of an oblate ellipsoid is easier in the xy – plane compared to the direction parallel to the z axis. Fig 2.6 provides the demagnetization factors for various shapes.

Figure 2.6: The demagnetization factors for various shapes [32].

In the next section, the origin and the role of magnetic anisotropies are discussed. Magnetic anisotropy strongly affects the shape of the hysteresis loop and controls the coercivity and remanence; it is therefore of considerable practical importance and it is used in the design of most magnetic materials of commercial importance.

2.6 Magnetic Anisotropies:

The theory of ferro- and ferrimagnetism is based on exchange forces. These forces can be so

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strong that suitable materials are spontaneously magnetized even in the absence of an applied field. Yet, in the laboratory we need to apply magnetic fields to saturate a ferro- or ferrimagnetic material. In some cases, the material in bulk form has a remanence of nearly zero, the reason is that each domain is spontaneously magnetized to saturation but the direction of magnetization varies from domain to domain. The net vector sum of all the domains therefore produces a near zero total magnetization. The dependence of magnetic properties in a preferred direction is called magnetic anisotropy. Magnetocrystalline and shape anisotropy are relevant to this work.

2.6.1 Magnetocrystalline anisotropy: The most common type of anisotropy is magnetocrystalline anisotropy which is caused by the spin-orbit interaction of the electrons. The electron orbits are linked to the crystallographic structure which interacts with electron spins to preferentially align the spins along well-defined crystallographic axes along which the magnetization of the ferromagnet is easy. Fig 2.7 shows the easy axis of magnetization for b.c.c. iron, f.c.c. nickel and hcp cobalt. In Fig 2.7 we see that Fe has three easy axes corresponding to the three $[100]$ directions, Ni has 4 easy axes corresponding to the body diagonal $[111]$ directions. Co has only a single easy axis of magnetization along the c-axis $[0001]$. Thus, cobalt is the only magnetically uniaxial crystal among these three ferromagnets [3].

Cobalt has a hexagonal crystal structure at room temperature; the hexagonal crystal axis is the direction of easy magnetization. The magnetocrystalline energy is usually small compared to the exchange energy, but the direction of magnetization is determined only by the anisotropy because the exchange interactions adjust in such a way that moments are parallel ^[27].

Figure 2.7: Easy and hard axis for (a) bcc iron (b) fcc nickel and (c) hcp cobalt [5].

2.6.2 Shape anisotropy:

Coupling of the shape of a particle to the direction of magnetization gives rise to a magnetostatic effect, known as shape anisotropy. The magnetostatic energy density (E_m), or self energy, of the particle is given by^[3],

$$E_m = -\frac{\mu_0}{2} (\overline{M} \cdot \overline{H_d}) \quad (2.6)$$

where μ_0 is the permeability of free space, H_d is the internal demagnetizing field and M is the magnetization. When the magnetization points in the direction of lowest demagnetizing field, the energy of the particle is minimized. In the case of a prolate ellipsoid (the ellipsoid in Fig. 2.5 with minor axis of equal magnitudes and axis of symmetry, a , parallel to the z direction) if M forms an angle θ with the z -axis the magnetostatic energy density (E_m) is given by

$$E_m = \frac{\mu_0 M_s^2}{2} (N_{\perp} \sin^2 \theta + N_{\parallel} \cos^2 \theta) \quad (2.7)$$

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where, $N_{//}$ is the demagnetization factor along the symmetry axis and $N_{\perp}$ is a demagnetization factor along any axis perpendicular to the axis of symmetry.

By rearrangement, we can write,

$$E_m = \frac{\mu_0 M_s^2}{2} (N_{\perp} - N_{//}) \sin^2 \theta + \frac{\mu_0 M_s^2}{2} N_{//} \quad (2.8)$$

For materials with uniaxial shape anisotropy, the anisotropy constant K_s , is given by

$$K_s = \frac{\mu_0 M_s^2}{2} (N_{\perp} - N_{//}) \quad (2.9)$$

Uniform magnetization of the particles is favored by the exchange energy within the particles as well as the anisotropy energy. Since nanoscale magnetic materials are studied in this work, an understanding of the energy concepts in nanoscale magnets is of interest, as discussed in following section.

2.7 Energy Concepts in Nanoscale Magnets:

The magnetic free energy determines the local magnetization of a magnet. The free energy character of this functional is related to the atomic origin of magnetism. The magnetization is obtained by tracing the local (or global) minimum of magnetic free energy F , as a function of the external magnetic field. The corresponding magnetization state at minimum free energy results in magnetic hysteresis ^[31, 33-37].

The magnetic free energy F , mainly consists of four terms,

$$E = E_{\text{ex}} + E_K + E_{\text{ms}} + E_H \quad (2.10)$$

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where E_{ex} , E_K , E_{ms} , and E_H are the exchange contribution, uniaxial anisotropy contribution, magnetostatic self interaction energy and the Zeeman term, respectively.

The exchange contribution to the free energy is given by,

$$E_{ex} = \int A[(\nabla m_x)^2 + (\nabla m_y)^2 + (\nabla m_z)^2]dV \quad (2.11)$$

where, A is the exchange stiffness, and $m = M / M_s$ is the reduced magnetization and V is the volume of uniformly magnetized grain. The other energy terms (E_i) can be written as integrals over free energy densities $\eta_i(r)$, so that,

$$E_i = \int \eta_i(r)dV \quad (2.12)$$

The leading second order uniaxial anisotropy contribution is,

$$E_K = K_u V \sin^2 \theta \quad (2.13)$$

where K_u is the first anisotropy constant and θ is the angle between $\mathbf{M}$ and the easy axis of magnetization. For ellipsoidal grains magnetized along a principal axis the magnetostatic self interaction energy can be written as,

$$E_{ms} = \frac{1}{2} N M_s^2 \quad (2.14)$$

where N is the demagnetizing factor. This term represents the magnetostatic dipole interaction of the atomic magnetic moments inside the grain. The magnetostatic interaction of the magnet with an external magnetic field is described by the Zeeman term, (2.15)

$$E_H = -H M_s V \cos \alpha$$

where, α is the angle between the applied field and the magnetization vector.

In the next section we describe the synthesis and characterization of magnetic nanostructures.

2.8 Synthesis and Characterization of Magnetic Nanostructures: A Literature Review:

Controlled self assembly of magnetic nanoparticles has drawn considerable interest as it offers a convenient tool to develop high density data storage devices ^[37-39]. In order to fabricate such patterned magnetic media, assembly of the magnetic elements is required. For high density magnetic recording, remanence and coercivity values higher than those of conventional soft magnetic materials are some of the desired properties. Since magnetic spherical nanoparticles do not provide shape anisotropy, synthesis of magnetic nanoelements with different shapes are of particular interest; cube ^[43], disk^[23, 44], rod ^[23, 44], wire^[45], ring ^[20], chain of spheres ^[46] and bowl ^[16, 18] geometries have been synthesized in addition to spherical nanoparticles ^[47] (Fig. 2.8). Shape anisotropy is an important tool to alter the magnetic properties. Such anisotropic structures have so far been mainly studied for cobalt, nickel, iron and their alloys.

Two schemes are commonly used to form such structures. In the first scheme, shapes are formed by incorporating materials into templates having the inverse interstitial structure of the desired shape ^[48, 49]. The magnetic elements will have a periodic arrangement if the interstitials are in an ordered array. The second scheme comprises the formation of magnetic nanoparticles by various chemical synthesis techniques, followed by their self assembly ^[23, 46].

This section reviews the various strategies to synthesize self assembled magnetic nanostructures. Various methods of synthesizing magnetic nanostructures, which includes

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template directed assembly of magnetic nanostructures as well as colloidal chemical synthesis of magnetic nanoelements and their assembly are presented.

Figure 2.8: Shapes of different magnetic nanostructures.

2.8.1 Top down and Bottom up approaches, general: Both “top down” and “bottom up” approaches can be used fabricate nanoscale features. The “top down” method is a process in which patterns are directly fabricated on the substrates while in the “bottom up” approach, physically or chemically synthesized components are arranged in the desired structure. The chemical synthesis of magnetic nanoelements with their self assembly involves either interactions between the nanoelements or embedding the nanoelements in the template possessing the desired geometry. Here, we review “bottom up” approaches as well as a combination of “bottom up and “top down” approaches for the fabrication of magnetic

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nanostructures. “Top down” methods such as conventional e-beam lithography are limited by their high cost and low throughput, while the “bottom up” method is a facile method; however it is difficult to achieve long range order using the bottom-up approach.

In the bottom up approach, nanoparticles are mainly synthesized by chemical routes followed by their assembly mediated by various interaction forces. In the combination of “top down” and “bottom up” approaches, the desired template is first made followed by the filling of the material in the template. One of the most widely used methods of template production is anodization of aluminum which provides an anodized aluminum oxide (AAO) porous film with aligned pores^[48]. Nanosphere lithography^[18] is one of the best examples of the “bottom up” approach; it has widely been used for making nanodots^[49] and nanobowls^[18]. For example, to prepare nanodots, a self assembled monolayer of Polystyrene (PS) spheres is used as the template and material is deposited in the interstitial spaces of the template. Two and three dimensional magnetic nanobowls can also be fabricated by nanosphere lithography. In other “bottom up” approaches, the size and shape of the nanoparticles can be controlled using different surfactants and these anisotropic particles can be self assembled by controlling the interactions among the particles e.g., self assembled magnetic nanorings^[20] can be synthesized by a dipole directed self assembly process.

These template assisted assembly experiments have mainly used AAO templates [Fig. 2.9 (a)], 2-D monolayers of PS spheres [Fig. 2.9 (b)] or 3-D closed packed colloidal templates of PS spheres [Fig. 2.9 (c)]. A description of template assisted assembly is provided in the next section. In order to synthesize magnetic nanostructures of different sizes and shapes, two strategies have been used, template assisted assembly and colloidal chemical synthesis. The following section describes the template assisted assembly technique by which ordered array of nanowires have been produced using AAO templates^[48], mesoporous silica templates^[50]

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and self assembled diblock copolymer templates ^[51]. The synthesis of nanodots using a monolayer of PS spheres and nanobowls using 3-D colloidal templates of PS or silica spheres is also described.

In the next section, a description of the synthesis of templated nanowires using various templates is presented. Prior work, state of the art and current challenges which have been examined in this thesis are provided.

Figure 2.9: SEM micrographs of the templates for the fabrication of magnetic nanostructures (a) AAO template (b) 2-D monolayer of PS nanospheres (c) 3-D colloidal template of PS nanospheres of 300 nm diameter.

2.8.2 Templated Nanowires (a Top Down approach)

Magnetic nanostructures with high aspect ratio (wires) are of great interest due to their magnetic anisotropy which enhances the coercivity ^[48, 50-83]. Metallic and magnetic nanowires have been studied for applications in high density data storage devices ^[51], magnetic sensing and as well as bioengineering applications such as cell separation ^[8].

Fabrication of elongated nanostructures and arranging them into large arrays is quite a challenging task by conventional lithography. Instead, these issues can be tackled by utilizing

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chemical synthesis methods; utilization of nanoporous membranes has been favored as templates by many researchers. In this technique, a porous membrane with well aligned cylindrical pores is filled with the desired material resulted in wires inside the pores^[48, 50-83]. Filling of the pores can be carried out by various methods such as electrodeposition, vacuum infiltration, external magnetic field assisted infiltration of magnetic nanoparticles and super critical fluid (SCF) inclusion techniques^[50].

Magnetic nanowires exhibit uniaxial anisotropy with the easy axis along the wire axis, the shape anisotropy gives rise to perpendicular magnetic anisotropy. Such nanowires can therefore exhibit coercivity value useful for patterned magnetic media, for which reasonably high coercivity is required in order to prevent the data being erased by stray fields generated in the pattern.

2.8.2.1 AAO template:

The anodic aluminum oxide (AAO) template provides an affordable template for the synthesis of nm-scale porous structures^[48], it consists of close-packed cells in a local hexagonal arrangement, with pores at their centers. AAO templates are produced by electrochemical oxidization of aluminum in the presence of an acidic medium, typically the AAO membrane can be separated from the remaining aluminum foil using a 2% HgCl₂ solution or by reversing the applied voltage of anodization to a negative bias. It consists of a hexagonally packed two-dimensional (2-D) array of cylindrical pores with a uniform size. The pore spacing and size can be controlled by altering the voltage and current density; the pore diameter can be adjusted in the range 5–200 nm. Immersing the samples in 1% phosphoric acid for different time durations can widen the pores without changing the center to center spacing. These methods produce hexagonal patterns with extended long-range

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order. Magnetic materials can be electrodeposited into these pores by AC electrodeposition, producing isolated needle-like particles which are of interest for perpendicular magnetic recording. The pore diameter in the AAO templates can also be controlled.

Electrodeposition of ferromagnetic materials such as Fe, Co and Ni into the pores can be carried out using their aqueous salt solution. To make deposition easier, boric acid, usually 25-45 g l⁻¹ (pH value 3-4) is used and an inhibitor, such as citric acid or ascorbic acid, is used in order to prevent oxidation of ferrous materials to ferric materials.

2.8.2.1.1 Prior Work and State of the Art: Nanowires of iron and cobalt using the AAO template with pore sizes in the range of 12 – 72 nm were prepared by Benfield et al.^[65, 66] The nanowire system was characterized by EXAFS, XANES, X-ray diffraction and SAXS to study their structure and bonding. Fe nanowires in the size range of 12 nm–72 nm were found to be structurally very similar to bcc bulk iron. They had a strong preferred orientation within the alumina pores. A mixture of h.c.p. and f.c.c. structures was obtained for cobalt nanowires but there was no clear relationship established between the ratio of the volume fraction of h.c.p. to f.c.c. phases on pore size or preparation conditions. The pH value of the deposition electrolyte also affects the crystal structure of cobalt. The magnetic properties of the nanowire arrays are a function of the crystal structure and wire shape which introduces magnetocrystalline and shape anisotropy respectively. When the magnetocrystalline anisotropy is weak, shape anisotropy dominates the effective anisotropy and results in high coercivity and squareness along the nanowire axis. This effect has been observed in the case of b.c.c. Fe and f.c.c. Ni nanowires with small diameter. In case of Co, for sufficiently large diameters, nanowires grow along the planes perpendicular to the c-axis. In such cases, a competition between shape anisotropy and magnetocrystalline anisotropy takes place. As the wire diameter decreases, this difference can be expected to increase because a change in

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texture takes place and the wire axis will be along the c-axis. Ideally, a square hysteresis should be obtained when the applied field is parallel to the wire axis and no hysteresis should be exhibited when the applied field is perpendicular to the wire. This behavior provides a bi-stable orientation of the magnetic moments (parallel and antiparallel to the wire axis) which is highly desired for data storage.

A number of groups have studied the synthesis of Fe, Co and Ni nanowires by the electrodeposition of the relevant materials into the pores of the AAO templates. The coercivity values along the wire axis have been reported in the range of 2100-2700 Oe for Fe, 1100-2400 Oe for Co and 400 - 950 Oe for Ni^[33]. FeCo alloy nanowires of 50 nm diameter and 1 μm length were prepared using an AAO template and the dependence of structural and magnetic properties on annealing conditions was studied^[62]. After annealing, the coercivity value was found to be as high as 2800 Oe and the squareness was 0.9 compared to the as synthesized sample which exhibited a coercivity of about 1500 Oe and squareness of about 0.7.

Cobalt oxide nanotubes have been produced by the calcination of cobalt nanowires. In this process^[73], Co nanowires are first formed in AAO templates by electrodeposition. Calcination at 600⁰C for 20 h changed the morphology of wires into tubes. Nanotube formation consists of four processes: oxidation, phase transition, evaporation and crystallization. The f.c.c. phase of cobalt is more prone to oxidation compared to the hcp phase, this difference in the oxidation properties of the two phases can be considered as a precondition for tube formation.

2.8.2.2 Mesoporous silica template: Mesoporous silica templates combined with the supercritical fluid (SCF) inclusion phase technique can also be used for the fabrication of

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metal and metal oxide nanowires and nanotubes ^[50].

2.8.2.2.1 Prior Work and State of the Art: The supercritical fluid (SCF) inclusion phase technique has been used to form nanowires and nanotubes of cobalt, copper and iron oxide. By this technique, nanotubes of metal and metal oxalate of various thicknesses can be synthesized by controlling the concentration of the precursors. Control of the synthesized phases can also be achieved by suitable solution density ^[50].

2.8.2.3 Block copolymers: Ultrahigh density nanowires arrays can be synthesized using self assembled diblock copolymer templates as described below.

2.8.2.3.1: Prior Work and State of the Art: Ultrahigh density nanowire arrays can be grown in self assembled diblock copolymer templates ^[51]. The templates are typically made of polystyrene (PS) and polymethylmethacrylate P(S-b-MMA). A high density of nanopores were fabricated using the equilibrium self assembly morphology of asymmetric diblock copolymers as a template, nanowires of cobalt with densities in excess of 1.2×10^{12} wires/inch² have been fabricated by direct current electrodeposition. Magnetic measurements on an array of 14 nm nanowires with an aspect ratio of 36 showed coercivity values of 3000 Oe at 5K and 800 Oe at 300 K when the field direction was parallel to the wire axis.

2.8.2.4: Filling of Nanowire Templates:

In this technique, the interstitials of porous alumina templates are filled with magnetic nanoparticles using vacuum and simultaneous magnetic field assisted infiltration. The magnetic particles aggregate within the pores and form wires.

2.8.2.4.1: Prior Work and State of the Art: Magnetic nanowires can be synthesized into

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the pores of AAO template by vacuum assisted infiltration of nanoparticles in the presence of an external magnetic field. By this technique, cobalt ferrite (CoFe_2O_4) nanopillars composed of about 8 nm diameter particles in an AAO template were obtained ^[52]. The room temperature coercivity of the as synthesized sample was ~ 100 Oe because most of these particles are superparamagnetic, hence the magnetization direction of such particles are randomized by thermal fluctuations. The particles which are infiltrated into the pores are separated by an organic coating and they interact via weak dipolar interactions. If the organic coating is removed by combustion, the particles aggregate the form of pillars. After aggregation into pillars with 60 nm diameter and lengths of hundreds of nanometers, superparamagnetic properties were suppressed and coercivity values of 1600 Oe were achieved.

In this work, vacuum assisted infiltration of aqueous solution of precursors was preferred over the supercritical fluid inclusion (SCF) technique because aqueous solutions can be more readily synthesized compared to supercritical fluids. AAO templates are more easily available than mesoporous silica or diblock co-polymer templates, hence it has been used in this work. Instead of using electrodeposition as a process to fill the pores of AAO template, we have chosen a novel technique where pores of the templates are filled with the aqueous precursor solutions and materials formation takes place within the pores, this technique fills the pore more homogenously and avoids “shadowing effects”. This technique is versatile and can be extended to a wide range of materials and alloy compositions. Further, unlike the electrodeposition process we do not need to coat an additional conducting layer in the vacuum infiltration technique, such a conducting layer can affect the magnetic properties.

In the next section, we describe the synthesis of curved magnetic nanostructure, state of the art and selected current issues which this thesis has studied.

2.8.3: Templated Nanobowls (a Top Down Approach)

This section describes the synthesis of nanodots and nanobowls by template assisted assembly using nanosphere lithography and the filling of colloidal crystals method.

2.8.3.1: Nanosphere Lithography:

Nanosphere lithography (NL) ^[84] is a cost effective technique to fabricate long range periodic 2-D or 3-D ordered arrays. Submicron metal dots with excellent edge definition can also be fabricated by electron beam lithography but low processing speed and high cost are constraints in these processes. In recent years, nanosphere lithography has shown great promise in achieving periodic arrays of metal dots or bowl like arrays ^[84-104]. If the spheres are in contact with each other and material cannot reach the regions of contact, “dots” are formed in the interstitial spaces whereas if materials reach the point of interconnections a “bowl” like morphology is observed. In this process self assembled monolayers or 3-D closed packed templates of nanospheres are used as a mask for metal deposition in the interstices of the template. Metal can be deposited by electrodeposition or infiltration techniques. Polystyrene (PS) spheres are widely used for mask formation. The procedure for patterning using NL involves three processes: mask formation by the self-assembly of nanometer or micrometer - size spheres, film deposition through the resulting mask followed by the removal of mask. This method has been used extensively to produce nanostructures of different materials.

The size of the metal dots can be controlled by the diameter of the PS spheres; a simple etching process to remove the PS spheres is another attractive feature of this technique. The removal of polystyrene spheres can be performed by either annealing or washing in toluene.

For a monolayer template, the resulting magnetic array structure consists of triangular dots of size $0.233D$, where D is the diameter of the nanospheres. For a bilayer, diamond-shaped islands of reduced size of $0.155D$ can be produced. By using a 3-D colloidal template, a 3-D interconnected magnetic network with a nanobowl structure on the surface can be fabricated which provides enhanced coercivity due to shape anisotropy. This 3-D network has interconnections within the same layer as well as the underlayer. 3-D closed packed templates of monodispersed PS^[18] or PMMA^[85] spheres have been used and the interstitial spaces of these templates can be filled either by electrodeposition^[85] or by the chemical conversion route^[18].

2.8.3.2: Filling of colloidal crystals: In this technique, magnetic nanoparticles are formed within the interstitials of the templates by chemical conversion of precursors. Two types of strategies are commonly used, precipitation of metal salt by thermal decomposition and reduction of the metal salts using a suitable reducing agent.

2.8.3.2.1 Prior Work and State of the Art: Yan et al^[11] have reported the formation of 3-dimensionally ordered macroporous alloys of $\text{Ni}_x\text{Co}_{1-x}$ (solid solution) and Mn_3Co_7 (an intermetallic compound), in which precipitation of mixed metal salts (acetate precursors) within the interstitials of a colloidal template of poly(methyl methacrylate) (PMMA) spheres was employed, however large volume shrinkage (up to 30%) and cracking of the material were observed. Since the precursor metal salts occupy a greater volume than the final alloy, such volume shrinkage was observed. Such volume shrinkage was due to the greater volume of the precursor metal salts compared to the final alloy. In order to fabricate structures without volume shrinkage, Bartlett et al^[12] have used electrochemical deposition to fabricate macroporous structure of cobalt and nickel iron alloy without volume shrinkage. Templates of self assembled 0.20, 0.50, 0.75 or 1.00 μm diameter PS latex spheres were used for the

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fabrication of cobalt, iron, nickel, and nickel-iron alloy nanostructures. Coercivity of Co nanostructures were found to be in the range of 28 Oe to 288 Oe.

Krivorotov et al ^[104] have studied the magnetic properties of macroporous cobalt prepared by colloidal crystal templating using PMMA spheres as templates. The samples were prepared by thermal decomposition of cobalt oxalate in the interstitial spaces of the template; this thermal treatment also removes the template. Exchange bias was observed which was attributed to antiferromagnetic CoO which forms when the cobalt sample was exposed to air. Iskandar et al ^[92] have reported that the macroporous structure of FePt nanoparticles infiltrated into a PS colloidal template shows extremely high coercivity values of up to 10 kOe after annealing. Periodic macroporous structures of Ni and NiO with 250-500 nm diameter monodisperse voids have been reported by Yan et al ^[105], precipitation and subsequent chemical conversion of the precursors was conducted within the templates. Xu et al ^[106] have synthesized periodic nickel sphere arrays, the coercivity and squareness values were 100 G and 0.028 respectively for out of plane magnetization and 90 G and 0.225 for in plane magnetization, respectively. Yoshikawa et al ^[107] have reported the synthesis and characterization of magnetic hollow spheres of Co₃O₄ and fcc Co using polystyrene beads. Magnetic measurements on the Co₃O₄ sample showed a large remanent magnetization while the Co sample exhibited ferromagnetic properties similar to that of bulk f.c.c. cobalt. This technique is not limited only to magnetic materials, other materials have also been fabricated in macroporous structures, e.g., macroporous CdSe macroporous solids of high- and low-refractive indexes have been prepared for photonic band gap materials applications ^[108, 109]. CdSe nanocrystals were used as building blocks to create the macroporous material.

This filling of colloidal crystals technique was used to synthesize nanobowl arrays in this work. We had observed that precipitation of acetate precursors used by Yan et al. ^[11] leads to large volume shrinkage. Hence we used metal chloride precursors and the desired materials

were formed by borohydride reduction of their aqueous solutions. The complete filling of the interstitials was ensured by multiple infiltrations which minimizes the volume shrinkage. Filling of colloidal crystals by electrodeposition was avoided as it greatly restricts the choice of materials and processing conditions.

A literature survey conducted on the templated assembly of magnetic elements showed that various types of templates can be used to synthesize magnetic nanostructures. Table 2.2 summarizes the advantages and disadvantages of various types of templates.

Table 2.2: The advantages and disadvantages of various kinds of templates used to create patterned magnetic structures.

Template	Advantages	Disadvantages
Lithographically patterned templates	High resolution, long range periodic order	Low throughput (e-beam lithography) High cost (X-ray lithography)
PS Template	Long range order, fast preparation, easy template removal, better size control, low cost	Fragile templates (should be handled carefully)
AAO Template	Long range order, low cost	Brittle templates, template fabrication is complicated compared to PS templates, size control is not as easy as PS templates
Mesoporous Silica	Small pore sizes	Complicated process to prepare supercritical fluid

It was noticed that lithographically patterned templates are limited by their high cost and low throughput while colloidal crystal templating provides a low cost and high throughput route to synthesize magnetic nanostructures. Similarly, the AAO templated assembly technique is also a low cost and high throughput technique to create magnetic nanostructures. Mesoporous silica templates have the disadvantage of using supercritical fluid as the

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precursor. The disadvantage of using colloidal crystal or AAO templates is their fragile nature. After reviewing these advantages and disadvantages of various templates, it was decided to use PS templates to create curved nanostructures and AAO templates to synthesize elongated nanostructures.

In the next section, a description of the bottom up approach of the synthesis of magnetic nanostructures is presented. Various synthesis techniques along with their state of the art, current challenges and relevance to this thesis are outlined.

2.8.4 Direct chemical synthesis of magnetic nanoparticles and self-assembly (a Bottom Up approach)

The synthesis of nanoparticles with controlled size, shape and size distribution has been extensively pursued, discrete magnetic nanoparticles in the size range of 2-20 nm are of interest for pattern magnetic media with storage densities of multiTb/inch². Several techniques such as hydride reduction ^[22, 110], reverse micelle technique ^[111-120], thermolysis ^[121-145] and the polyol method ^[24, 146-147] have been used for the synthesis of such nanoparticles. As mentioned earlier, spherical nanoparticles do not provide shape anisotropy, hence there has been intensive interest in synthesizing magnetic nanoparticles of non-spherical geometries. In this section, we will review the synthesis of magnetic nanoparticles by reverse micelle technique, thermolysis and polyol methods.

2.8.4.1 Borohydride reduction to prepare Fe and Co:

Reduction of metal salts is a facile method to synthesize nanoparticles and has been extensively used for the synthesis of ferromagnetic nanoparticles. Ferromagnetic nanoparticles of Co, Ni and Fe have been prepared by this technique. CoCl₂, FeCl₂ and FeSO₄ are the most widely used salts for the synthesis while KBH₄ and NaBH₄ are used as

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reducing agents. For example, Co nanoparticles are synthesized by the reduction of CoCl_2 by NaBH_4 ; a typical chemical reaction is,

The complicated part of this method is the removal of boron in order to produce elemental Co. Co_2B and $\text{Co}(\text{BO}_2)_2$ products are the primary product, the process by which Co is obtained is considered to be the pyrolysis of a mixture of Co_2B and $\text{Co}(\text{BO}_2)_2$ in air to produce Co and B_2O_3 ^[22],

The other possibility is the sacrificial oxidation of Co_2B which gives Co and B_2O_3 as final product ^[22].

2.8.4.1.1 Prior Work and State of the Art: Glavee et al ^[22, 110] have synthesized cobalt nanoparticles by borohydride reduction of cobalt salt, the formation of metal boride was observed. They have explained the chemistry of borohydride reductions and suggested a scheme for metal boride to metal reduction. Zhang et al ^[46] have performed the borohydride reduction of metal salts in the presence of an external magnetic field and synthesized chains of spheres of Co-B and Fe-Co-B compounds.

2.8.4.2 Reverse micelle synthesis:

Since the magnetic properties of nanoparticles depend on size, shape and crystallinity, considerable effort has been made to control these factors as well as the assembly of particles

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in regular arrays. In particular, shape anisotropy has a large influence on the magnetic properties. Rod-shaped nanoparticles exhibit shape anisotropy in addition to crystalline anisotropy, which enhances their coercivity. Surfactant (surface active agents) based templates can be used to control the particle size. Surfactants are molecules that lower surface tension; these molecules consist of hydrophobic hydrocarbons which are attracted to oil and hydrophilic components which are attracted to water. When a surfactant is added, the hydrocarbon chains tend to self associate in order to minimize contact with the water molecule, this results in the formation of various aggregates. Aggregates are not formed when water is able to solublize the polar head of the alkyl chains equally ^[111-120].

(a) Normal micelles:

When surfactant molecules have a very large polar head and a small chain forming a cone shape, self association of chains take place to form spherical aggregates. This is known as a normal micelle. In a normal micelle, the inner core is formed by chains and outer surface by head-groups.

(b) Reverse micelles:

If the surfactant has a small polar head and branched hydrocarbon chains, formation of spherical reverse micelles can take place. In a reverse micelle, head groups form the inner core while chains form the outer surface. When two reverse micelles meet, they form two distinct micelles via the exchange of their water content. The size of reverse micelles increases linearly with the amount of water added to the system. When the surfactant system contains a high concentration of oil and water, change in the shape and dimensions of the aggregates is observed as interconnected water channels or cylinders ^[111].

The most widely surfactant system used in the synthesis of magnetic nanoparticles is sodium bis(2-ethylhexyl)sulfosuccinate (AOT)^[111-117]. However other systems like sodium dodecylsulphate (SDS), cetyltrimethylammonium bromide (CTAB) have also been used. Nanoparticles can be formed by creating water in oil microemulsion using AOT. The water in oil microemulsion consists of a bulk oil phase, a small amount of water, and a surfactant, resulting in the formation of reverse micelles in the solution. Ordinarily water is very insoluble in oil phases and vice versa, however with the incorporation of a surfactant, water becomes miscible in the oil phase. This occurs because a surfactant such as sodium bis(2-ethylhexyl)sulfosuccinate (AOT), consists of two main entities; a hydrophilic head group and a hydrophobic tail group. The head group ‘likes’ the polar water environment and will attach to the water molecules. The tail group ‘likes’ the non-polar oil environment and attaches to the oil molecules forming a bridge between the two immiscible phases and creating a single phase.

This arrangement leads to the formation of thermodynamically stable, spherical reverse micelles. The water cores of these reverse micelles are only a few nanometers in diameter and can act as nanoreactors for aqueous reactions. In the case of the synthesis of cobalt nanoparticles, a reduction of cations occurs within the reverse micelle cores to produce stable particles. A schematic of the reverse micelle synthesis of cobalt nanoparticles is provided in Fig. 2.10. The products of these reactions are nanoparticles that range in size from 4 - 18 nm. The size of the particles can be controlled by varying the water to surfactant (w) ratio.

Figure 2.10: Schematic of the synthesis of cobalt nanoparticles by the reverse micelle technique.

2.8.4.2.1 Prior Work and State of the Art: Petit et al ^[117] were the first to report the self organization of cobalt nanoparticles in 2-D superlattices. A comparison of the magnetic properties of the isolated magnetic particles and organized particles was also presented. Self assembly was achieved by a balance between hard-sphere repulsion and van der Waals attraction forces, the nanoparticles were organized in a hexagonal network. An increase in the blocking temperature was observed when particles are arranged in a 2-D hexagonal network and this effect was attributed to interparticle interactions.

Lisiecki et al ^[47] have reported the synthesis of cobalt nanocrystals with rather narrow size distribution, $R (= [NaBH_4]/[Co(AOT)_2])$ equal to 0.5 and w equal to 40 were used and local self organization of Co nanocrystals was obtained. For higher R values, a compact hexagonal network of cobalt nanocrystals was produced. Multilayers of cobalt nanocrystals were also produced by depositing material on amorphous carbon, however some local disorder was observed. It was concluded that to obtain self organization, the size distribution has to be less than 13%.

2.8.4.3 High temperature decomposition:

Decomposition of organometallic precursors by thermolysis is a simple method for the synthesis of nanoparticles ^[122-145]. In this technique, nanoparticle growth is controlled by the decomposition temperature. To protect the particles from coalescence, different polymers and capping agents are used. Next section describes the prior work and state of the art related to the synthesis of monodisperse nanoparticles, their assembly and the effect of surfactants on nanoparticles shape.

2.8.4.3.1 Prior Work and State of the Art: Sun et al ^[122] have produced self assembled superlattices of FePt; it was shown that these chemically and mechanically robust assemblies can support high-density magnetization reversal transitions. FePt nanoparticles were chosen because the magnetic stability of individual particles scales with the anisotropy constant and the particle volume, small FePt particles may be suitable for future ultrahigh-density magnetic recording. It was demonstrated that an assembly of magnetic nanocrystals as small as 4 nm can support stable magnetization reversal transitions at room temperature. FePt nanoparticles in the size range of 3 nm to 10 nm with a standard deviation of less than 5 % were synthesized. Self assembly of these particles in 3-dimensional superlattices has also been reported. These particles were synthesized by the reduction of platinum acetylacetonate and decomposition of iron pentacarbonyl in the presence of oleic acid and oleyl amine stabilizers. Self assembly was achieved by dispersing the particles in a non polar solvent, this leads to self assembly by evaporation of the solvent. By the self assembly of 6 nm Fe₅₀Pt₅₀ particles, h.c.p. three dimensional superlattices were achieved, the interparticle distance and superlattice symmetry can be altered by changing the alkyl group on the stabilizers. Temperature dependent magnetic measurements suggest that the superparamagnetic behavior can be blocked at temperatures between 20 to 30 K.

Sun et al ^[123] have also demonstrated the synthesis of cobalt nanoparticles and their assembly in the form of superlattices. High temperature solution phase reduction of cobalt chloride in the presence of oleic acid and trialkylphosphine stabilizers was used. A phase transformation from the ϵ -Co to h.c.p.-Co at 300⁰ C was observed, the ϵ -phase has a structure similar to the β -phase structure of Mn. Puentes et al ^[124] have synthesized 3-17 nm diameter spherical ϵ -cobalt nanocrystals by rapid pyrolysis of cobalt carbonyl. Self assembly of these particles was achieved via evaporation at low rates in a controlled atmosphere.

Table 2.3 summarizes the advantages and disadvantages of three commonly used chemical synthesis techniques that can be used for the synthesis of magnetic nanoparticles.

Table 2.3: Advantages and disadvantages of three commonly used chemical synthesis techniques for synthesis of patterned magnetic media.

Chemical Synthesis Technique	Advantages	Disadvantages
Borohydride Reduction	Simple experimental procedure, high yield	Wide size distribution
Reverse Micelle	Simple experimental setup, narrow size distribution	Low yield, complicated surfactant removal process
High temperature decomposition	Narrow size distribution	Cumbersome experimental set-up, nanoparticles can sinter during high temperature decomposition

A major portion of the work reported in this thesis has used the borohydride reduction

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technique (section 2.8.4.1). This technique was chosen because of its simplicity over other available techniques such as reverse micelle technique which requires tedious surfactant removal process and usually has a low yield. High temperature decomposition process was not used due to (a) the complicated experimental set-up, (b) it is a high temperature process and (c) the nanoparticles undergo sintering which causes loss of ordering and aggregate formation. The chemistry of borohydride reduction of metal salt has been shown easier to result in high quality product; procedures such as removal of byproducts from the sample have been demonstrated. A relatively broad size distribution of the nanoparticles is the disadvantage of the borohydride reduction process, but in this work synthesis was mainly carried out within the interstitials or pores of a template; hence this disadvantage does not significantly affect the product. A broad size distribution was observed only in magnetic field induced assembly, where a non-constrained synthesis of Co nanoparticles was carried out. In this work, size selection of nanoparticles was carried out using the centrifugation process.

2.8.5: Direct Synthesis of anisotropic nanoparticles

In this section, state of the art of various synthesis processes to synthesize anisotropic particles is described. These shapes include rods, cube, ring, anisotropic platelets and diabolos.

2.8.5.1 Prior Work and State of the Art: The synthesis of rod shaped nanoparticles by the controlled growth of monodispersed spherical particles was reported by Hyeon et al ^[121] In this process, 2 nm spherical iron nanoparticles were first synthesized by thermal decomposition of organometallic precursor in the presence of a stabilizing surfactant. The spherical nanoparticles were transformed into nanorods via an oriented attachment mechanism.

A synthetic procedure developed for CdSe nanorods was extended to the synthesis of cobalt nanorods by Alivisatos et al ^[23, 142] who also reported the synthesis of hcp-Co disks, which were described as nanorods. Tilting experiments in the TEM were used to verify the disk shape of these crystals. In this synthesis process, dicobalt octacarbonyl, $\text{Co}_2(\text{CO})_8$, in o-dichlorobenzene solution was injected into hot (185°C) o-dichlorobenzene solution containing oleic acid and trioctylphosphine oxide (TOPO). Quenching of the reaction mixture shortly after injection generated relatively uniform sized cobalt nanorods with a hcp crystal structure. Further thermal aging for several minutes transforms the high energy hcp rod shaped particles to monodisperse spherical ϵ -Co nanocrystals, this phase transformation was explained as a result of reduction of surface energy. The ratio of surfactant concentration to precursor concentration can be used to control the size of the nanoparticles.

An important factor for the synthesis of disk shaped nanoparticles is the use of two different surfactants which modulates the relative growth rates of different phases. In this case, at a fixed oleic acid concentration, the length of nanorods was found to be proportional to the TOPO concentration. These uniform sized particles were used for self assembly and the formation of superstructures such as ribbons of nanorods.

Self assembly in a hexagonal or square array can be achieved by controlling the size, size distribution, shape and magnetic properties. Bao et al ^[144] have presented the mechanism of self organization of single domain (diameter < 70 nm) cobalt nanoparticles. In such particles, exchange interaction couples the atomic magnetic moments and they can be considered as large magnetic dipoles. Cobalt particles less than 10 nm in size exhibit superparamagnetism and their magnetic moments are free to rotate in random directions, in bigger particles the magnetic dipole moment is fixed along the easy axis, these particles prefer an arrangement in which the magnetostatic energy is minimized. Self assembly to form superstructures can be

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achieved when a colloidal solution is allowed to evaporate in a controlled manner, particles migrate to their lowest energy sites during evaporation. This can be achieved by slow evaporation at room temperature using high boiling solvents e.g. o- dichlorobenzene. Finally, the balance of surface tension, van der Waals forces and magnetic interactions control the arrangement of the assembly. The self assembly of cobalt nanoparticles mediated by magnetic interactions has been explained by Bao et al ^[145] on the basis of competing interactions (steric, van der Waals, depletion or magnetostatic), a variety of nanocrystal arrays have been produced as hexagonal closed packed arrays, square packed arrays with bimodal size distribution, linear chain of larger spheres (~18 nm), and lyotropically ordered of disk shaped particles of low and high concentrations.

Shukla et al ^[43] have reported the chemical synthesis of FePt nanoparticles with shapes that are close to rectangles and cubes. Assembly of these nanoparticles was performed by depositing onto surfaces where shape anisotropy directs these nanocubes to assemble along the oriented crystallographic axes. In this work, nanoparticles with diameter in the range of 4-10 nm were produced; self assembly was observed in the form of arrays with locally square symmetry, which has higher packing density than spherical nanoparticles. These arrays consists of nanocubes oriented with their [100] axes aligned along the surface normal. Such self assembled arrays may be useful to develop patterned media.

Tripp et al ^[20, 133], have reported the presence of flux closure states in single walled cobalt nanorings, each ring consisted of six nanoparticles of average diameter 27 nm synthesized by dipole directed self assembly. Since the exchange length of cobalt is ~7 nm, cobalt particles are expected to show single domain behavior in this size regime, the formation of domain walls is energetically expensive in this size range. Self assembly of weakly ferromagnetic cobalt nanoparticles into rings with discrete particles was performed. It was suggested that chain and bracelet formation are governed by the magnetic moments of Co nanoparticles and

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competition between dipolar interactions and non directional van der Waals interactions takes place at small distances. It was concluded that ring self assembly occurs in solution and can be produced by chain degradation.

Reduction of cobalt acetate in a liquid polyol can be used to synthesize cobalt based anisotropic platelets, rod or diabolo shaped ^[24] particles, their anisotropic shape results in high coercivity values. Co and Co₈₀Ni₂₀ particles in the size range of 25-100 nm with different shapes have been observed, it was found that anisotropic particles form in the case of the hcp phase (with a low probability of stacking faults) while a major fcc phase (with higher probability of stacking faults) leads to isotropic shapes.

2.8.6 Magnetic field assisted assembly: Chain of spheres:

For ferromagnetic particles, intrinsic moments are large resulting in strong magnetic dipolar interactions; this suggests the feasibility of directed assembly driven by external magnetic fields. A magnetic field causes a net torque on the particles which acts to align the particles with the field direction. The potential energy of the system is given by,

$$E = -\vec{m} \cdot \vec{H} = -mH \cos \theta \quad (2.19)$$

where, m is the dipole moment, H is the magnetic field strength and θ is the angle between dipole moment vector and magnetic field direction. A non-uniform field is generated by each dipole in addition to the uniform external field. This non uniform field affects the behavior of the surrounding dipoles in the solution; in a non-uniform field the resultant force on a dipole has a non-zero value which accelerates the dipole in the direction of the field gradient. This mechanism can lead to a chain of spheres morphology ^[46, 154 - 157] when an external magnetic field is applied to magnetic nanoparticles. The resulting chain possesses shape anisotropy

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which significantly affects the magnetization reversal process. A chain of single domain magnetic nanoparticles has advantages, e.g., chains of spheres dispersed in polymer matrices may be useful for longitudinal or perpendicular recording ^[51]. Earlier, little attention was paid to the effect of a magnetic field on the movement and self-assembly of magnetic nanocrystallites; recently, self assembly under the influence of an external magnetic field has drawn attention and a significant influence of magnetic field on the movement and assembly of magnetic particles was observed ^[156].

2.8.6.1 Prior Work and State of the Art: Zhang et al. ^[46, 154, 155] have presented the formation of chains of nanometer sized Fe spheres (20 – 70 nm) by borohydride reduction of Fe²⁺ salt in the presence of an external magnetic field. Saturation magnetization values of 160 emu/g and coercivity value of 1300 Oe were achieved. Experiments were also carried out with Co, Fe and Ni and it was concluded that magnetic interaction between adjacent particles plays an important role in chain formation while crystallinity and boron concentration plays an indirect role on magnetic properties. Chains of spheres of silica coated cobalt nanoparticles (magnetic pearl necklaces) of 32 ± 5 nm diameter organized by applying a weak external magnetic field was demonstrated by Maceira et al ^[156] A quantitative molecular dynamics simulation, taking realistic magnetic parameters into account, was performed to understand chain formation due to magnetic dipolar forces.

When Co nanoparticles are not exposed to an external magnetic field, ferromagnetic particles magnetize one another by dipolar interactions in arbitrary random directions. When an external magnetic field is applied, however, particles tend to align along the magnetic lines of force and favor the formation of linear chains, thus dipole directed self assembly takes place ^[157]. In the case of single domain particles, large magnetic moments and magnetic interactions were observed and nearly parallel wires can be achieved by this process.

Processing based on a biomimetic mechanism has been proposed to synthesize submicron scale ordered chains of amorphous cobalt and Co-B alloys on a solid support ^[158]. In this process, magnetotactic bacteria were used as the template to direct the fabrication of submicron chains of Co-B alloys. Magnetotactic bacteria contain one or more linear protein chains and nanosized magnetite (Fe_3O_4 , 40~100 nm) and/or greigite (Fe_3S_4 , 40~100 nm) which are usually arranged in the protein chains. Magnetic crystals impart magnetic moment to the bacteria which enables them to align and subsequently migrate along geomagnetic field lines. In addition to an external magnetic field, mediation of soluble starch can also play a role in pattern formation ^[158]. Borohydride reduction of Co^{2+} ions complexed to soluble starch was performed in the presence of an external magnetic field and Co-B alloys formed as arrays along the field lines.

In this work, the magnetic field assisted assembly technique has been used to synthesize Co nanowires less than 10 nm in diameter which may be useful in achieving high data storage density. Since nanoparticles less than 10 nm in diameter can be obtained by borohydride reduction of metal salts followed by size selection, we have used this magnetic field assisted technique to align particles to form nanowires. This thesis also explores the magnetization reversal behavior of these nanowires.

The next chapter describes our results on colloidal crystal templated assembly of cobalt and cobalt ferrite nanobowls arrays and their surface, structural and magnetic properties.

Chapter 3

Synthesis and Characterization of Curved Magnetic Nanostructures

3.1 Introduction:

This chapter describes the template directed self assembly of cobalt and cobalt ferrite nanobowl arrays. Magnetic nanostructures with curved shapes such as nanobowls or nanocaps can significantly control the magnetization reversal ^[159, 160] and hence alter the coercivity value. The new generation of magnetic data storage is likely to rely on patterned magnetic media, hence a study of periodic arrays of nanoelements with curved surfaces are relevant to such applications. Colloidal crystal templating is a low cost and quick speed method to produce nanobowl arrays ^[16, 18]. In this work, chemical synthesis techniques have been combined with colloidal crystal templating to produce ordered array of magnetic nanobowls. This technique can produce periodic assemblies in the centimeter range which is not feasible by physical techniques such as sputtering or template free chemical synthesis techniques. These nanobowl arrays were synthesized by the borohydride reduction ^[22] of metal salts within the interstitials of a template. Structural, surface and magnetic properties of these nanostructures were studied. The morphology and structural properties were found to have a profound effect on magnetic properties. Hollow sphere and nanowire morphologies were also produced by varying the synthesis and annealing conditions. Both, cobalt and cobalt ferrite nanobowls exhibit enhanced coercivity value compared to their bulk or thin film counterpart.

In the next section, results and discussion on the synthesis and characterization of cobalt nanobowl arrays are provided.

3.2 Synthesis and Characterization of Cobalt Nanobowl Arrays:

This section describes the morphological, surface, structural and magnetic properties of cobalt nanobowl arrays. First, we provide the synthesis of cobalt nanobowl arrays of 1 μm diameter and optimization of synthesis condition to obtain metallic cobalt. The optimized synthesis route was then extended to synthesize cobalt nanobowl arrays of 200 and 100 nm diameter.

3.2.1: Morphological, Surface and Structural properties:

Ordered interconnected cobalt nanobowl arrays were fabricated by using colloidal templates of 1 μm polystyrene (PS) spheres (Fig 3.1). First, nanoparticles were synthesized within the interstitials of the template by borohydride reduction of cobalt salt. Aqueous solutions of cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) and sodium borohydride (NaBH_4) were impregnated into the interstitials of the PS template by the vacuum assisted infiltration technique. Next, the polystyrene template was removed by a sequence of annealing at 500^o C for 3 h in N_2 atmosphere (sample set 1) and toluene etching resulting in an ordered interconnected nanobowl array. The SEM micrograph shows nanobowl arrays of size 300 μm x 200 μm (Fig 3.2) thus this technique can achieve assembly over a large area. Fig 3.3 (a) presents a SEM micrograph of the nanobowl array in a 60 μm x 45 μm region which shows the domain structure of the network. These domains are inherited from the domains in the colloidal template, which were formed during self-assembly of the polystyrene (PS) spheres. The Fourier transform of the selected region of Fig 3.3 (a) shows sharp peaks which confirm the

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crystalline order of network within each domain [Fig 3.3 (b)].

Figure 3.1: SEM micrograph of 3-D colloidal template of 1 μm polystyrene spheres, used as a template for the fabrication of nanobowl array.

Figure 3.2: Low magnification SEM micrograph of nanobowl array annealed at 500⁰ C for 3 h in nitrogen atmosphere.

Figure 3.3: (a) Low magnification SEM micrograph of a nanobowl array annealed at 500⁰ C for 3 h followed by toluene etching showing distinct domains (set 1), (b) Fourier transform of selected area of the micrograph shown in Fig 4.3 (a), (c) and (d) SEM micrographs of the nanobowl array in distinct domains.

The previous literature had pointed out the disadvantages of the infiltration approach such as large volume shrinkage and cracking of the material ^[11]. A smaller molar volume of the final material compared to the precursors could be one reason for volume shrinkage. Another reason for volume shrinkage and the presence of cracks observed by previous researchers could be the fact that the synthesis step of metal formation inside the interstitials of the

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colloidal template includes heat treatment therefore competition between weight loss of PS spheres and metal formation takes place. In our approach, cobalt salt is chemically reduced inside the interstitial spaces of the colloidal template and filling of the interstitial spaces by the material is ensured by multiple infiltrations. Once the material is filled in the interstitials, it acquires the shape of a bowl and then annealing of the sample is carried out for template removal. Since annealing of the sample for template removal is done after the formation of bowl structure by the material, the volume shrinkage is minimized as the average diameters of the bowls are $\sim 1\ \mu\text{m}$ [Fig 3.3 (c) and 3.3 (d)] which is the same as the PS sphere diameter used in the template. The circular mouths of the bowls confirm that in this region, the thickness of the topmost layer is equal to the radius of the PS spheres used in the template. The walls of the bowl are of $< 100\ \text{nm}$ dimensions. High magnification SEM micrographs [Fig 3.3 (c) and 3.3 (d)] show two distinct domains in the array and also reveal interconnections within the network. In Fig 3.3 (c), point A is an example of interconnection within the same layer while the point B is an example of the interconnection with the underlayer. These interconnections are the point of contacts of spheres in the colloidal template, precursors could not infiltrate at these points. Usually, template removal can be accomplished by either annealing the sample or by toluene etching but in this work, a combination of these two processes was employed. The advantage of this sequence is evident in Fig [3.4 (a) to (c)].

When the sample is annealed at 500°C for 3 h in N_2 atmosphere [Fig 3.4 (a)], considerable amount of PS residues can be observed due to incomplete burnout of PS spheres under inert atmosphere. The sample [Fig 3.4 (b)] which is only washed with toluene shows that material formation is not continuous inside the interstitials. The samples for which the template removal was carried out by combined sequence of annealing and toluene etching shows a

continuous formation of cobalt inside the interstitials [Fig 3.4 (c)]. When we anneal the sample, interparticle bonding between the particles becomes stronger in order to reduce surface energy, leading to the formation of a continuous structure inside the interstitials [16, 18]. Annealing the sample is also important to crystallize the sample, since the as-synthesized sample is amorphous [Fig 3.5 (a)]. In the previous literature on similar type of structures in binary and ternary oxide systems, it has been suggested that washing in a solvent is a better technique to remove templates [162] but we find that in our case, a combination of annealing and washing with a solvent was essential for effective template removal as well as to crystallize the material.

Figure 3.4: SEM micrograph of (a) nanobowl structure annealed at 500⁰ C for 3 h in N₂ atmosphere (b) nanobowl structure without annealing and only washed in toluene (c) SEM micrograph of the nanobowl structure annealed at 500⁰ C for 3 h in N₂ atmosphere followed by toluene etching (set 1).

X-ray diffraction patterns of as synthesized samples and samples which were annealed at 500⁰ C for 3 h in N₂ atmosphere (set 1) are provided in Fig 3.5. The as synthesized sample [Fig 3.5 (a)], which was only etched with toluene and not annealed, is amorphous while set 1 sample [Fig 3.5 (b)] is comprised primarily of the Co₃(BO₃)₂, Co(BO₂)₂ and Co₃B, the

majority phase is $\text{Co}_3(\text{BO}_3)_2$. The as synthesized sample was found to be amorphous because the reaction temperature (room temperature) is much less than the glass transition temperature. The presence of boron in the sample stabilizes the amorphous structure at room temperature. A similar observation was made by Wonterghem et al ^[163] in which they synthesized small alloy nanoparticles by reduction of metal ions by KBH_4 in aqueous solution.

Figure 3.5: X-Ray diffraction pattern of as synthesized sample (a), and sample annealed at 500°C for 3 h in N_2 atmosphere (set 1) (b).

The formation of Co_2B (an intermediate) takes place, this phase is subsequently converted into $\text{Co}(\text{BO}_2)_2$ after longer period (~ 15 min) of reaction. Upon heat treatment of this product, a solid state reaction converts $\text{Co}(\text{BO}_2)_2$ to $\text{Co}_3(\text{BO}_3)_2$. Additional XRD lines from Co_3B were

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also observed. The detailed mechanism of the formation of the Co_2B , $\text{Co}(\text{BO}_2)_2$ and $\text{Co}_3(\text{BO}_3)_2$ phases has been described elsewhere ^[22, 110]. For set 1, the $\text{Co}_3(\text{BO}_3)_2$ phase does not get converted to Co when annealed in N_2 atmosphere because of the absence of oxygen ^[22].

In set 1, although we achieved the morphology with minimal volume shrinkage, the nanobowls were composed of cobalt borate $\text{Co}_3(\text{BO}_3)_2$ instead of cobalt. So, to fabricate nanobowl arrays of metallic cobalt, another template was infiltrated with the same processing condition as for set 1 except that for this set annealing was performed at 400°C for 4 h in air (sample set 2). Fig 3.6 (a) shows a typical SEM micrograph of set 2, in which an ordered array of bowls with hexagonal mouths is shown. The non-circular (hexagonal) opening of the bowls indicates that the thickness of the topmost layer is greater than the radius of the bowl. A scheme of calculation of the diameter of the bowl has already been suggested [Fig 3.6 (b)]^[164]; here we suggest a simpler scheme which is presented with the SEM micrograph. If we inscribe the hexagonal shape in a circle, the diameter of the circle can be used to obtain bowl radius. From the SEM micrograph and geometrical calculations, the diameter of the bowl is estimated as $\sim 1\ \mu\text{m}$ which is same as the diameter of the PS sphere in the template this shows that volume shrinkage is minimized.

Figure 3.6: (a) SEM micrograph of nanobowl array annealed at 400⁰ C for 4 h followed by toluene etching (set 2), (b) a scheme for estimation of bowl diameter is also shown.

Nanobowl arrays of 200 nm and 100 nm diameters were also synthesized. Fig 3.7 (a) and (b) present the SEM micrographs of the template of 200 nm PS spheres and the resulting nanobowl array, respectively, while Fig 3.7 (c) and (d) present the SEM micrograph of the template of 100 nm PS spheres and the resulting nanobowl array, respectively. These nanobowls arrays were fabricated using the same borohydride reduction technique and annealing sequence of 400⁰ C for 4 h followed by toluene etching as that used for nanobowl

arrays of 1 μm diameter from sample set 2. The wall sizes for the nanobowls of 200 nm and 100 nm diameter were found to be 42 and 33 nm, respectively [Fig 3.7 (b) and (d)].

Figure 3.7: SEM micrograph of (a) PS template of 200 nm spheres (b) resulting nanobowl array from 200 nm PS template (c) PS template of 100 nm spheres (d) resulting nanobowl array from 100 nm PS template.

The XRD pattern (Fig. 3.8) of the sample set 2 reveals the presence of two distinct phases of cobalt and the absence of $\text{Co}_3(\text{BO}_3)_2$. Thus, upon annealing in air, $\text{Co}_3(\text{BO}_3)_2$ decomposes into metallic Co and B_2O_3 [22]. It is suggested that B_2O_3 remained in the toluene. To determine the percentage of each phase present in the sample, the XRD pattern was analyzed by Rietveld analysis (Fig. 3.8), which shows 68% of hexagonal

cobalt (ϵ -phase) and 32% of f.c.c cobalt (α -phase) is present in the sample. The crystallite size of the ϵ -cobalt is calculated to be 8 nm and that of the α -cobalt is 35 nm. No cobalt oxide peaks were observed in the XRD pattern [Fig 3.8].

Figure 3.8: Rietveld refined X-ray diffraction profile of cobalt nanobowls (set 2). The Bragg markers from top to bottom belong to ϵ - and α - cobalt respectively. Experimental data are shown as continuous line overlaying a simulated pattern (circles). The lower trace is the difference between the calculated and experimental intensities.

In order to study the chemistry of borohydride reduction and the presence of two phase crystal structure, cobalt nanoparticles were synthesized by the borohydride reduction of cobalt salt and their surface and structural characterization was carried out. Fig. 3.9 (a) presents the TEM micrograph of Co nanoparticles annealed at 400⁰ C for 4 h in air,

nanoparticles in the size range of 3-35 nm were observed. Fig. 3.9 (b) shows a high resolution micrograph of a typical Co nanoparticle after annealing at 400⁰ C for 4 h.

Figure 3.9: (a) BF-TEM micrograph of Co nanoparticles synthesized by borohydride reduction of cobalt salt annealed at 400⁰C for 4 h in air (b) high resolution TEM micrograph of a typical cobalt nanoparticle.

The chemistry of borohydride reduction of cobalt salt leading to the formation of Co is as follows; Co₂B and Co (BO₂)₂ are formed as the primary product ^[22, 110] (Eq. 3.1 to Eq 3.3) [22].

The process by which Co is obtained is considered to be the pyrolysis of a mixture of Co₂B and Co (BO₂)₂ in air, yielding Co and B₂O₃ (Eq 3.4 and Eq 3.5) ^[22],

The other possibility is the sacrificial oxidation of Co₂B again yielding Co and B₂O₃ as the final product ^[22].

The removal of B₂O₃ [Eq. (3.4) and (3.5)] was carried out by washing the sample in DI water, the samples were then characterized by XRD and XPS techniques. A number of studies have been performed to study the final product of the reactions, however most of these studies have used XRD techniques, and surface characterization of Co formation using the XPS technique has received little attention. Legrand et al ^[165] have presented XPS characterization of Ni nanoparticles synthesized by the reverse micelle technique, NiB₂ or a mixture of metallic Ni and Ni-B compounds were formed depending on the atmosphere used for synthesis. In this study, surface characterization includes use of XPS technique. The XPS spectra before and after washing in DI water are presented in Fig. 3.10 (a) and (b), respectively. The XPS spectrum before washing shows peaks corresponding to Co 2p_{3/2}, and B 1s and O 1s [Fig. 3.10 (a)]. High resolution spectra of B 1s, O 1s, Co 2p_{3/2}, were collected in their respective energy ranges [Fig 3.11 (a)-(c)]. The peak position of B 1s at 193.58 [Fig 3.11 (a)] confirms the formation of B₂O₃ and also precludes the possibility of Co-B. The high resolution spectrum of O 1s fits with the peaks at 536.80, 533.20 and 531.49. The O 1s peaks at 536.80 and 531.49 correspond to –OH bonds or Co₃O₄ at the surface, respectively. The peak at 533.20 shows the presence of B₂O₃, the peak at 782.83 corresponds to 2p_{3/2} while the peak at 786.55 is the satellite peak. The XPS spectrum after washing in DI water [Fig 3.11

(b)] indicates that most of the B_2O_3 was removed. Quantitative analysis shows that the concentration of boron present in the sample was reduced from 15.6 at. % to 4.1 at. % after washing in DI water.

Figure 3.10: XPS survey scan collected on cobalt nanoparticles annealed at 400⁰ C (a) before and (b) after washing in DI water. Decreased intensity of B 1s peak is highlighted by ellipse.

Figure 3.11: High resolution XPS spectra of cobalt nanoparticles after annealing at 400°C (before washing). (a) B 1s (b) O 1s and (c) Co 2p_{3/2}.

The structural properties were investigated by the X-ray diffraction technique. Fig 3.12 (a) and (b) shows the XRD pattern of the cobalt nanoparticles annealed at 400⁰ C before and after washing, respectively. It is evident that the B₂O₃ peak is absent in the XRD pattern of the sample after washing. Two phase microstructure of cobalt [α -cobalt (f.c.c.) and ϵ -cobalt (h.c.p.)] was observed in the XRD pattern.

Figure 3.12: XRD pattern of cobalt nanoparticles after annealing at 400⁰ C for 4 h (a) before and (b) after washing in DI water.

Cobalt exhibits h.c.p. crystal structure below 420⁰C and f.c.c crystal structure at higher temperatures. The thermodynamics of cobalt at room temperature can be used to explain this phenomenon ^[166]. The free energy of formation of the f.c.c. phase, starting from the h.c.p. phase, is given by,

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$$\Delta G^{\varepsilon \rightarrow \alpha} = \Delta H^{\varepsilon \rightarrow \alpha} - T\Delta S^{\varepsilon \rightarrow \alpha} \quad (3.6)$$

Where ΔG , ΔH and ΔS , respectively represents the free energy, enthalpy and entropy of transformation from the ε to α phase, and T is the temperature. For cobalt, $\Delta H^{\varepsilon \rightarrow \alpha}$ and $\Delta S^{\varepsilon \rightarrow \alpha}$ are positive, thus the enthalpy term favors the hexagonal phase while the entropy term opposes it. At room temperature, the enthalpy term dominates and the phase is hexagonal, while at higher temperatures the entropy term dominates yielding the f.c.c phase. Since the h.c.p. and f.c.c structures differ only by the stacking sequence of close packed atomic layers (ABCABCABC for f.c.c and ABABAB for h.c.p.) stacking faults as observed in TEM micrograph [Fig 3.9 (b)] can facilitate this h.c.p. to f.c.c phase transformation.

3.2.1.1 Cobalt Hollow Spheres:

During the synthesis of cobalt nanobowl arrays, hollow spherical morphologies were also observed [Fig 3.13]. Fig. 3.14 [(a)-(c)] presents a schematic of the formation of two different curved morphologies (viz. nanobowl and hollow sphere) ^[16]. Fig. 3.14 (a) shows an ordered close packed PS sphere template. Nanoparticles are formed by in situ reduction within the interstitial space of PS spheres and thus acquire the shape of the spheres [Fig. 3.14 (b)]. Vacuum suction was applied to infiltrate the precursors into the underlayers which led to the formation of thicker layers of nanoparticles in the underlayers compared to the top layer. When an etching sequence is applied to remove the PS spheres, unlike the underlayers which are supported by the upper layers in the network, the topmost layer adopts a bowl shape morphology instead of the hollow sphere morphology. Removal of the PS spheres from the underlayers resulted in a hollow sphere morphology [Fig. 3.14 (c)]. The thickness of the

nanobowls in the top layer is less than the diameter of the PS spheres while the thicknesses of the hollow spheres in underlayers are equal to the diameter of the PS spheres used in the template. Formation of hollow spheres can also occur due to over infiltration of precursors leading to the formation of hollow sphere morphology in the top layer as well.

Figure 3.13: SEM micrograph cobalt nanostructure synthesized by colloidal crystal templating leading to hollow sphere morphology.

Figure 3.14: Schematic for the formation of nanobowls and hollow spheres using colloidal crystal templating.

3.2.1.2 Nanobowl to Nanowire Transformation:

The stability of bowl structure against high temperature annealing was investigated. High temperature annealing of nanobowls results in nanowire formation. The SEM micrographs of nanowire obtained by annealing 1 μm and 200 nm diameter nanobowls at 600⁰C for 3 h [Fig 3.15 (a) and (b)] reveal nanowire morphology. The average diameter of nanowires were found to be 53 nm for 1 μm nanobowls and 26 nm for 200 nm nanobowls samples, respectively.

Fig 3.15: SEM micrograph of cobalt nanobowls arrays (a) of 1 μm diameter and (b) 200 nm diameter annealed at higher temperature (600⁰C) showing nanowire morphology.

XRD data presented in Fig 3.16 reveals the presence of cobalt oxide instead of cobalt in the sample. Annealing at higher temperature (600⁰C) leads to the formation of high temperature f.c.c phase which is less stable in air ^[73] resulting in cobalt oxide (Co₃O₄) formation. The peaks observed in the XRD pattern can be indexed as (111), (220), (311), (400), (422), (511), (440), (620) and (533) planes of a cubic unit cell. This oxide formation at high temperature annealing could be a possible reason for nanowire formation as observed in SEM micrographs [Fig 3.15 (a) and (b)]. The density of Co₃O₄ (6110 kg/m³, equivalent to a molar

volume of $39.4 \times 10^{-6} \text{ m}^3/\text{mol}$) is significantly less than the density of Co (8900 kg/m^3 , equivalent to a molar volume of $6.6 \times 10^{-6} \text{ m}^3/\text{mol}$). The increase in molar volume of Co_3O_4 compared to Co (~ 6 -fold) gives rise to large compressive stresses. In order to relieve these compressive stresses, protrusion of nanowires takes place as observed in Fig 3.15 [(a) and (b)]. A similar observation was made in the case of intermetallic formation in relation to Sn whiskers^[167]. Such methods are of interest in microelectronics applications.

Fig 3.16: XRD pattern of the cobalt nanobowls arrays of $1 \mu\text{m}$ diameter and annealed at 600°C corresponding to the formation of Co_3O_4 .

3.2.2 Magnetic Properties:

The magnetization curve for samples from set 1 is presented in fig 3.17. Low saturation magnetization (3.6 emu/g) and coercivity (15.9 Oe) was observed due to borate formation in the sample (Fig 3.5).

Figure 3.17: Magnetization curve of the sample annealed at 500⁰ C for 3 h in N₂ atmosphere followed by toluene etching (set 1).

Magnetic measurements were carried out on the Co nanobowl arrays (set 2) and the magnetization curve is given in Fig. 3.18 (a) which shows that the saturation magnetization is 57.6 emu/g. This value was less than the saturation magnetization of bulk cobalt (168 emu/g). This reduction of saturation magnetization of nanostructures compared to their bulk counterpart may be attributed to surface antiferromagnetic oxidation (as observed in XPS spectra in Fig 3.10, where the formation of Co₃O₄ is evident) as well as due to surface spin disorder effect ^[168, 169]. The coercivity value of set 2 samples was found to be 507.5 Oe which is higher than the coercivity of the randomly dispersed cobalt nanoparticles synthesized by the same technique and annealing sequence (391.3 Oe) [Fig 3.18 (b)]. The saturation magnetization of randomly dispersed nanoparticles was 62.3 emu/g. The magnetic properties of the nanobowl arrays with 200 nm and 100 nm bowl diameter show coercivity values of 526.2 Oe and 572.1 Oe [Fig 3.19 (a) and (b)], respectively which indicates that coercivity decreases with bowl diameter. The saturation magnetization of 200 nm and 100 nm bowl diameters were found to be 55.5 and 54.7 emu/g, respectively [Fig 3.19 (a) and (b)].

Morphological features and magnetic properties of nanobowl arrays of 1 μm , 200 nm and 100 nm diameter are provided in Table 3.1.

Fig 3.18: Hysteresis loop of cobalt nanobowls arrays with 1 μm diameter annealed at 400 $^{\circ}\text{C}$ for 4 h (a), and cobalt nanoparticles annealed at 400 $^{\circ}\text{C}$ for 4 h (b).

Figure 3.19: Hysteresis loop of cobalt nanobowls arrays (a) of 200 nm diameter and (b) 100 nm diameter annealed at 400 $^{\circ}\text{C}$ for 4 h followed by toluene etching.

Table 3.1: Magnetic properties of cobalt nanoparticles and nanobowl arrays.

Average Bowl Diameter (nm)	Average Wall size (nm)	Saturation Magnetization (emu/g)	Coercivity (Oe)
Randomly Dispersed Co nanoparticles	-	62.3	391.3
1 μm	70	57.6	507.5
200 nm	42	55.5	526.2
100 nm	33	54.7	572.1

Table 3.2 presents a brief overview of the work performed by various groups on the synthesis of similar structures called macroporous, hollow sphere and nanobowl. Their synthesis technique and magnetic properties are also provided in the table. The coercivity values we have obtained for cobalt nanobowls arrays were found to be much higher than previously reported values for cobalt thin films e.g. 42 Oe by Bartlett et al^[12] and 28 Oe by Zhukov et al^[170], they have synthesized a similar structure by colloidal crystal templating combined with electrodeposition technique, they^[12] have obtained a coercivity of 42 Oe and 288 Oe for macroporous structures of 1 μm and 200 nm, respectively which shows that coercivity increases with decreasing pore size consistent with our observation. Zhukov et al^[170] have also observed the same trend in their experiments on macroporous cobalt structure. Liu et al^[151] have reported Ni hollow spheres with a coercivity value of 102 Oe. Ishkandar et al^[92] have reported coercivity of around 10 kOe for macroporous FePt structure. Although FePt structures show great potential in the area of data storage devices due to their high coercivity

value in $L1_0$ phase, however annealing at high temperature to obtain this $L1_0$ phase usually leads undesirable sintering and lose of long range order.

Table 3.2: A comparison of synthesis techniques and coercivity values reported by other groups with our results.

Nanostructure	Materials	Synthesis technique	Coercivity	Group
Macroporous	Co, Ni, Fe	PS template/ Electro deposition	42-288 Oe (Co), 164 Oe for Ni, 66 Oe for Fe	Bartlett et al [12]
Macroporous	Co, Fe, Ni, $Ni_{1-x}Co_x$	PMMA and PS templates, chemical conversion	Not Reported	Yan et al ^[11]
Macroporous	FePt	PS template/vacuum infiltration of nanoparticles	10 kOe	Iskandar et al ^[92]
Hollow Spheres	Ni	Hydrothermal synthesis	102 Oe	Liu et al ^[151]
Macroporous	Co	PS template/electro deposition	80-1170 Oe	Zhukov et al [170]
Nanobowl	Co and Co ferrite	PS template/ chemical conversion	508-572Oe (Co) 299 -862 Oe (Co-ferrite)	This work

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We have observed that the coercivity values obtained for curved surfaces are greater than their nanoparticle and thin films counterparts. TEM observation shows nanoparticles of < 7 nm diameter [Fig 3.9 (a)] which may be affected by thermal fluctuations, however the particles are synthesized within the interstitials of a template, they form aggregates in the shape of larger size walls of bowls, hence they are unaffected by thermal fluctuations leading to increased coercivity. In the present work, shell thicknesses were found to be 70 nm, 42 nm and 33 nm for 1 μ m, 200 nm and 100 nm bowl diameter, respectively. These values are greater than the exchange length of Co (7 nm) ^[3, 5] and hence thermal fluctuations are not expected, resulting in high coercivity for cobalt nanobowls compared to nanoparticles. Compared to thin films, coercivity of curved structures was higher which can be attributed to domain wall pinning due to the network structure and interconnections present in the arrays as well as domain wall curvature. Previous studies of thin films on curved surfaces have also shown increased coercivity in curved structures compared to flat thin films ^[160], in earlier studies, magnetic domains which showed serpentine like structure have been imaged ^[160]. Here we discuss the effect of domain wall curvature on coercivity value.

Skomski ^[161] has studied the effect of domain wall curvature on coercivity [Fig 3.20]. He has considered a plane wall parallel to the crystallographic c-axis, whose position was parametrized by a displacement parameter ξ . In this case, free energy is given as,

$$E = -2\mu_0 M_s H L^2 \xi + \langle \gamma(\xi) \rangle L^2 \quad (3.7)$$

where, M_s is the magnetization, H is the magnetic field, γ is the domain wall energy, L^2 is the wall area and $\langle \dots \rangle$ denotes the average over the wall area. Now, considering the curved domain wall, displacement is a function of wall element and can be written as, $\xi = \xi(u, v)$, where u and v are the Cartesian coordinates. In terms of $\xi(u, v)$, total energy is given as,

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$$E = -2\mu_0 M_s H \int \xi(u, v) du dv + \gamma \sqrt{1 + \left(\frac{\partial \xi}{\partial u}\right)^2 + \left(\frac{\partial \xi}{\partial v}\right)^2} du dv \quad (3.8)$$

The wall curvature can be calculated by approximating the wall inside a given cell by a segment of a sphere of radius R [Fig 3.20]. Now, to investigate the domain wall curvature effect on coercivity, a pinning term $\Delta E = 2\pi R_0 f(\xi_0)$ is added to the free energy term given in eq. 3.8. The function $f(\xi_0)$ denotes the dependence of wall energy on the wall position at the cell boundary. From Fig 3.20, a maximum displacement can be formulated as,

$$h = R - \sqrt{R^2 - R_o^2} \quad (3.9)$$

Figure 3.20: A curved domain wall with the curvature of a sphere of radius R [161].

Now, the total energy can be written as,

$$\frac{E}{\pi} = -2\mu_0 M_s H \left(\frac{h^3}{6} + \frac{h R_0^2}{2} + R_0^2 \xi_0 \right) + \sigma (R_0^2 + h^2) + 2R_0 f(\xi_0) \quad (3.10)$$

The expression of coercivity (H_c) can be derived by minimizing E with respect to ξ_0 ,

$$H_c = \max \left(\frac{\partial f}{\partial \xi_0} \right) / \mu_0 M_s R_0^2 \quad (3.11)$$

which shows that coercivity is inversely proportional to the curvature which is consistent with our experimental observations for curved nanostructure compared to thin film structures. Further, as the bowl diameter decreases, the curvature also decreases leading to an increase in coercivity value consistent with our experimental results. Domain wall pinning due to the network structure of spherical shells can also lead to high coercivity. The shell structure is composed of nanoparticles and hence can be considered as a rough surface, this roughness also causes domain wall pinning.

3.3 Synthesis and Characterization of Cobalt Ferrite Nanobowls:

To examine the versatility of this synthesis technique, magnetic cobalt ferrite nanobowl arrays were also synthesized using colloidal crystal templates. These arrays were formed by vacuum assisted infiltration of precursors in the interstitial spaces of 3-dimensional close packed polystyrene (PS) templates. The templates were removed by a combined sequence of annealing and toluene etching resulting in cobalt ferrite nanobowl arrays. A morphological investigation of the mechanism of the formation of such nanobowls is presented. Structural properties investigated by XRD techniques show the effect of annealing temperature on the

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crystallinity of the material. The effect of shape and magnetocrystalline anisotropy on the magnetic properties was studied.

3.3.1 Morphological, Surface and Structural properties:

Mixtures of aqueous solutions of iron and cobalt salts and sodium borohydride were infiltrated inside the interstitial spaces of 3-D close packed template of PS spheres. The topmost layer of the as synthesized sample, for which the template was removed by toluene etching, shows a bowl like morphology with shell thicknesses in the sub-100 nm regime [Fig 3.21 (a)]. Discontinuous formation of material can be observed within the interstitials similar to the results obtained for the synthesis of cobalt nanobowls. The dark regions are the interconnections within the network arising from the point of contact of the PS spheres. Fig 3.21 [(b) and (c)] presents the morphology of samples for which template removal was carried out by annealing at 400⁰ C for 4 h followed by toluene etching. The top layer of the structure exhibits nanobowl formation Fig 3.21 (b). On the other hand, the morphology of underlayers is very similar to the hollow spheres Fig 3.21 (c). The hollow nature of these spheres has been confirmed by the broken spheres [shown in the inset of Fig 3.21 (c)]. The interconnections were not evident, indicating that precursors had over infiltrated within the interstitials. When the sample is annealed at 500⁰ C for 4 h in air, nanobowl shape was not retained, instead the sample was broken Fig 3.21 (d).

Figure 3.21: Morphology of as synthesized cobalt ferrite nanobowl samples (a) as synthesized (b) annealed at 400°C for 4 h in top layer (c) annealed at 400°C for 4 h in underlayers (d) annealed at 500°C for 4 h.

To show the effect of this bowl structure on properties, nanoparticles were synthesized by the same borohydride reduction technique without using templates. Fig 3.22 shows the TEM micrograph of the particles which shows the formation of polydisperse nanoparticles in the size range of 5 nm – 45 nm.

Figure 3.22: TEM micrograph of the as synthesized cobalt ferrite nanoparticles.

The structural properties of the sample were investigated using the XRD technique. The XRD patterns of the samples are presented in Fig 3.23 [(a), (b) and (c)] which show the effect of annealing temperature on the crystallinity. Fig 3.23 (a) shows the XRD pattern of the as synthesized nanobowl sample which reveals an amorphous structure. Annealing results in crystallization, the major peak observed for samples annealed at 400⁰ C for 4 h [fig 3.23 (b)] can be indexed as the (311) plane of a cubic unit cell of CoFe₂O₄ structure (JCPDS card no. 22-1086) , while the peaks observed for samples annealed at 500⁰ C for 4 h [Fig 3.23 (c)] can be indexed as the (200), (311), (400), (422), (511), (440) and (622) planes of a cubic unit cell which corresponds to that of CoFe₂O₄ structure (JCPDS card no. 22-1086). However, energy dispersive X-Ray spectroscopy (EDS) results of the sample annealed at 400⁰ C show that the atomic percentage of Co, Fe and O is 25%, 25% and 50%, respectively (Co:Fe $\approx$ 1:1)

which is same as the Co/Fe ratio in precursor, consistent with the value (0.81) reported by Li et al. for 1:1 molar ratio of Co/Fe in precursor solution. Li et al.^[171] also observed the spinel cobalt ferrite structure for 1:1 molar ratio of Co/Fe in the precursor solution in agreement with our result. The EDS results of the sample annealed at 500⁰ C show that the 1:1 atomic ratio of Co/Fe was retained.

Figure 3.23: X-Ray diffraction pattern of the cobalt ferrite nanobowls samples (a) as synthesized (b) annealed at 400⁰ C for 4 h (c) 500⁰ C for 4 h.

Surface characterization of cobalt ferrite nanoparticles was performed using the XPS technique. Fig. 3.24 (a) shows the XPS spectrum of as synthesized cobalt ferrite nanoparticles, while the Fig 3.24 [(b) and (c)] presents the XPS spectrum of cobalt ferrite nanoparticles annealed at 400⁰ C before and after washing the nanoparticles in air. The observed peaks can indexed as B 1s, C 1s, O 1s, Fe 2p_{3/2} and CO 2p_{3/2}. It is evident that high intensity peak of B at 192.2 is observed in only Fig 3.24 (b). Reduction of solution mixture of cobalt and iron salts in inert atmosphere leads to the formation of Co- Fe-B or Co-Fe-B-O compounds and that is why no B₂O₃ peak is observed in Fig 3.24 (a). When we anneal the product in air, boron oxidizes into B₂O₃ which is observed in Fig 3.24 (b). This B₂O₃ content can be removed by washing into DI water [Fig 3.24 (c)].

Figure 3.24: XPS spectra of cobalt ferrite nanoparticles (a) as synthesized (b) after annealing at 400⁰C before washing in DI water and (c) after annealing at 400⁰C followed by washing in DI water.

3.3.2 Magnetic Properties:

The magnetic behavior of cobalt ferrite nanoparticles and nanobowls were measured and their hysteresis curves are presented in Fig 3.25 to 3.27. The magnetic properties are tabulated in Table 3.3. The saturation magnetization values of as synthesized cobalt ferrite nanoparticles and nanobowls were found to be 23.9 emu/g and 21.4 emu/g, respectively [Fig 3.25 (a) and (b)]. The coercivity of the as synthesized nanoparticles and nanobowls arrays were found to be 215.9 Oe and 299.0 Oe, respectively. [Fig 3.25 (a) and (b)]. The cobalt ferrite nanoparticles annealed at 400⁰ C exhibited saturation magnetization of 71.4 emu/g and 62.1 emu/g and coercivity values of 237.2 Oe and 862.8 Oe, respectively [Fig 3.26 (a) and (b)]. The saturation magnetization values for cobalt ferrite nanoparticles and nanobowls annealed at 500⁰ C were found to be 79.6 emu/g and 69.0 emu/g, respectively and the coercivity values were 282.7 Oe and 349.0 Oe, respectively [Fig 3.27 (a) and (b)]. The saturation magnetization of the particles and nanobowls array increased on increasing the annealing temperature due to increased crystallinity of the material [Table 3.3].

Figure 3.25: Hysteresis loop measured on as synthesized cobalt ferrite nanoparticles (a), and cobalt ferrite nanobowls array (b).

Figure 3.26: Hysteresis loop measured on cobalt ferrite nanoparticles (a), and cobalt ferrite nanobowls array (b), after annealing at 400⁰ C for 4 h in air.

Figure 3.27: Hysteresis loop measured on cobalt ferrite nanoparticles (a), and cobalt ferrite nanobowls array (b), after annealing at 500⁰C for 4 h in air.

Table 3.3: Magnetic Properties of cobalt ferrite nanoparticles and nanobowl arrays before and after annealing.

Annealing	Nanoparticles		Nanobowls	
Temperature	M _s (emu/g)	H _c (Oe)	M _s (emu/g)	H _c (Oe)
As synthesized	23.9	215.9	21.4	299.0
400 ⁰ C	71.4	237.2	62.1	862.8
500 ⁰ C	79.6	282.7	69.0	349.0

Many groups have reported the synthesis of cobalt-ferrite nanostructures in the form of nanoparticles, nanowires, thin films and hollow spheres^[52, 172-175]. A brief overview of these nanostructures and their coercivity values are provided in Table 3.4. Lee et al^[172] have reported the synthesis of cobalt ferrite nanoparticles at elevated temperature with a room temperature coercivity value of 460 Oe while Bhattacharya et al^[173] have synthesized superparamagnetic cobalt ferrite nanoparticles. Jung et al^[52] have synthesized cobalt ferrite nanowires by infiltration of nanoparticles within pores of anodized aluminum oxide templates. A considerable change in coercivity with annealing temperature was observed, it increased from 100 Oe to 1600 Oe after annealing at 600⁰C. Lin et al^[175] have reported cobalt ferrite hollow spheres with the coercivity values in the range of 0-374 Oe. The effect of annealing on coercivity was also studied by Wang et al^[174] for cobalt ferrite thin films, they observed coercivity values in wider range from 10 Oe to 7500 Oe.

Table 3.4: A comparison of coercivity of cobalt ferrite nanostructures as reported by other groups with our results.

Co-ferrite nanostructure	Annealing temperature (T)	Coercivity (H _c) (Room Temperature)		Group
Nanoparticles	300 ⁰ C	460 Oe		Lee et al ^[172]
Nanowires	As synthesized	100 Oe		Jung et al ^[52]
	600 ⁰ C	1600 Oe		
Nanoparticles	295 ⁰ C	0 Oe		Bhattacharyya et al ^[173]
Thin films	As synthesized/ 500 ⁰ C/700 ⁰ C/900 ⁰ C/1100 ⁰ C/1200 ⁰ C	Hc _{//}	Hc _⊥	Wang et al ^[174]
		10 Oe/50	10 Oe/25Oe	
		Oe/2600	/2200	
		Oe/7500	Oe/6100	
		Oe/5700	Oe/5100	
		Oe/2000Oe	Oe/1300 Oe	
Hollow spheres	Cobalt ferrite	Poly (MMA-co-MAA) spheres/chemical conversion	0 – 374 Oe	Lin et al ^[175]
Nanobowls	As synthesized/400 ⁰ C/500 ⁰ C	299.0 Oe/862.8 Oe/349.0 Oe		This work

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The difference in coercivities of nanoparticles and nanobowls arrays was found to be 39%, 264% and 23.4% for as synthesized sample and the samples annealed at 400^o C and 500^o C, respectively [Table 3.3] which exhibits shape effect. In a typical TEM micrograph (Fig 3.22), Co-ferrite nanoparticles in less than 10 nm size range were also observed which are expected to be in superparamagnetic regime, on the other hand when the particles are synthesized in the interstitials of a colloidal template, particles are aggregated in the larger size walls of the bowls and hence are unaffected by the thermal fluctuations leading to higher coercivity. Recently, a difference in coercivity (~26 %) of such morphologies of nickel has been reported^[176]. The coercivity values obtained for nanobowl arrays (299 Oe- 862.8 Oe) in this work is much greater than the coercivity of Co-ferrite thin films annealed at the same temperature (10-50 Oe)^[174]. This behavior may be attributed to the coercivity dependence of domain wall curvature as discussed for Co nanobowls and thin films earlier in this chapter (Eq. 3.11).

3.4 Summary:

Chemical synthesis of cobalt nanobowl arrays with diameter of 1 μm , 200 nm and 100 nm and wall sizes in the sub-100 nm range directed by colloidal crystal templated assembly was carried out. Borohydride reduction of cobalt salts within the interstitials of colloidal crystal templates of PS spheres followed by annealing resulted in Co nanobowl arrays. The chemistry of borohydride reduction leading to removal of undesired boron contents was established by surface and structural characterization. Two phase (h.c.p. + f.c.c) microstructure was observed for cobalt with planar defects. High temperature annealing of nanobowls resulted in the formation of nanowires. Coercivity of nanobowl arrays was found to be greater than their thin film or nanoparticle counterparts. Cobalt ferrite nanobowl arrays were synthesized by borohydride reduction of aqueous solution mixture of cobalt and iron

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salts within the interstitials of colloidal templates of PS spheres. Annealing led to improved crystallinity and hence the high magnetization values. The coercivity value of cobalt ferrite nanobowls was found to be greater than that of nanoparticles and thin films.

In this chapter, it was shown that nanobowl structures can be fabricated over a fairly large area using colloidal crystal templated assembly and chemical synthesis techniques, such a methodology may be useful to fabricate patterned magnetic media for data storage applications. Due to minimum volume shrinkage, the morphology of the nanobowl arrays were spatially ordered, this good spatial ordering is a necessity for patterned media. The coercivity values reported here, i.e., in the range of 500 to 1000 Oe are well suited for data storage applications.

In the next chapter, synthesis and characterization of cobalt nanowires by magnetic field induced assembly and cobalt nanowire arrays by AAO template assisted synthesis is presented.

Chapter 4

Synthesis and Characterization of High Aspect Ratio Cobalt Nanostructures

4.1 Introduction:

This chapter describes the synthesis and characterization of elongated cobalt nanostructures in random orientation as well as periodic arrays by magnetic field induced assembly and anodized aluminum oxide (AAO) template assisted assembly, respectively.

The borohydride reduction of cobalt salt technique was used to synthesize cobalt nanoparticles. Randomly oriented cobalt nanowires of average diameter 4.8 nm were synthesized by magnetic field induced assembly of cobalt nanoparticles, the wires consisted of both h.c.p. and f.c.c. Co and the magnetic properties of these nanowires showed the effect of shape anisotropy. The magnetic properties were compared with the theoretical predictions. A periodic assembly of wires was not achieved since wire formation occurs within a liquid.

Template-free self assembly over a large area is difficult task to achieve, however synthesis of periodic nanostructures over a large area can be achieved by template assisted assembly techniques with the additional advantage that anisotropy can be simultaneously introduced. Such periodic arrays of Co nanowires offer great potential in the area of high density data storage devices. In this work, template assisted assembly technique using AAO templates was employed to synthesize cobalt nanowires in a periodic assembly. The morphology, surface and structural characterization and magnetic property evolution is presented.

4.2 Magnetic Field Induced Synthesis of Cobalt Nanowires:

In chapter 3, we have described the synthesis of cobalt nanobowls (sample set 1 and sample set 2). Synthesis of cobalt nanoparticles (sample set 3) in the size range of 3-35 nm by borohydride reduction of cobalt salt followed by annealing at 400⁰C for 4h and washing in DI water [Fig 3.9 (a)] was also described in chapter 3. Size selection of the nanoparticles from sample set 3 was carried out by centrifugation at 4000 rpm. The average diameter of the nanoparticles after size selection (sample set 4) was found to be 4.3 nm with a standard deviation of 1.77 nm [Fig 4.1].

Figure 4.1: BF-TEM micrograph of Co nanoparticles annealed at 400⁰C after size selection (sample set 4).

An external magnetic field of 0.35 T was applied for 1 h to both sets of nanoparticle suspensions (sample set 3 and sample set 4). Fig 4.2 (a) shows the macroscopic view of the particles in an external magnetic field which reveals that the particles can be aligned in the external magnetic field. TEM studies reveal aligned nanoparticles in the size range of 20-35

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nm [Fig 4.2 (b)] for sample the set 3 prior to exposure of magnetic field. Fig 4.2 (c) shows the TEM micrograph of sample set 4 prior to exposure of magnetic field which shows nanowires with an average diameter of 4.8 nm.

Figure 4.2: (a) Macroscopic alignment of magnetic nanoparticles in an external magnetic field, BF-TEM micrographs of Co nanoparticles annealed at 400⁰C exposed to an external magnetic field of 0.35 T for 1 h (b) before size selection (sample set 3) (c) after size selection (sample set 4).

Ferromagnetic particles exhibit large dipolar interactions due to high intrinsic moments which enable them to assemble along the external magnetic field direction. Particles are aligned in field direction due to a torque which develops due to equal and antiparallel forces on a dipole resulting from the Zeeman interactions in a uniform magnetic field ^[177] [Fig 4.3]. A non-uniform field is generated by each dipole, in addition to the uniform external field. This non uniform field affects the behavior of the surrounding dipoles in the solution; in such a non-uniform field the resultant force on a dipole has a non-zero value which accelerates the dipole in the direction of the field gradient. The suspension of the particles was ultrasonicated for TEM sample preparation but the chain structure remained intact [as observed in TEM micrographs Fig 4.2 [(b) and (c)] due to residual magnetic and Van der Waals interactions.

Figure 4.3: Schematic of magnetic field induced alignment of magnetic nanoparticles in an external magnetic field.

Magnetic measurements on sample sets 3 and 4 were performed using a vibrating sample magnetometer. The magnetization curves of sample sets 3 and 4, before and after exposure to an external magnetic field, are presented in Fig 4.4 and 4.5, respectively. The magnetic properties of both sets of samples are summarized in Table 4.1. The saturation magnetization of sample set 3 was found to be 62.3 emu/g [Fig 4.4 (a)] while the size selected particles show an unusually high saturation magnetization of 151.3 emu/g [Fig 4.5 (a)], close to that of

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bulk cobalt (168 emu/g). This high magnetization value of nanoparticles can arise due to the high fraction of surface atoms. Due to these surface atoms, the electronic structure of the atoms is modified by the different symmetry at the surface, this enhances the atomic moment since the lack of orbital overlap at the surface causes band narrowing ^[178]. High magnetization values are desirable in many applications, e.g., cell sorting, since it enables particles to be separated from the suspension at relatively low fields.

The coercivity values before size selection were found to be higher than those of size selected particles, the coercivity value of sample set 3 was 391.3 Oe [Fig 4.4 (a)] much higher than that of sample set 4 (153.2 Oe) [Fig 4.5 (a)]. For cobalt, the critical size for single domain region is 70 nm ^[28], for single domain particles, magnetization reversal does not take place by domain wall motion, instead the whole magnetization vector rotates, this process requires more energy and hence high coercivity was observed ^[27]. Sample set 4 consists of polydisperse particles in the 3-35 nm range, since many of the particles are in the single domain range, high coercivity is observed. The coercivity of nanomagnetic particles decreases as particle size approaches the superparamagnetic limit ^[5] (Fig 2.4 in chapter 2), hence low coercivity (153.2 Oe) was observed for size selected particles of 4.3 nm average size.

Figure 4.4: Magnetization curves measured on the cobalt nanoparticles annealed at 400°C before size selection (sample set 3) (a) before exposure to magnetic field (b) after exposure to magnetic field of 0.35 T for 1 h. Inset shows the portion of the curve where it touches the axis.

Figure 4.5: Magnetization curves measured on the size selected cobalt nanoparticles annealed at 400°C (sample set 4) (a) before exposure to magnetic field (b) after exposure to magnetic field of 0.35 T for 1 h. Inset shows the portion of the curve where it touches the axis.

Table 4.1: Magnetic properties of Co nanoparticles annealed at 400⁰C (sample set 3 and sample set 4) before and after exposure of an external magnetic field.

	Sample set 3 (before size selection)		Sample set 4 (after size selection)	
	Before exposure to external magnetic field	After exposure to external magnetic field	Before exposure to external magnetic field	After exposure to external magnetic field
Saturation Magnetization(M_s) (emu/g)	62.3	70.8	151.3	162.3
Coercivity (H_c) (Oe)	391.3	572.3	153.2	251.5
Squareness (S_Q)	0.25	0.32	0.08	0.12

The saturation magnetization values of sample set 3 before and after exposure to an external magnetic field was 62.3 emu/g and 70.8 emu/g, respectively [Fig 4.4 (a) and (b)] revealing that magnetization increased after exposure to an external magnetic field. A similar trend was obtained for sample set 4, the saturation magnetization increased from 151.3 emu/g to 162.3 emu/g [Fig 4.5 (a) and (b)]. Typical values for saturation magnetization of cobalt nanostructures reported earlier are 111 emu/g for the wire morphology^[158] and 124.6 emu/g for the belt morphology^[19]. A comparison of our results for cobalt nanowires with other groups is summarized in Table 4.2. Niu et al^[158] have synthesized Co nanowires of ~ 13 μ m diameter by magnetic field induced assembly with a coercivity value of 389 Oe. Cheng et al^[177] have also created chain of spheres by magnetic field induced assembly using 15 nm nanoparticles and

obtained a low coercivity of 50 Oe. Xie et al ^[19] have synthesized an elongated morphology called “nanobelts” with a coercivity of 410.6 Oe.

Coercivity values for both sample sets 3 and 4 increased after exposure to an external magnetic field. For sample set 3, coercivity values before and after exposure to an external magnetic field were found to be 391.3 Oe and 572.3 Oe [Fig 4.4 (a) and (b)], respectively, larger than the coercivity previously reported for micron size nanowires (389 Oe). For sample set 4, the coercivity increased from 153.2 Oe to 251.5 Oe [Fig 4.5 (a) and (b)] larger than the previously reported value of 15 nm Co particles (50 Oe) aligned by an external magnetic field ^[177]. The squareness also increased from 0.25 to 0.32 for sample set 3 [Fig 4.4 (a) and (b)] and 0.08 to 0.12 for sample set 4 [Fig 4.5 (a) and (b)]. Enhancement in the coercivity of wire shaped magnetic nanostructures imply that a higher magnetic field is needed to reverse magnetization for elongated nanostructures compared to randomly dispersed Co nanoparticles.

Table 4.2: A comparison of magnetic properties of elongated Co nanostructures synthesized by template free techniques with our results.

Morphology	Diameter	Magnetization (room temperature)	Coercivity (room temperature)	References
nanowire/chain	~13 μm	111 emu/g	389 Oe	Niu et al ^[158]
Chain	15 nm	Not reported	50 Oe	Cheng et al ^[177]
Chain	32 nm	Not reported	Not Reported	Maceira et al ^[156]
nanobelt	200-500 nm	124.6 emu/g	410.6 Oe	Xie et al ^[19]
nanowire/chain	Sub-10 nm	153.2 emu/g	251.5 Oe	This work
	20-35 nm	70.8 emu/g	572.3 Oe	This work

In previous reports on magnetic field induced assembly of Co nanowires, the coercivity values were not compared to any theoretical models. In this work, the coercivity values obtained for the nanowires synthesized by magnetic field induced assembly of the nanoparticles in sample set 3 and sample set 4 were compared to Jacobs and Bean's^[15] model.

4.2.1 Magnetization Reversal in Magnetic Chains of Spheres:

Studies of magnetization reversal in elongated nanostructures mainly deal with nanowires, modeled as perfect infinitely long cylinders or prolate ellipsoids. Two types of reversal mechanisms, coherent rotation and curling are usually studied^[61]. In the coherent rotation processes, the dipole moment rotates uniformly during the reversal process [Fig 4.6 (a)] and the coercivity is given as $2\pi M_s$ ^[61]. When the radius of the wire is larger than the coherent length (15 nm), the magnetization reversal model is usually be the curling mechanism [Fig 4.6 (b)] for which the coercivity is given by^[61],

$$H_c = 2.16\pi \frac{A}{M_s r^2} \quad (4.1)$$

where A ($= 1.30 \times 10^{-6}$ erg/cm for Co) is the exchange constant, M_s is the saturation magnetization and r is the radius of the wire. Modes of magnetization reversal by coherent rotation and curling are presented in Fig 4.6.

Considering the case of sample 3 [saturation magnetization (M_s) = 70.8 emu/g ($= 630.1$ emu/cm³)]. Coercivity value for coherent rotation process is given by $2\pi M_s$ from which we get theoretical coercivity value of 3957 Oe. For curling mode of reversal we calculate the coercivity value using eq 4.1 with $M_s = 70.8$ emu/g ($= 630.1$ emu/cm³) and $r = 20$ nm which gives a coercivity value of 3611.7 Oe. Both of these values are much greater than our experimental value of 572.3 Oe [Fig 4.4 (b)].

Figure 4.6: Modes of magnetization reversal by (a) coherent rotation and (b) curling [5].

In previous studies on nanowires, Chen et al^[61] have also observed such discrepancies which arise due to ignorance of imperfections in the structure of real nanowires. These imperfections are the point of contacts between two spheres, since in our case the wires were synthesized by aligning particles and cannot be treated as cylindrical nanowires. These nanowires are basically chains of spheres. In the presence of imperfections, due to the localized nature of magnetization reversal, a decrease in coercivity is expected^[33]. Chen et al^[61] have studied the magnetization reversal mechanism in magnetic nanowires. In this case nanowires were treated as chains of spheres. Magnetocrystalline anisotropy was ignored because it is usually much smaller than shape anisotropy. They suggested that imperfections in the nanowires lead to the absence or weakening the local exchange interactions. Jacobs and Bean^[15] proposed a model for the magnetic properties of chain of spheres. According to their symmetric fanning model, the spheres in a chain are considered as single domain with

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no exchange interactions between adjacent spheres. The magnetization reversal processes by symmetric fanning is presented in Fig 4.7.

Figure 4.7: Magnetization reversal in chains by symmetric fanning [15].

Considering each sphere as a dipole of moment μ and diameter a , the dipoles make angles θ_i and θ_j , with the vector joining them. For the symmetric fanning [Fig 4.7], mechanism $\theta = \theta_1 = -\theta_2 = \theta_3 = \theta_4, \dots$. In order to find the expression for the coercivity value, the total energy of the system is minimized with respect to its angle parameter (θ) which gives an expression for the equilibrium field at a given angle. The total energy of the system was shown to be the sum of the interdipole magnetostatic energy (term 1 and 2 in eq 4.2) and the field energy in an applied field H (term 3 in eq 4.2), with the field directed opposite to the magnetization direction of the chains ^[15]:

$$En = \left(\frac{\mu^2}{a^3} \right) nL_n (\cos 2\theta - 3 \cos^2 \theta) + \left(\frac{\mu^2}{a^3} \right) nM_n (1 - 3 \cos^2 \theta) + n\mu H \cos \theta. \quad (4.2)$$

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where

$$L_n = \sum_{j=1}^{(n-1)/2 < j \leq (n+1)/2} [n - (2j - 1)] / n(2j - 1)^3 \quad (4.3)$$

$$M_n = \sum_{j=1}^{(n-2)/2 < j \leq (n/2)} (n - 2j) / n(2j)^3 \quad (4.4)$$

Here a is diameter of the spheres, n is number of the spheres and aspect ratio of the nanowires and μ is the dipole moment of a single sphere $= \pi a^3 M_s / 6$.

After minimizing the energy with respect to its angle parameter, the expression for the coercivity obtained is,

$$H_{c,n} = \pi(6M_n + 2L_n)M_s / 6 \quad (4.5)$$

We used this model to evaluate coercivity values for both sample sets 3 and sample sets 4.

4.2.1.1 Numerical Calculations:

Eq. 4.5 was used to evaluate coercivity for both sample sets 3 and 4. For sample set A, the average number of particles in a chain (n) was 15 hence the value $(6M_n + 2L_n)$ is equal to 2.6 (eq. 4.3 and 4.4). Substituting the value of $(6M_n + 2L_n)$ and M_s from Table 4.1, we find the predicted coercivity for sample set A as 857.3 Oe (eq. 4.5). For sample set B, the average number of particles in a chain (n) was 20 and hence the value of $(6M_n + 2L_n)$ can be calculated as 2.7 (eq. 4.3 and 4.4). Substituting these values of $(6M_n + 2L_n)$ and M_s from Table 4.1, we calculate the coercivity value for sample set B as 2040.9 Oe (eq. 4.5).

Before making the comparison of experimental and theoretical values, we discuss the size dependent behavior of magnetic properties.

Exchange forces are the short range interaction responsible for the alignment of magnetic dipole moments. Particles much larger than the exchange length ($D \sim 10 \lambda_{\text{ex}}$) break into domains in order to reduce their magnetostatic energy [Fig 4.8 (a)]. In the size range of the magnetic nanoparticles of a few λ_{ex} [Fig 4.8 (b)], domain wall formation is energetically expensive and no domain formation takes place. For very small particles smaller than the exchange length, magnetization of the particle may be switched due to thermal fluctuation and hence exhibit superparamagnetism^[3] [Fig 4.8 (c)].

(a) Multidomain particle
($D \sim 10 \lambda_{\text{ex}}$)

(b) Single domain particle
($D \sim \lambda_{\text{ex}}$)

(c) Superparamagnetic particle

Figure 4.8: Magnetization configuration of (a) multidomain (b) single domain and (c) superparamagnetic particle [3].

In numerical calculations for sample set 3, the experimental value differed from Jacobs and Bean's model by $\sim 33\%$. Sample set 3 has a wide particle size distribution as it contains particles in the size range of 3-35 nm. Statistical analysis made on the basis of 100 particles in the TEM micrographs shows that in sample set 3, 52% of the particles are less than or equal to 7 nm size while 48% of the particles are greater than 7 nm [Fig 4.9 (a)]. Since the exchange length of the cobalt nanoparticles is 7 nm, only particles are in size range of greater

than 7 nm particles size are likely to be in the single domain regime. Particles in the size range of less than 7 nm are likely to be in the superparamagnetic regime and do not satisfy the assumption of Jacobs and Bean's model ^[15]. The thermal fluctuation of superparamagnetic particles leads to a decrease in coercivity, hence the experimental value was found to be less than the theoretical value [Fig 2.4 in chapter 2]. In sample set 3 and sample set 4 all the particles were seen less than the upper limit for single domain size range 70 nm ^[28] [Fig 4.9 (a) and Fig 4.9 (b)], it is unlikely that the particles are in the multidomain regime.

For sample set 4, ~ 8-fold difference was observed between for the experimental value compared to the theoretical value. In sample set 4, the statistical analysis was made on the basis of 100 particles in the TEM micrographs. The percentage of the particles in less than 7 nm was observed to be 89 % which are expected to be in superparamagnetic regime resulting in a decrease in coercivity, hence the lower coercivity was observed [Fig 2.4 in chapter 2]. Only 11 % particles were in the single domain region [Fig 4.9 (b)] and hence the coercivity value is dominated by superparamagnetic particle.

Figure 4.9: Number of particles (%) less and greater than 7 nm size range in (a) sample set 3, and (b) sample set 4.

In the next section, synthesis and characterization of cobalt nanowires in a periodic array using anodized aluminum oxide template and their structural and magnetic properties are presented.

4.3 AAO Template Directed Synthesis of Cobalt Nanowire Arrays:

This section describes the chemical synthesis of cobalt nanowires in periodic arrays by borohydride reduction within the pores of an AAO template. Cobalt nanowires were formed by borohydride reduction of cobalt salt in the pores of anodic aluminum oxide (AAO) templates; the samples were annealed in order to produce nanowires with the h.c.p. crystal structure. Microstructural investigations were carried out using SEM, TEM and AFM while structural properties were characterized using XRD analysis. The morphology and the crystal structure was varied through the template geometry and annealing temperature, respectively. Magnetic property measurements by VSM showed that shape played an important role in altering the magnetic properties and magnetization cross over behavior for high aspect ratio nanowires was observed.

4.3.1 Synthesis and Characterization:

To introduce shape anisotropy along with periodicity, synthesis of cobalt nanoparticles inside pores of AAO templates was carried out. Two types of templates were used to fabricate the nanowires, one with $35\text{ nm} \pm 5\text{ nm}$ pore size and $30\text{ }\mu\text{m}$ thickness and another with $200\text{ nm} \pm 25\text{ nm}$ pore size and $65\text{ }\mu\text{m}$ thickness were used. Fig 4.10 (a) and (b) shows the top view and cross section of the templates of 35 nm pore size while Figure 4.10 (c) and (d) illustrates the corresponding SEM micrographs for the template with 200 nm pores. The surfaces of the templates were also characterized by atomic force microscopy (AFM) [Fig 4.11 (a) and (b)]

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for templates with 35 nm pore diameter and Fig 4.11 (c) and (d) for 200 nm pore diameter template. The RMS roughness values for the templates with 35 nm and 200 nm pore diameters were found to be 5.5 nm and 15 nm, respectively. Fig. 4.12 [(a) and (b)] are SEM micrographs of both the templates after infiltration of the precursors inside the pores, followed by annealing at 350⁰C for 3 h in air. Fig 4.12 (a) is a SEM micrograph of Co nanowires formed in the template of 35 nm pore diameter while Fig 4.12 (b) shows the SEM micrograph of Co nanowires of 200 nm template from which the mean values of wire to wire spacing for 35 nm and 200 nm templates were found to be 117 nm and 450 nm, respectively.

Figure 4.10: The SEM micrographs of the AAO template with 35 nm pore diameter (a) top surface (b) cross section, and the AAO template with 200 nm diameter (a) top surface (b) cross section.

Figure 4.11: AFM images of the surface of the AAO template (a) with 35 nm pore size (b) corresponding 3-D AFM image, and (c) with 200 nm pore size (d) corresponding 3-D AFM image.

The surfaces of the infiltrated templates were observed by atomic force microscopy. Fig 4.13 (a) and (b) presents the AFM image and 3-D profile of the template with 35 nm pore size respectively while Fig 4.13 (c) and (d) presents the same for the template with 200 nm pore size. The RMS roughness values of the infiltrated templates of 35 nm and 200 nm pore diameter were found to be 18.7 nm and 47.0 nm, respectively [Fig 4.13 (b) and (d)], indicating that the surfaces of the infiltrated templates are rougher compared to the surfaces of the templates before infiltration [Fig 4.11 (b) and (d)]. During the infiltration of the precursors some aggregation of particles [Fig 4.13 (a) and (c)] takes place on the surface resulting in increased roughness.

Figure 4.12: SEM micrographs of Co nanowires formed in (a) AAO template with 35 nm pore diameter and (b) AAO template with 200 nm pore diameter.

Since the borohydride reduction process produces Co-B compounds, these compounds were converted to cobalt by a controlled annealing process. The sample was heated to 350⁰ for 3 h in air in order to produce cobalt. A discussion on the formation of cobalt by borohydride reduction has been presented elsewhere ^[22]. The initially amorphous sample could be

converted to the h.c.p. crystal structure. The f.c.c. phase was avoided since it is more prone to oxidation to Co_3O_4 .

Figure 4.13: AFM images of the surface of the Co filled AAO templates (a) with the 35 nm pore size (b) corresponding 3-D AFM image, and (c) with the 200 nm pore size (d) corresponding 3-D AFM image.

Fig 4.14 shows the XRD pattern of the arrays of nanowires of 35 nm and 200 nm diameter annealed at 350⁰C for 3 h; a high intensity diffraction peak corresponding to the (0002) planes of h.c.p. cobalt is observed, this (0002) texture is a result of the growth axis being perpendicular to the close packed planes (the aluminum peaks arise from the sample holder used for XRD experiments). In previous studies of Co nanowires, different crystal structures of cobalt have been reported. Nanowires of cobalt with AAO templates with pore sizes in the range of 12 – 72 nm were prepared by Benfield et al ^[66] and a mixture of h.c.p. and f.c.c. phases was obtained; however there was no clear relationship between the volume fraction of the h.c.p. phase relative to the f.c.c. phase and the pore size or preparation conditions.

Figure 4.14: XRD pattern of the Co nanowires formed in the AAO template of 35 nm and 200 nm pore size.

Fig 4.15 (a) and (b) presents the hysteresis loops for 35 nm diameter wires when the magnetic field was applied parallel and perpendicular to the axis respectively, while Fig 4.15 (c) and (d) presents the corresponding results for the hysteresis loop measured for the 200 nm diameter nanowire arrays. The coercivity value obtained for 35 nm nanowire arrays was found to be 428 Oe and 458 Oe respectively for the applied field perpendicular and parallel to the axis. For 200 nm nanowire arrays, the coercivity value obtained was 416 Oe and 444 Oe for applied field perpendicular and parallel to axis, respectively.

Table 4.3 presents the coercivity values of Co nanowires synthesized by template directed assembly by various groups ^[179-183]. Nanowires with diameters in the range of 9 – 400 nm with coercivity values in a wide range from 145 Oe to 2200 Oe have been reported. Bantu et al ^[179] have synthesized nanowires in AAO templates and studied the coercivity dependence on synthesis conditions and length of the wires. They have concluded that reduction potential or the electrolyte concentration does not affect the magnetic properties but the length of the wire plays an important role (this aspect is discussed in section 4.3.2). Khan et al ^[181] synthesized nanowires of 78 nm (length -0.84 μ m) and 18 nm (length-1.1 μ m) and concluded that $H_c(\perp)$ decreases with increasing nanowire diameter. Zeng et al ^[182] have studied the effect of nanowire diameter, center to center spacing and wire length on coercivity values. It was reported that if the diameter and pore spacing is constant, coercivity increases with wire length and saturates when the ratio of length/diameter exceeds 5. They observed that coercivity decreases monotonically with increasing wire diameter except for the smallest wire diameter (9 nm). In our case, $(H_c)_{//200\text{ nm}}$ (444 Oe) is less than $(H_c)_{//35\text{ nm}}$ (458 Oe) which follows the same trend.

Figure 4.15: Magnetization hysteresis loop measured on the nanowires formed in the AAO template with 35 nm pore size (a) when the magnetic field was applied parallel to axis (b) when the magnetic field was applied perpendicular to axis, and AAO template with 200 nm pore size (a) when the magnetic field was applied parallel to axis (b) when the magnetic field was applied perpendicular to axis.

Table 4.3: A comparison of coercivity of Co nanowires synthesized by AAO template directed assembly with previous work.

Deposition Technique	Diameter (length)	Coercivity (Room Temperature)	Group
Electrodeposition	100 nm, 200 nm, 400 nm. (Varying length)	145 – 304 Oe	Bantu et al ^[179]
Electrodeposition	78 nm (0.84 μ m)	1549 Oe ($\perp$) 711 Oe (II)	Khan et al ^[181]
	18 nm (1.1 μ m)	597 Oe ($\perp$) 567 Oe (II)	
Electrodeposition	9 - 21 nm (1-5 μ m)	1700 – 2100 Oe	Zeng et al ^[182]
Electrodeposition	35-400 nm	200-2200 Oe	Ounadjela et al ^[183]
Vacuum Infiltration	200 nm (65 μ m)	444 Oe (II) 416 Oe ($\perp$)	Present work ^[180]
	35 nm (30 μ m)	458 Oe (II) 428 Oe ($\perp$)	

Our coercivity values are less than those observed by Chen et al (1700-2100 Oe) which can be attributed to the fact that wire diameter in our case (35 and 200 nm) are greater than the diameter they have used (9-21 nm). Interestingly, we have observed that that the coercivity values were not much different when the applied magnetic field was parallel or perpendicular

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to wire axis. For 200 nm wire diameter $H_{c//}$ and $H_{c\perp}$ were found to be 444 Oe and 416 Oe, respectively, while for 35 nm diameter $H_{c//}$ and $H_{c\perp}$ were found to be 458 Oe and 428 Oe, respectively. This can be explained in terms of magnetization cross over as discussed in the next section.

4.3.2 Magnetization Crossover:

For wire diameters of 35 nm and 200 nm, not much difference was observed when the applied magnetic field was parallel or perpendicular to the wire axis [Fig 4.15, (a)-(d)] which can be explained if magnetocrystalline anisotropy, dipolar interactions and demagnetizing fields are considered. Bantu et al ^[179] developed a model to explain such behavior. They have studied two dimensional arrays of parallel Co wires where each wire is considered as a magnetic dipole. They considered an array formed by a square dipole mesh size 'd' with magnetic moments parallel to the axes of the wires. The total effective magnetic field ($H_{|| \text{ eff}}$) acting on each wire is,

$$H_{|| \text{ eff}} = 4.2 \frac{\mu}{d^3} + \frac{2k}{M_s} \quad (4.6)$$

where, μ ($= M_s V$) is the magnetic moment of the dipole, M_s is the saturation magnetization of the bulk material, V is its volume and k is the magnetocrystalline anisotropy of cobalt. The first and second terms in Eq. 4.6 are the dipolar interactions among the wires and the field associated with the magnetocrystalline anisotropy of cobalt, respectively. For h.c.p. cobalt at room temperature, $M_s = 1422 \times 10^3 \text{ A m}^{-1}$ and $k \approx 5 \times 10^5 \text{ J/m}^3$.

For the array with the magnetic moments aligned perpendicular to the axes of the wires, the total field on each wire can be given as,

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$$H_{\perp eff} = -2.1 \frac{\mu}{d^3} + 2\pi M_s \quad (4.7)$$

In Eq. 4.7, the first and second terms correspond to the dipolar interactions and demagnetizing field of each wire, respectively. As the positive terms in Eq. 4.6 and 4.7 indicate directions opposite to the magnetization vector, one can expect a cross over of magnetization with a change in volume of the wires. The condition of cross over of the magnetization is obtained by equating Eq. 4.6 and 4.7 which gives the following condition,

$$\left(\frac{V}{d^3} \right)_{critical} \approx 0.21 \quad (4.8)$$

For (V/d^3) values greater than 0.21, the easy axis of magnetization lies perpendicular to the wire axis while for values lower than 0.21, the easy axis will be parallel to the wire axis [Fig 4.16 (a) and (b)]. In our case (V/d^3) ratio of both the nanowire arrays (35 nm and 200 nm) was calculated to be 18.0 and 22.3 respectively; much higher than the critical value. Hence cross over of magnetization is expected, implying that the direction perpendicular to the wire axis is the easy direction of effective anisotropy. Thus the difference in the hysteresis loops of short wires is substantial while for long wires they superimpose.

The correlation of magnetic properties with wire diameter, length and crystal structures has been discussed in the literature ^[179, 181-184]. It has been suggested that as wire diameter decreases, a change in texture takes place and wires can grow parallel to the close packed planes. When the pore diameter is very small, wire growth is strongly confined in one direction by the pore walls, fast nucleation at the pore walls can result in textured growth with close packed planes parallel to the wire axis ^[166]. Low magnetostatic interactions within

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the patterned arrays prevent the data from switching and hence it is highly desirable for data storage devices. In next section, a quantitative estimation of magnetostatic interactions within both the arrays of nanowires (200 nm and 35 nm diameter) is presented.

Figure 4.16: Relative directions of magnetization and wire axis for (a) $V/d^3 \geq 0.21$ (b) $V/d^3 < 0.21$.

4.3.3 Magnetostatic Interaction in Nanowire Arrays:

In an array of dipoles of length of l and moment $m (= M_s V)$, the field created at distance x in the direction perpendicular to the dipole can be given as ^[185],

$$H_x = \frac{\mu}{\left(x^2 + \frac{l^2}{4}\right)^{3/2}} \quad (4.9)$$

The magnetostatic interaction in both 35 nm wires and 200 nm wires have been calculated using the expression given in Eq. 4.9. For 35 nm diameter Co nanowire, magnetic field created by a nanowire on adjacent nanowire was calculated to be 0.6 Oe. For 200 nm

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diameter wires, the magnetic field created by a nanowire in adjacent nanowire was calculated to be 4.2 Oe. These values are small in compared to their coercivity values, suggesting that switching will not occur in such nanowire arrays by stray magnetic field developed due to magnetostatic interaction.

4.4 Summary:

Elongated magnetic nanostructures in both, random orientation and periodic arrays have been synthesized and their morphology, structure and magnetic properties were investigated. Unusually high magnetic moment (151.3 Oe) was observed for the size selected cobalt nanoparticles with an average diameter of 4.3 nm synthesized by borohydride reduction of cobalt salt. An external magnetic field induced assembly technique was used to align the nanoparticles into nanowires. Coercivity of Co nanowires synthesized by magnetic field induced assembly showed enhanced coercivity compared to their nanoparticle counterpart due to shape anisotropy which opposes magnetization reversal. The coercivity value of the nanowires deviated from the theoretical predictions of fanning reversal mode due to thermal fluctuations. Chemical synthesis of Co nanowires of 200 nm and 35 nm diameter within the pores of AAO templates was performed. These nanowires exhibited (0002) texture with an interesting magnetization cross over behavior and small magnetostatic interactions.

It was demonstrated in this chapter that elongated nanostructures can be fabricated using chemical synthesis techniques, nanowires with an average diameter of 4.8 nm can be useful to increase storage density. The magnetization reversal behavior of these nanowires has been discussed. The coercivity values are in a range which is appropriate for data storage media. AAO template assisted assembly of nanowires shows that the nanowires can be assembled in a periodic large area network, as required for patterned magnetic media.

The next chapter presents work on synthesis of cobalt chains of spheres and chains of ellipsoids by thermal decomposition of cobalt oxalate nanorods. A morphological investigation on the rod to sphere fragmentation followed by their structural and magnetic properties are provided.

Chapter 5

Synthesis and Characterization of Chains of Co Nanoparticles

5.1 Introduction:

This chapter presents a synthesis technique to produce chains of cobalt nanoparticles; which is simpler than processes such as borohydride reduction^[22], decomposition of organometallic precursors^[23] or magnetic field induced assembly^[171]. The major advantage of this method is the absence of byproducts such as surfactants or boron residues. Thermal decomposition of cobalt oxalate nanorods prepared by the chemical reaction of cobalt acetate and oxalic acid led to the formation of chains of Co spheres. Microstructural observations show that these rods change to chains via an intermediate ellipsoidal shape. Structural observations reveal the presence of two distinct phases (ϵ -cobalt and α -cobalt), TEM studies suggest that low energy stacking faults were responsible for the phase transformation between the two cobalt allotropes. The magnetic properties and magnetization reversal processes of such elongated magnetic nanostructures is presented.

5.2 Synthesis and Characterization:

Fig 5.1 presents the SEM micrograph of the cobalt oxalate nanorods synthesized by the chemical reaction of cobalt acetate and oxalic acetate followed by annealing at 90⁰ C for 10 h. After annealing the sample at 90⁰ C, rod shaped precipitates with an average diameter (2 R₀) and average length (L) of 32 nm and 260 nm, respectively, were observed. Fig 5.2 shows

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a typical XRD pattern of the sample annealed at 90⁰C, showing the formation cobalt oxalate with two distinct amounts of water of crystallization, CoC₂O₄.4H₂O and CoC₂O₄.2H₂O. Cobalt oxalate is chosen as the precursor due to its low temperature of decomposition to Co. The d-metal oxalates can decompose to metals via two processes ^[186];

Figure 5.1: SEM micrograph of cobalt oxalate nanorods obtained by chemical reaction of cobalt acetate and oxalic acid followed by heat treatment at 90⁰ C for 10 h.

The strength of M-O and C-O bonds in the oxalate decides which mechanism of decomposition will occur. If the C–O bond is stronger, decomposition reaction follows Eq. 5.1, a metal and CO₂ is produced. When the M–O bond is stronger than C–O bond, decomposition reaction follows Eq. 5.2 metal oxide and carbon dioxide form. Previous

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studies^[186] have shown that the activation energy of CoC_2O_4 decomposition to Co is $198.3 \pm 2.9 \text{ kJ mol}^{-1}$.

The decomposition temperature from Co oxalate to Co was found in earlier studies to be 400°C ^[186], hence these cobalt oxalate nanorods were annealed at 400°C for 150 min and 180 min respectively. SEM micrographs of the samples annealed at 400°C at 150 min and 180 min are presented in Fig 5.3 [(a) and (b)]. Fig 5.3 (a) shows the ellipsoidal particles in the chains while Fig 5.3 (b) shows chains of spheres.

Figure 5.2: XRD pattern of cobalt oxalate nanorods obtained by chemical reaction of cobalt acetate and oxalic acid followed by heat treatment at 90°C for 10 h.

Figure 5.3: SEM micrograph of cobalt, (a) chains of ellipsoids obtained by annealing cobalt oxalate nanorods at 400⁰ C for 150 minutes and (b) cobalt chains of spheres obtained by annealing the cobalt oxalate nanorods at 400⁰ C for 180 minutes. A high resolution micrograph of cobalt chains of spheres is presented in the inset of Fig 5.3(b).

The instability of a cylindrical rod under the influence of capillarity or surface tension has been studied previously ^[187]. Chemical potential gradient induced by perturbations in the rod direction acts as a driving force for this process. According to Plateau's prediction, a liquid cylinder of radius R_0 is unstable to radial perturbations whose wavelength λ exceeds the circumference of the cylinder. The energy of the cylinder is decreased by a transformation of a cylinder into a row of spherical particles for a fixed volume. This work was extended by Rayleigh who performed linear stability analysis of periodic perturbations of nonviscous liquid jets ^[187]. This perturbation approach was extended to solids by Nichols and Mullins ^[187- 189].

Their analysis was based on the instability of an infinite cylindrical rod with initial

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unperturbed radius R_0 with isotropic surface energy, against a sinusoidal radial perturbation of the form ^[188],

$$r = R_0 + \delta \sin (2\pi/\lambda) z \quad (5.3)$$

where R_0 is initial radius of the rods (unperturbed), δ is amplitude of the perturbation, λ is wavelength of the perturbation and z is coordinate along the symmetry axis of the rod.

Their work showed that instability of the rods would occur for perturbation of wavelength greater than the rod circumference, i.e., $\lambda_{\min} = 2\pi R_0$. A specific wavelength of perturbation ($\lambda_{\max}$) provides the maximum growth rate of perturbation. The value of $\lambda_{\max}$ is dependent on the mass transport mechanism which is responsible for the decay process.

A schematic of the formation of chains of spheres from rods with increasing time is provided in Fig. 5.4. Nichols ^[189] has proposed two modes of fragmentation of the rods, ovulation and spheroidization, depending on the aspect ratio of the rod. He has predicted a critical length-to-diameter ratio ($L/2R_0$) of 7.2, below which only one spheroidal particle results (spheroidization) and above which two or more are formed (ovulation). Experimentally, an aspect ratio of the nanorods of 8.1 was observed in the present work hence the rods were fragmented in a row of spheres (ovulation), in agreement with Nichols prediction ^[189]. Fragmentation via ovulation has also been observed by Molares et al ^[187] for Cu nanorods and Karim et al ^[188] for Au nanorods.

Figure 5.4: Schematic of the formation of chains of spheres from rods with increasing time.

The Nichols and Mullins model ^[188] is based on isotropic surface energy and isolated cylindrical rods, they predicted $\lambda_{\max} = 8.89, 9.02$ and $12.96 R_0$ for surface diffusion, and internal-volume and external-volume diffusion, respectively. The average radius (R_0) of the cobalt oxalate rods was found to be 16 nm while the average radius of spherical particles in chains of spheres was found to be 22 nm. According to the Rayleigh criterion, $r = 1.89 R_0$ from which radius of the spherical particles should be 30 nm compared to the experimental value of 22 nm. The decreased diameter of cobalt particles in the chains of spheres is due to volume shrinkage of cobalt oxalate precursor during thermal decomposition. Cobalt oxalate undergoes ~ 30 percent of volume shrinkage during thermal decomposition to cobalt which suggest the radius of the spherical particle after fragmentation should be $(0.7)^{1/3} \times 30 \text{ nm} = 26.6 \text{ nm}$, close to our experimental value of 22 nm. Fragmentation of Au nanowires was also studied by Karim et al ^[188], average spacing and radius of spherical particles were found to be greater than theoretical predictions with standard deviation of 17-32 % and 8-10 %, respectively.

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respectively. This deviation was attributed to surface energy anisotropy, presence of a substrate and aperiodic perturbation.

Molares et al ^[187] have studied the fragmentation of Cu nanowires of 38 nm ($2 R_0$) diameter and 1.7 μm (L) length in which average spacing between spherical particles (λ_m) after fragmentation and radius of the particles (r) were found to be 165 ± 57 nm and 36.5 ± 4.5 nm respectively in excellent agreement with Nichols and Mullins model. The fragmentation of Co stripes into a chain of nanodroplets upon ion beam bombardment has been studied by Lian et al ^[14], λ_m and r were found to be consistent with the Nichols and Mullins model but no magnetic properties were reported.

The average spacing (λ_m) between the spheres in a chain was found to be 40 nm which is much smaller than the prediction of Nicholas and Mullins criterion for surface diffusion ($\lambda_m = 8.89 R_0$) according to which $\lambda_m \sim 142$ nm. This difference can be attributed to magnetic interactions between magnetic nanoparticles. The field of a magnetic dipole ($\vec{H}$) at a distance r away from the center of dipole is given as ^[3],

$$\vec{H} = \frac{1}{4\pi t^3} [3(m \cdot \hat{t})\hat{t} - \vec{m}] \quad (5.4)$$

Where, $\hat{t}$ is the unit vector of vector $\vec{t}$ and m ($= M_s V$) is the magnetic moment of the dipole. Here we consider that the row of spheres of 22 nm radius has formed according to Nicholas and Mullins criterion with $\lambda_m \sim 142$ nm. The field of a magnetic dipole on its nearest neighbor can be calculated (by Eq. 5.4) as 15.3 Oe, using magnetic moment (m) = 55.5 emu/g (from Table 5.1) and t ($= \lambda_m \sim 142$ nm), this field attracts the neighboring particles, hence the particles in the chain were in close contact. Recently, fragmentation of Cu ^[187], Au ^[188] and Co nanorods ^[14] to chain of spheres has been reported.

The XRD pattern of samples annealed at 400⁰C (Fig. 5.5) shows that two allotropes [ϵ -cobalt (h.c.p.) and α -cobalt (f.c.c.)] were formed. A TEM micrograph of stacking faults observed in cobalt nanoparticles is provided in the inset of Fig 5.5. The low stacking fault energy (25 mJ m⁻²) associated with cobalt facilitates the h.c.p.:f.c.c. phase transformation since h.c.p. and f.c.c. structures are different only in the stacking sequence of close packed atomic layers [ABCABCABC for f.c.c. and ABABAB for h.c.p.]^[166]. The absence of cobalt oxide peaks in the XRD pattern shows that the decomposition reaction follows Eq. 5.1^[186],

Figure 5.5: XRD pattern of the cobalt chains of spheres obtained by annealing the cobalt oxalate nanorods at 400⁰ C for 3 h. TEM micrograph of a typical Co particle is shown in the inset.

Magnetic property measurements show that the coercivity value of chains of ellipsoids (633.2 Oe) is higher than that of the coercivity value of chains of spheres (514.3 Oe) [Fig 5.6]. The squareness value for chains of ellipsoids (0.47) was also found to be slightly higher than the chains of spheres (0.44). Saturation magnetization of chains of spheres and chains of ellipsoids were 55.5 emu/g and 53.7 emu/g, respectively. Magnetic properties of chains of spheres and chains of ellipsoids are presented in Table 5.1.

Figure 5.6: Magnetization curves measured on chains of ellipsoids and chains of spheres synthesized by thermal decomposition of cobalt oxalate.

Table 5.1: Magnetic properties of chains of spheres and chains of ellipsoids.

Nanostructure	Saturation magnetization (M_s) (emu/g)	Coercivity (Oe)	Squareness (S_q)
Chains of spheres	55.5	514.3	0.44
Chains of ellipsoids	53.7	633.2	0.47

In chapter 4, a magnetization reversal mechanism for the cobalt chains of spheres was discussed. In the present case, particles in nanowires are usually prolate and not spherical; a modification in Jacobs and Bean's model can be made where the magnetostatic self-interaction energy of each particle is changed during the magnetization reversal. For chains of prolate ellipsoids, the total energy can be given as ^[61],

$$E_m = \left(\frac{\mu^2}{b^3} \right) m L_m (\cos 2\theta - 3 \cos^2 \theta) + \left(\frac{\mu^2}{b^3} \right) m M_m (1 - 3 \cos^2 \theta) + 2\pi m (N_{\perp} - N_{\parallel}) M_s \sin^2 \theta + m \mu H \cos \theta. \quad (5.6)$$

Here b is the distance between the centers of two ellipsoids of ellipsoid and m is the number of ellipsoids.

$N_{\perp}$ and $N_{\parallel}$ are the demagnetization factors of the ellipsoid perpendicular and parallel to the nanowire. The expression for coercivity can be obtained by minimizing the energy with respect to its angle parameter,

$$H_{c,m} = \left(\frac{\mu}{b^3} \right) (6M_m + 2L_m) + 4\pi (N_{\perp} - N_{\parallel}) M_s \quad (5.7)$$

Inserting the expression for the dipole moment,

$$\mu = \pi a^2 b M_s / 6 \quad (5.8)$$

The expression for coercivity can be written as,

$$\begin{aligned} H_{c,m} &= \frac{1}{\alpha^2} \pi (6M_m + 2L_m) M_s / 6 + 4\pi (N_{\perp} - N_{\parallel}) M_s \\ &= \frac{1}{\alpha^2} \pi (6M_{(n/\alpha)} + 2L_{(n/\alpha)}) M_s / 6 + 4\pi (N_{\perp} - N_{\parallel}) M_s \end{aligned} \quad (5.9)$$

where, α ($= b/a$) is the aspect ratio of ellipsoid and n is the aspect ratio of the wire.

For a prolate ellipsoid (Fig 5.7), the demagnetization factor along the symmetry axis $N_{\parallel}$ is given by,

$$N_{\parallel} = \frac{1}{\alpha^2 - 1} \left[\frac{\alpha}{\sqrt{\alpha^2 - 1}} \ln(\alpha + \sqrt{\alpha^2 - 1}) - 1 \right] \quad (5.10)$$

where α (c/a) is the aspect ratio of the ellipsoid.

Figure 5.7: Prolate ellipsoid

In general, the demagnetization factor along the symmetry axis ($N_{||}$) and the demagnetization factor along any axis perpendicular to the axis of symmetry ($N_{\perp}$) are related to each other by the following expression.

$$N_{||} + 2N_{\perp} = 1. \quad (5.11)$$

5.2.1: Numerical Calculations:

(a) For Co chains of spheres: The average number of particles (n) in the chains of spheres [Fig 5.3 (b)] was found to be 8 from which the value of $(6M_n + 2L_n)_{n=8}$ can be calculated as 2.4. Substituting this values of $(6M_n + 2L_n)$ and M_s [Table 5.1] in eq. 4.5, theoretical coercivity value $(H_c)_{\text{Theoretical}}$ of the chains of spheres was calculated as 620.3 Oe while the experimental coercivity $(H_c)_{\text{Experimental}}$ value was found to be 514.4 Oe (Table 5.1)

(b) For Co chains of ellipsoids: The average length of major (c_{average}) and minor axis (a_{average}) of ellipsoidal particles were found to be 95 nm and 72 nm, respectively [Fig 5.3 (a)], the aspect ratio (α) of the particles is 1.3. Average number of particles (m) in a chain is 8 while the aspect ratio of the nanowire (n) is 10.4, the value of $(6M_{n/\alpha} + 2L_{n/\alpha})$ is 2.4. Using Eq. 5.10 and 5.11, the values of $N_{||}$ and $N_{\perp}$ were calculated as 0.26 and 0.37, respectively. Substituting these calculated values of $(6M_{n/\alpha} + 2L_{n/\alpha})$, $N_{||}$ and $N_{\perp}$ and M_s from Table 5.1 in eq. 5.9, the theoretical coercivity value $(H_c)_{\text{Theoretical}}$ can be calculated as 1015.4 Oe while the experimental $(H_c)_{\text{Experimental}}$ coercivity value was found to be 633.2 Oe (Table 5.1).

The numerical calculations showed that the experimental coercivity value of cobalt chains of spheres deviated by ~17 % compared to the theoretical prediction of Jacobs and Bean model, this may be attributed to surface oxidation of the particles. The coercivity value of the chain

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of ellipsoids deviated by ~37 % compared to the modified form of Jacobs and Bean's model [15]. Compared to the theoretically calculated values for coercivity for parallel rotation or curling mechanism, the fanning mechanism is the closest match with the experiments, hence it is suggested that the magnetization reversal mechanism in these chains occurs by fanning mechanism. Synthesis of cobalt chains of spheres by magnetic field induced assembly has been previously reported. Niu et al [158] have reported the chains of ~13 μm diameter and coercivity was found to 389 Oe. Cheng et al [177] have reported the chains of cobalt nanospheres of 15 nm diameter with a coercivity value of 50 Oe. The coercivity value of chain of spheres presented in this work was found to be greater than compared to the coercivity values reported by Niu et al [158] and Cheng et al [177]. The coercivity value obtained in this work is also greater than that of nanobelts (410.6 Oe) [19].

5.3 Summary:

This chapter presents the synthesis and characterization of cobalt chains of nanoparticles (average radius 22 nm) by thermal decomposition of cobalt oxalate nanorods (average radius 16 nm) driven in part by Rayleigh instability effects [186, 188]. The shape transition from cobalt oxalate nanowires to cobalt chains of spheres via an ellipsoidal shape was in accordance with the ovulation process predicted by Nichols [189]. Structural properties reveal two phase crystal structure (h.c.p. + f.c.c.) of cobalt. Low energy stacking faults were found to be responsible for this phase transformation. The magnetic property of chains of ellipsoids and chains of spheres were determined, the coercivity of chains of ellipsoids was greater than that of chains of spheres. In order to investigate the magnetization reversal mechanism of these chains, the magnetic properties were compared with a modified form of the Jacobs and Bean's [15] model which suggests that magnetic reversal in these chains proceeds via the fanning mechanism [61].

The work presented in this chapter shows a morphological transition from magnetic nanowires to chains of spheres and chains of ellipsoids. This technique is a facile method to synthesize Co nanoparticles and nanochains. The change in magnetic properties was modeled by a modified form of the theory of Jacobs and Bean. The small size of these nanostructures makes them potentially useful to achieve high storage density. The magnetization reversal behavior of these nanochains was discussed. The coercivity values are broadly in the range required for patterned magnetic media.

The next chapter presents the major conclusions of this thesis.

Chapter 6

Conclusions and Future Work

This chapter presents the significant findings of this thesis and the scope of future work which could be made by utilizing the results obtained in this work.

6.1 Conclusions:

In the present work, directed self assembly of chemically synthesized magnetic nanostructures in curved and elongated shapes relevant to future high density data storage media was studied. Both these morphologies significantly affect the magnetization reversal process; hence shape can be used to alter coercivity. The nanostructures were synthesized by chemical methods because this method offers better scope for varying size, shape and surface modification compared to usual physical methods such as sputtering. The shapes studied in this work, e.g., bowl and wire, chain of spheres etc. are difficult to form by conventional physical techniques. Morphological investigation, surface and structural characterization and magnetic property evaluation was carried out. The experimental techniques used included SEM, TEM, XRD, VSM and XPS. The effect of shape of nanoelements on the magnetic properties such as magnetization, coercivity and squareness was evaluated. The following conclusions were reached from the study:

(1) Chemical synthesis of cobalt nanobowl arrays of 1 μm , 200 nm and 100 nm diameters directed by colloidal crystal templated assembly was carried out. Long range periodicity relevant to future patterned high density data storage media was observed. These cobalt nanobowl arrays were synthesized by borohydride reduction of cobalt salt within the

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interstitials of a close packed PS template. The chemistry of borohydride reduction leading to synthesis of cobalt nanoparticles was studied; interestingly, undesired byproducts could be removed by a novel annealing and washing sequence. The effect of annealing temperature and atmosphere was found to be important to obtain metallic cobalt. A two phase (h.c.p. and f.c.c.) microstructure with planar defects was observed. Shape effects on magnetic properties of these arrays were studied, it was observed that coercivity increases with decreasing bowl diameter, these values are also higher than the coercivity of their nanoparticle or thin film counterparts. High temperature annealing of cobalt nanobowl arrays led to the formation of nanowires.

(2) Cobalt ferrite nanobowl arrays of 1 μm diameter were synthesized by colloidal crystal templated assembly. In this case, an aqueous solution mixture of cobalt and iron salt was reduced within the interstitials of close packed PS template. Structural properties revealed a single phase cubic crystal structure. The effect of annealing on morphology, structural properties and magnetic behavior was studied. It was found that annealing results in improved crystallinity and saturation magnetization. The coercivity of nanobowl arrays was found to be higher than their nanoparticles counterpart again due to shape effects.

(3) Size selected Co nanoparticles with average diameter of 4.3 nm showed unusually high magnetic moment (151.3 emu/g). An external magnetic field induced assembly technique was used to align randomly dispersed Co nanoparticles into nanowires, the coercivity of the nanowires was found to be greater than their nanoparticle counterpart. Such an increase was attributed to the shape anisotropy of the wire morphology which opposes the magnetization reversal. The coercivity values deviated from the theoretical predictions of fanning reversal mode due to thermal fluctuations at small size range.

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(4) Chemical synthesis of periodic arrays Co nanowires of 200 nm and 35 nm diameter was directed by the pores of AAO templates. Structural properties showed (0002) texture as a result of the growth axis being perpendicular to the close packed planes. The coercivity of the wires were found to be similar when the magnetic field was applied parallel and perpendicular to the wires due to magnetization cross over. Small magnetostatic interactions were found for both sets of nanowire arrays.

(4) Cobalt chains of spheres and chains of ellipsoids were synthesized by thermal decomposition of cobalt oxalate nanorods. It was observed that the nanorods were decomposed to chains of spheres via intermediate ellipsoidal shape. This rod to chain of spheres fragmentation was partially driven by the Rayleigh instability effect. The kinetics of fragmentation was compared to the theoretical predictions of Rayleigh and Nichols and Mullins and reasonable agreement was found. Structural properties revealed a two phase microstructure (h.c.p. and f.c.c.). The coercivity of these chains was found to be in closest match with the fanning reversal mode.

6.2 Future Work:

This section presents the scope of future work which can be extended from this work. This work provides a platform to further research in the area of patterned nanomagnetic media for high density data storage devices. The chemical synthesis techniques used in this work are versatile in terms of materials selection and could be extended to a wide range of magnetic materials in future work.

(a) 3-D Arrays of magnetic nanobowls:

The synthesis of nanobowls arrays could be extended to a range of other sizes of PS spheres.

Scaling down to < 100 nm PS spheres may lead to novel magnetic properties due to surface effects. Magnetization reversal studies in curved nanostructures can be understood using magnetic force microscopy (MFM). Nanobowls with wall dimension close to exchange length of cobalt may lead to novel magnetic properties. Synthesis of nanobowls arrays can be extended for other materials also, FePt can show potential application for data storage point of view if the high coercivity L_{10} phase is achieved at comparatively lower temperature. In present work, it was found that temperature range around 600° C is not appropriate to maintain bowl like morphology. If an improvement in this technique is made in such a way that bowl-like morphology is maintained at higher temperatures, cobalt ferrite nanobowls can exhibit high coercivity in the range of few kOe.

(b) Nanowires:

The magnetic nanowires of radius smaller than those presented in this work can be employed to examine the size effects and magnetic properties. Mesoporous silica templates can also be used to synthesize nanowires of smaller diameters. The aspect ratio can be altered in order to investigate its effect on textured growth or magnetization cross over behavior. The nanowire synthesis with $(V/d^3 < 0.21)$ can be performed so that the absence of magnetization cross over. In case of very small pore sizes, supercritical fluid (SCF) inclusion technique can be used to fill the pores.

Magnetic field induced assembly work presented in this thesis suggests that magnetic particles can be arranged in the direction of magnetic field. Further, these particles can be arranged in various morphologies using magnetic field in various directions. One of the potential geometry is a ring-like structure useful in future MRAM (magnetic random access

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memory) devices. Nanorings are expected to show flux closure state which is capable to store data in clockwise and anti clockwise directions and hence no power is required to store data.

In this thesis, collective magnetic properties have been measured using VSM. Magnetic behavior of single nanobowls and their domain structure or magnetization reversal process can be studied using magnetic force microscopy (MFM) or Magnetic Optical Kerr Effect (MOKE). Low temperature magnetic measurements could be useful in studying the superparamagnetic behavior of nanoparticles. It would be advantageous in investigating the temperature dependence of magnetic properties such as magnetization and coercivity.

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Appendix A

The details of the instruments and software used for characterization and analysis in this work are provided in Table A.1.

Table A.1: Nanostructures and their characterization techniques.

Nanostructure	Characterization: Instrumentation	Software/Databases etc. used for analysis
Co nanobowl	SEM: JSM-6360 (JEOL) and JSM-5410 LV (JEOL) scanning electron microscope XRD: Shimadzu 6000 Lab X diffractometer (Cu K α radiation) VSM: Lakeshore 7404 vibrating sample magnetometer (Lakeshore Cryotronics)	Fourier Transform: CRISP. XRD database: Joint Committee on Powder Diffraction Standards (JCPDS) Rietveld Refinement: TOPAS R (2.1)
Co ferrite nanobowl	SEM: JSM-6340 F (JEOL) scanning electron microscope TEM: JEM-2010 (JEOL) transmission electron microscope XRD: Shimadzu 6000 Lab X (Cu K α radiation) VSM: Lakeshore 7404 vibrating sample magnetometer (Lakeshore Cryotronics)	XRD database: JCPDS
Co nanoparticles and nanowires	TEM: JEM-2010 (JEOL) scanning electron microscope XRD: Shimadzu 6000 Lab X (Cu K α radiation) VSM: Lakeshore 7404 vibrating sample magnetometer (Lakeshore Cryotronics). XPS: PHI 5600 XPS.	XRD database: JCPDS XPS database: NIST XPS database and Computer added surface analysis XPS (CASAXPS).
AAO template directed synthesis of nanowire arrays	SEM: JSM-6360 (JEOL) and JSM-6340 F (JEOL). XRD: Shimadzu 6000 Lab X diffractometer (Cu K α radiation) AFM: DI 31,002 atomic force microscope. VSM: Lakeshore 7404 vibrating sample magnetometer (Lakeshore Cryotronics).	XRD database: JCPDS
Co chain of spheres and chain of ellipsoids.	SEM: JSM-6340 F (JEOL) scanning electron microscope TEM: JEM-2010 (JEOL) scanning electron microscope XRD: Shimadzu 6000 Lab X (Cu K α radiation) VSM: Lakeshore 7404 vibrating sample magnetometer (Lakeshore Cryotronics).	XRD database: JCPDS

List of Publications

International Journals:

- (1) Srivastava, A.K., & Ramanujan, R. V. (2009). **Invited Book Chapter**. Self Assembly of Magnetic Nanomaterials, H.S. Nalwa (ed.), *Magnetic Nanostructures*, American Scientific Publishers. In Press.
- (2) Srivastava, A.K., Madhavi, S., White, T. J., & Ramanujan, R. V. (2007). Cobalt–ferrite nanobowl arrays: Curved magnetic nanostructures. *J. Mater. Res.*, 22, 1250-1254.
- (3) Srivastava, A. K., Singh, R. S., Sampson, K. E., Singh, V. P., & Ramanujan, R. V. (2007). Templated Assembly of Magnetic Cobalt Nanowire Arrays. *Metal. Mater. Trans. A*, 38, 717-724.
- (4) Srivastava, A. K., Madhavi, S., White, T. J., & Ramanujan, R. V. (2006). The processing and characterization of magnetic nanobowls. *Thin Solid Films* 505, 93-96.
- (5) Srivastava, A.K., Madhavi, S., White, T. J., & Ramanujan, R. V. (2005). Template assisted assembly of cobalt nanobowl arrays. *J. Mater. Chem.* 15, 4424-4428.

International Conferences:

- (1) Srivastava, A.K., & Ramanujan, R. V., Chemical Synthesis and Characterization of Cobalt based Curved Magnetic Nanostructure Arrays, *5th Intl. Conf. on Materials Processing for Properties and Performance*, vol. 5, K.A. Khor, R. V. Ramanujan, C. P. Ooi, J. H. Zhao, W Zhou and L. G. Yu (eds.), Singapore, p. 84-85, (2006).
- (2) Ramanujan, R. V., & Srivastava, A.K., The Synthesis and Characterization of Magnetic Nanowires Formed in Nanoporous Templates, *5th Intl. Conf. on Materials Processing for Properties and Performance*, vol. 5, K.A. Khor, R. V. Ramanujan, C. P. Ooi, J. H. Zhao, W Zhou and L. G. Yu (eds.), Singapore, p. 86-87, (2006).