CHAPTER – 1

INTRODUCTION
Nanoscience and Technology

In 1959, the physicist Richard Feynman, Nobel Prize winner for Physics in 1965, came up with the brilliant concept of the nano, when he said, “there is plenty of room at the bottom” during a conference of the American Physical Society [1]. The term nano was derived from the Greek word nanos which means “dwarf”, but nano is infinitely smaller than a dwarf. It designates as a billionth of meter i.e. $10^{-9}$ meter [2]. Thus the science of nanostructures is often defined as dealing with the objects on a size scale of 1–100 nm. The properties of nanoscale materials and bulk materials are different due to the change in number of surface atoms, surface energy and hence their reactivity etc.

“Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale”. Bulk materials (the “big” pieces of materials we see around us) possess continuous (macroscopic) physical properties [3] the same applies to micron-sized material (e.g., a grain of sand). When particles are assumed nano-scale dimension, the principles of classical physics are no longer capable of describing their behavior (movement, energy).

Nanostructures may be compared [4] to a human hair which is ~50,000 nm thick whereas the diameters of nanostructures are ~0.3 nm for a water molecule, 1.2 nm for single-walled carbon nanotubes, and 20 nm for a small transistor. DNA molecules are 2.5 nm wide, proteins about 10 nm, and an ATP base biochemical motor about 10 nm. In addition, living systems work at the nanoscale. The application of nanoscience in practical devices is called nanotechnology. Nanotechnology is based on the manipulation, control and integration of atoms and molecules to form the materials, structures, components, devices and systems at the nanoscale. Nanotechnology is the application of Nanoscience especially to industrial and commercial objectives. All the industrial sectors rely on
materials and devices made of atoms and molecules. Thus, in principle all the materials can be improved with nanomaterials and all industries can be benefited from nanotechnology. In reality, as with any new technology, the “cost vs. added benefit” relationship will determine industrial sectors that will mostly benefit from nanotechnologies [5].

1.2 Properties of Nanomaterial

1.2.1 General Property of Nanomaterial

(A) Density of States

![Density of States](image)

Fig. 1.2.1(A): Quantization of density of states against energy values for bulk, 3D, 2D, 1D and 0D semiconductor.

The density of states is defined as the number of energy states present in the unit energy interval per unit volume. Due to the quantization of energy levels, the relationship between density of states and energy values are also dramatically modified for the low dimension semiconductors, as shown in the Fig.1.2.1A.

In the case of three-dimensional confined quantum dot, the energy states are determined in a few sharp discrete energy levels. The density of states of three dimensional electron gases (bulk semiconductor) is proportional to $E^{1/2}$. The density of states for the two dimensional structure is constant; it does not depend on the energy due to free motion of electrons. The density of states for a quantum wire can be shown to have inverse square root energy dependence ($E^{-1/2}$). The density of states of quantum dot is a delta function.
which is represented as \( \delta [E - E (n_x, n_y, n_z)] \), where \( E_{nx}, E_{ny}, \) and \( E_{nz} \) are the quantized energy in the confined \( x, y \) and \( z \) directions.

(B) Surface to Volume Ratio

![Graph showing surface/volume ratio as a function of particle size](image)

Fig. 1.2.2(B): Surface/volume ratio as a function of the particle size. (Ref. 6)

The two key factors the size and surface characteristics of nanoparticles (NPs) are controlling the properties of nanomaterials. For the spherical particles, surface to the volume ratio are inversely proportional to its radius \( R \), \( (S/V) \sim 3/R \). These two factors are interrelated when \( S/V \) ratio increases as the size decreases.

The surface atoms are chemically more active as compared to the bulk atoms because they usually have fewer adjacent coordinate atoms and unsaturated sites or more dangling bonds and surface spins. The imperfection and defects on the surface of particles also induce additional electronic states in the band gap, which act as electron or hole trap centers [6]. This empirical law gives proportion of surface atoms of 100\% for a size of 1\( \text{nm} \). Such a dramatic increase in the ratio of surface atoms to the interior atoms in nanomaterials leads to great changes in the physical and chemical properties of materials.

1.2.2 Magnetic Property

(A) Spin Ordering

Magnetic NPs show remarkable new phenomena such as high field irreversibility, high saturation field, superparamagnetism, extra anisotropy contributions, or shifted loops
after field cooling. The electronic band structure of material in the nanometer region is strongly affected by quantum confinement and high surface/volume ratio. The magnetic moment of a nanoparticle which results from both the spin moments and the orbital moments are closely related to its electronic structure. Size-dependent magnetic properties of individual NPs as well as the coupling between the NPs have been the main focus of physical property investigation of magnetic NPs. Two key issues dominate the magnetic properties of NPs ‘finite-size effects’ and ‘surface effects’ which give rise to various special features.

(i) Finite Size Effect

Magnetic properties are based on the magnetic domain structure of the magnetic materials. When the size of a magnetic material is reduced below from a critical value $2A^{1/2}/M_S$ ($A=$exchange constant, $M_S=$moment per unit volume), it becomes a single domain, and for typical material parameter is 10-100 nm. Single-domain particles can be described by assuming that all the atomic moments are rigidly aligned as a single ‘giant’ spin as shown in the Fig. 1.2.2(i). According to the magnetic domain theory, the critical size of the single domain is affected by several factors including the value of the magnetic saturation, the strength of the crystal anisotropy and exchange forces, surface or domain-wall energy, and shape of particles [7]. The finite size can effect on structural and magnetic order in NPs. Bond lengths at metal surfaces tend to contract at free surfaces, so the average lattice parameter of NPs are reduced. This increases the overlap between atomic orbitals and reduces the moment per atom, tending to mitigate the effect of the reduced coordination on the moment. The theoretical study on Fe, Co, and Ni free surfaces shows that the magnetic moment increases upto few atomic surfaces [8]. In many other studies of
supported Fe, Ni, Co particles, reduced moments were observed, but it is often difficult to distinguish an intrinsic size effect from chemical reaction or inter diffusion with matrix [9].

![Coercivity vs Nanoparticles radius graph]

**Fig. 1.2.2 (i)** Schematic illustration of the coercivity-size relations of small particles (ref.7)

(ii) Surface Effect

![Surface and core-spin alignment diagrams]

**Fig 1.2.2(ii)(a)** The surface and core-spin alignment of a single NP in a magnetic field. **(b)** Surface and Core-Spin configuration in the 3D FCC NP artificial ferromagnet, (ref 25).

As the surface/volume ratio increases on decreasing particle size, a large percentage of all the atoms in a nanoparticle are surface atoms. For example, face-centered cubic (FCC) cobalt with a diameter of around 1.6 nm, about 60% of the total number of spins is surface spins [10]. Owing to these large surface atoms the surface spins make an important contribution to the magnetization as shown in the Fig. 1.2.2(ii). This local breaking of the
symmetry might lead to changes in the band structure, lattice constant and atom coordination. Under these conditions, some surface or interface related effects take place, such as surface anisotropy, under certain conditions and core–surface exchange anisotropy can occur.

Surface effects can lead to a decrease of the magnetization of small particles, for instance oxide NPs, with respect to the bulk value. This reduction has been associated with different mechanisms, such as the existence of a magnetically dead layer on the particle’s surface, the existence of canted spins, or the existence of a spin-glass-like behavior of the surface spins [11]. Spin canting is a phenomenon through which spins are tilted by a small angle about their axis rather than being exactly co-parallel. A spin glass is a disordered magnet with frustrated interaction, augmented by stochastic position of spins. On the other hand, for small metallic NPs, for example cobalt, an enhancement of the magnetic moment with decreasing size was reported as well [12].

Another surface-driven effect is the enhancement of the magnetic anisotropy, $K_{\text{eff}}$, with decreasing particle size [13]. In magnetic anisotropy, magnetic moments (spins) are aligned in easy axis. This anisotropy value can exceed the value obtained from the crystalline and shape anisotropy is assumed to originate from the surface anisotropy. In a very simple approximation, the anisotropy energy of a spherical particle with diameter $D$, surface area $S$, and volume $V$, may be described by one contribution from the bulk and another from the surface, given by $K_{\text{eff}} = K_V + \left(\frac{6}{D}\right)K_S$, where $K_V$ and $K_S$ are the bulk and surface anisotropy energy constants respectively.

(B) Spin Waves

At the low energy collective excitations of the magnetic moments create spin waves. In bulk materials, this leads, to a decrease of the magnetization with temperature
according to Bloch’s law \( M(T) = M_0 (1-BT^b) \), where \( b=3/2 \). In magnetic NPs, the spin wave spectrum can become quantized and known as magnons due to the finite particle size. For particles on the order of a few nanometers or a few tens of nanometers, direct evidences of spin wave quantization are still lacking due to contribution of superparamagnetism to the temperature dependence and by the effect of deferent matrices for the particles.

The spin wave spectrum of NPs in principle can be measured directly by inelastic neutron scattering. However, the temperature dependence of the saturation magnetization on chemically synthesized core–shell [Mg]Fe, and [MgF2]Fe particles, show a strong deviation from Bloch’s law when particle diameter is below 15 nm [14]. This indicates that quantization effects could be pronounced when particle sizes are below to 10 nm.

(C) Thermal Activation

The magnetic anisotropy energy per particle which is responsible for holding the magnetic moments along a certain direction can be expressed as follows: \( E(\theta) = K_{\text{eff}} V \sin^2 \theta \), where \( V \) is the particle volume, \( K_{\text{eff}} \) anisotropy constant and \( \theta \) is the angle between the magnetization and the easy axis. The energy barrier \( K_{\text{eff}} V \) separates the two energetically equivalent easy directions of magnetization. With decreasing particle size, the thermal energy \( K_B T \), exceeds the energy barrier \( K_{\text{eff}} V \) and the magnetization is easily flipped. For \( K_B T > K_{\text{eff}} V \) the system behaves like a paramagnet, instead of atomic magnetic moments, now there is a giant (super) moment inside each particle named as superparamagnetic. Such a system has no hysteresis and the data of different temperatures superimpose onto a universal curve of \( M \) versus \( H/T \). The relaxation time of the moment of a particle \( t \) is given
by the Néel-Brown expression [15] where $K_B$ is the Boltzmann’s constant and $t \approx 10^{-9}$ s.

$$\tau = \tau_0 \exp \left( \frac{K_{\text{eff}} V}{K_B T} \right)$$  \hspace{1cm} (1)

If the particle magnetic moment reverses at shorter times than the experimental time scales, the system is in a superparamagnetic state, if not, it is called blocked state. The temperature which separates these two regimes are called blocking temperature $T_B$, can be calculated by considering the time window of the measurement. The blocking temperature depends on the effective anisotropy constant, the size of the particles, the applied magnetic field and the experimental measuring time.

### 1.2.3 Optical Property

The most prominent property of semiconductor nanocrystals is the massive changes in electronic structure as a function of size. As the size decreases, the electronic excitations shift into higher energy and the oscillator strength is concentrated into just a few transitions [6]. When the size of nanocrystals is smaller than the de Broglie wavelength, electrons and holes are spatially confined and electric dipoles are formed.

In this way discrete electronic energy level would be formed in all the materials. Similar to a particle in a box, energy separation between adjacent levels increases with decreasing dimensions [16]. These changes arise through systematic transformations in the density of electronic energy levels as the function of the size, result in strong variations in the optical and electrical properties with size.

### 1.2.4 Thermal Property

It is well known that melting temperatures of nanocrystals with free surfaces or deposited on inert substrates, including metallic [17], organic [18], inert gas [19] and semiconductor [20] crystals, drop as their sizes decrease due to huge fraction of surface
atoms in the total amount of atoms. The melting point depression of the crystals is roughly proportional to the reciprocal of their radius $r$ written as $T_r/T_0=1−C/r$. where $T_r$ and $T_0$ are the melting points of the nanocrystals and the corresponding bulk crystals and $C$ denotes a material constant. As the dimension goes down to nanoscale, the size of NPs is comparable to the wavelength and hence the mean free path of the phonons. So that the phonon transport within the material will be changed significantly due to phonon confinement and quantization of phonon transport resulting in modified thermal properties.

1.2.5 Electrical Conductivity

When the critical dimension of thin films and nanowires are smaller than the electron mean free path, the motion of electrons will be interrupted through collision with the surface. The collision takes place due to thermal fluctuation, impurity, lattice defects, grain boundary and inelastic surface scattering of electrons. Elastic surface scattering does not affect the conductivity while inelastic scattering decreases the conductivity. The surface impurity and roughness favor inelastic scattering. An increased surface scattering would result in reduced electron mobility and, thus, an increased electrical resistivity [21-22].

On the other hand, on decreasing particle size, band gap increases which affects the electrical conductivity. Some metal nanowires may undergo a transition to become semiconducting as their diameters are reduced below certain values, and semiconductor nanowires may become insulators [23].

1.3 Literature Survey

The aim of literature survey to summarize research work which has been attracted much attention over the current and last decades. This literature survey is based on synthesis and characterization of magnetic nanomaterials with special interest on Fe, Co, and Mn oxide NPs. Cai et al. [24] have synthesized FeO phase of iron oxide using laser
ablation in liquid and investigated size dependent optical properties. They have varied size of iron oxide NPs in PVA matrix and observed that optical absorption red shifted as particle size decreases which were due to lattice defects.

Lierop et al [25] have studied the system of crystalline and non crystalline iron oxide NPs and predicted useful information. The uncrystalized system exhibits a distinct frequency dependence on the blocking temperature $T_B$, and the crystal exhibited no observable blocking behavior with an essentially frequency independent peak. At the lower temperature magnetization decreases due to the quenching signature of dynamical freezing. $M_S(T)$ of uncrystalized NPs decreases like exponential at the very low temperature (0-15 K) while $M_S(T)$ of crystalline NPs of iron oxide gradually increases in the range of (0-10 K). This suggests that crystal’s magnetization behaves antiferromagnet at low temperature.

The individual iron-oxide NPs are especially sensitive to Fe vacancies distributed throughout the surface which provide a ‘‘throttled’’ single-domain state [26] with surface moments that are canted in a random fashion like a spin glass [27-28]. The surface spins reveal themselves in high magnetic field in monodispers system but at the low field it masks the inter particle magnetism (core spins). The crystal does not become superparamagnetic above 400 K this indicates that NPs-based dipolar ferromagnet preserves the low (nonzero) coercivity at all the temperatures where dipolar magnetism dominates. On increasing temperature 20-300 K the gradual increase in coercivity of crystal indicates fractional increase of surface spin.

In the case of noncrystalline ferromagnet, coercivity decreases on increase of temperature, due to magnetic anisotropy diminishing. Thus surface spins of NPs behave like low temperature resim for crystal and noncrystallized systems. The $M$ - $H$ loop does not depend on the temperature for the crystalline or noncrystalline systems; this may be
due to the thermal fluctuation of particle magnetization and interparticle interactions or increases in magnetic anisotropy. Berkowitz and co-workers [29] pointed out that reduction of the saturation magnetization $M_S$ is caused by competing antiferromagnetic exchange interactions at the surface.

Polarized neutron scattering and Mössbauer spectroscopy confirm the reduction in saturation magnetization, due to surface spin disorder in magnetic NPs [29-31]. Monty et al [28] have reported that the origin of ‘spin-glass’ like phase at the surface may be due to the existence of broken bounds and the translational symmetry breaking of the lattice. These effects generate randomness in the exchange interactions that extends to some atomic layers from the surface. The spin-glass phase remains up to the highest field used, and at that point ferromagnetic core and the spin-glass surface layer are well defined. Relaxation experiments and strong exchange anisotropy indicate existence of a FM core surrounded by a spin-glass surface layer.

UV- visible absorption spectroscopy is an important technique to characterize absorption, electronic and band structure of transition metal oxide NPs. Many authors have studied the UV-Visible absorption spectrum of iron oxide NPs. Minati et al. [33] have reported the optical band gap of maghemite 2.03 eV. Hematite $\alpha$-Fe$_2$O$_3$ possesses a band gap (2.2 eV) that lies in the visible range, and has a relatively high refractive index. Kuhaili et al. [33] have reported values of the indirect band gap in the range 1.38–2.09 eV and direct band gap in the range 1.95–2.35 eV of hematite. The energy band gap 2.2 eV of $\alpha$-Fe$_2$O$_3$ which arises from d – d transitions that are spin-allowed due to magnetic coupling between Fe atoms. A theoretical model reveals the absorption band gap 3.2 eV reported by Marusak et al [34]. Zhou et al. [35] have recorded absorption spectra of Fe$_3$O$_4$/Au NPs in UV- visible range and studied the SERS. Sahar et al. [36] have reported optical band gap
of Fe₃O₄ NPs embedded in glassy phases in the range of 2-2.5 eV. The study of optical property of iron oxide NPs suggest that, optical property of iron oxide depends on it’s different phases and it behaves like semiconductor with optical band gap in the range of 1.9- 2.5 eV depending on synthesis method and size of NPs.

FT-IR spectra of iron oxide reveal peaks at 694, 555 and 471 cm⁻¹ of Fe₂O₃ correspond to the metal-oxygen vibrational modes of the spinel compound. A sample containing an interface between a ferromagnet (FM) and an antiferromagnet (AFM) when cooled in a magnetic field may exhibit an additional unidirectional anisotropy due to magnetic coupling at the interfaces. This effect, called exchange biasing (EB), it was first discovered by C. P. Bean in oxidized Co NPs [37]. Bawendi et al. [38] have reported that thin (1.0 nm) CoO shell exhibits no exchange biasing and a partially oxidized thicker CoO shell (3.2) nm shows exchange biased and the sample fully oxidized to CoO loses exchange biasing. Enhancement of the thermal stability of the orientation of the magnetic moment is due to exchange biasing in the partially oxidized CoO.

Low-temperature paramagnetic responses in the partially and fully oxidized samples are due to defects in the CoO shell. Sundaresan et al. [39] have reported that the unpaired electron spins responsible for ferromagnetism in the NPs have their origin in the oxygen vacancies, especially on the surfaces of the oxide NPs. One may expect that electrons trapped in oxygen vacancies are polarized to give room-temperature ferromagnetism. Fittipaldi et al [40] have studied the quantum effect in magnetic NPs and reported that the energy gap between the first excited and the ground state are expected to decrease, as the number of magnetic ions increased. Bgdker et al [41] have studied surface effects in metallic iron NPs and concluded that Metallic iron particles with diameter down to about 2 nm have properties similar to bulk α-Fe.
The magnetic anisotropy energy constant increases with decreasing particle size, presumably because of the influence of surface effects. Chemisorptions of oxygen results in formation of a surface layer, which is ferromagnetically coupled to the core of the particles, which have a disordered spin structure [42]. The ferromagnetic and antiferromagnetic system of Co and CoO has shown magnetic exchange coupling induced at the interface between ferromagnetic and antiferromagnetic systems. This can provide an extra source of anisotropy and leading to magnetization stability. The coupling of FM particles with an AFM matrix can be a source of a large effective anisotropy, leading to a considerable increase of the NPs blocking temperature.

FM-AFM exchange coupling may be understood by assuming that the FM moments of the cobalt particles create an exchange field, $\mu_0 H_{ext}$, acting on the interface AFM moments of the CoO matrix. CoO is a collinear antiferromagnet. At a compensated interface and the number of AFM moments from each sublattice is the same, the resulting magnetization is zero and thus the coupling vanishes to first order. To second order, the exchange field induces a canting of the AFM moments, and a FM component is induced along the FM cobalt moments.

The coupling energy is $E = -1/2 \chi_{AF} \mu_0 H_{ext}^2$ where $\chi_{ext}$ the interface AFM susceptibility. The magnetic coupling of FM NPs with an AFM matrix is a source of a large effective additional anisotropy. This leads to a marked improvement in the thermal stability of the moments of the FM NPs [43]. Tegus et al. [44] have studied the magnetic refrigeration techniques based on the magnetocaloric effect (MCE) have recently been demonstrated as a promising alternative to conventional vapour-cycle refrigeration.
UV-Visible absorption spectra of cobalt oxide NPs have been studied for long time. Zhang et al. [45] have reported band gap of Co$_3$O$_4$ NPs in the range of 1.52 and 2.01 eV, Gupta et al. [46] have shown that Co$_3$O$_4$ band gap reduces from 1.67 to 1.52 eV on annealing at 800$^\circ$C. Patil et al. [47] have shown that there are two energy levels of the direct allowed transition at 2.0 and 1.3 eV in the Co$_3$O$_4$ thin films. The optical band gap of Co$_3$O$_4$ reported 0.8, 1.0, 1.3, and 2.1 eV, which are assigned as charge transfers from Co$^{+2}(\pi^*e)$ to Co$^{+2}(\pi^*t_2)$, from Co$^{+3}(\pi^2t_2)$ to Co$^{+2}(\sigma^*t_2)$, and from O$^-2(\pi^*\Gamma)$ to Co$^{+2}(\sigma^*t_2)$, respectively [48-49].

Farhadi et al. [50] have reported band gap of spinal Co$_3$O$_4$ NPs 2.20 and 3.55 eV. Multiple band gaps 2.06 and 1.44 eV of cobalt oxide nanocrystals of size 10–15 nm, suggested that the higher band gap (2.28 eV) should be associated with the O$^{-}\text{II}\rightarrow$Co$^{\text{II}}$ charge transfer process (basic optical band gap energy or valence to conduction band excitation). The presence of Co$^{(\text{III})}$ centers in Co$_3$O$_4$ gives rise to a sub-bandgap located inside the energy gap. Hence the 1.57 eV band gap can be related to the O$^{-}\text{II}\rightarrow$Co$^{\text{III}}$ charge transfer (with Co$^{\text{III}}$ located below the conduction band). Raman spectra of cobalt oxide NPs show that A$_{1g}$, E$_g$ and the three F$_{2g}$ modes are Raman active. From the five F$_{1u}$ modes four are infrared active and one is an acoustic mode. The remaining F$_{1g}$, 2 A$_{2u}$, 2 E$_u$ and 2 F$_{2u}$ modes are inactive. Two distinguishable Raman peaks at 463 and 527 cm$^{-1}$ which can be assigned to the Raman active modes of Co$_3$O$_4$ [51].

Gu et al [52] have studied the optical absorption spectra that indicate the direct band gap of Co$_3$O$_4$ varied from 3.11 and 1.62 to 3.29–3.98 eV after introducing Li ion. Raman spectrum of the Co$_3$O$_4$ nanocrystals are prepared after Li addition. Four peaks at 482, 521, 618, and 690 cm$^{-1}$ can be observed, which correspond, to the E$_g$, F$^{1}_{2g}$, F$^{2}_{2g}$, and A$_{1g}$ modes of crystalline Co$_3$O$_4$ respectively. Liang et al. [53] have reported the synthesis
of tetragonal Mn$_3$O$_4$ phase and show a size in the range of 7.1-9.2 nm. Park et al. [54] have reported that MnO and Mn$_3$O$_4$ single crystal nanowires can be excellent ferromagnetic nanomaterials below room temperature. The temperature-dependent magnetization and magnetic hysteresis curves suggest the Curie temperature of 12 and 43 K for the MnO and Mn$_3$O$_4$ nanowires, respectively. Weak ferromagnetism up to $T_C$ 250 K and a spin-glass-like behavior at temperature below $T_{SG}$ 30 K in nanoscale MnO particles are observed. $T_{SG}$ is considerably lower and $T_C$ is much higher than the Néel temperature $T_N=122$ K of bulk MnO. The effective diameter of magnetic NPs can be calculated using following equation derived by Langevin function [55-56].

$$d_{max} = \left[\frac{18K T(dM/dH)_{H=0}}{\Pi \rho M_S^2}\right]^{1/3}$$

d$_{max}$ determines the least upper bound of particle size from largest magnetization at initial applied external magnetic field. Where $k$ is the Boltzmann constant, $T$ is temperature, $dM/dH$ is the slope of the initial (virgin) magnetization curve, $\rho$ is the density, and $M_S$ is the saturation magnetization. Optical absorption band gap of MnO has been studied for long time using various techniques. The highest occupied states are formed by the O 2$p$ and Mn 3$d$ states.

Many authors have reported band gap of MnO in the range of 3.6 and 4.3 eV [57-59]. The crystal-field splitting DCF between $t_{2g}$ and $e_g$ states have been calculated from experimental results to be between 0.7 and 1.25 eV and exchange splitting between $t_{2g}$ or $e_g$ states of different spin directions are considerably larger than 4.5 eV [60]. Franchini et al. [61] have studied MnO system using density functional theory approach and found that MnO behaves like intermediate Mott Hubbard/charge-transfer compounds with electronic band gap of 4.02 eV.
Magnetic NPs are of great interest for researchers from a wide range of disciplines, including magnetic fluids [62] catalysis [63-64] biotechnology/biomedicine [65] magnetic resonance imaging [66-67] data storage [68] and environmental remediation [69-70]. Exchange biased nanostructures have found applications in many fields, such as permanent magnets, recording media, and spintronics. Magnetic NPs with good stability will be of great interest in catalysis and in biotechnology/biomedicine applications. Such magnetic NPs can be very useful to assist an effective separation of catalysts, nuclear waste, biochemical products, and cells [71-73]. A very promising application of magnetic NPs is in drug delivery as drug carriers is called “magnetic drug delivery” proposed in the 1970s by Widder et al [74].

1.4 Brief Summary

Present thesis deals with the synthesis of iron, cobalt, manganese and Li doped ZnO diluted magnetic semiconductor nanomaterials. PLA and co-precipitation methods have been employed for the synthesis of nanomaterials. Various techniques such as XRD, UV-visible, PL, Raman, FTIR, VSM, TEM\SEM, have been employed to explore the optical, structural and magnetic properties. The chapter and section wise summary of the thesis is given as following.

Chapter 2, deals with the synthesis methodology and characterization techniques, it has two sections. Section 2.1 Synthesis methodology includes a brief introduction of PLA and co-precipitation methods. Section 2.2 Characterization Techniques introduces Nd: YAG laser, argon ion laser, PMT, and monochromator. This section consist characterization techniques which include XRD, UV-Visible, PL, Raman, FT-IR, VSM, TEM\SEM and thermal transport property.
Chapter 3, entitled “PLA of iron in aqueous media” describes synthesis of iron NPs using PLA in aqueous media and contains four sections. Section-3.1 deals with synthesis of FeO NPs in DD water and study of optical magnetic and thermal transport properties. Section-3.2 contains synthesis of iron NPs in CTAB liquid media and study of mix phase of FeO (OH) \ Fe₂O₃ NPs. Section-3.3 deals with synthesis of Fe₃O₄ NPs in SDS liquid media and study of optical and magnetic properties. Section-3.4 deals with laser ablation of bulk powder of Fe₂O₃ in different liquid media and study of optical and magnetic properties.

Chapter 4 deals with synthesis of cobalt nanomaterials using PLA in aqueous media. In this chapter, we have studied optical and magnetic properties of cobalt nanomaterials and contain three sections. Section 4.1 contains synthesis of Co₃O₄\Co NPs in DDW and study of optical magnetic and thermal transport properties. Section 4.2 deals with synthesis of cobalt nanomaterials in CTAB liquid media while Section 4.3 deals with synthesis of cobalt in SDS liquid media and study their optical and magnetic properties.

Chapter 5 includes synthesis of manganese oxide \ hydroxide NPs in aqueous media using PLA and contains three sections. Section 5.1 deals with synthesis of MnO NPs in DD water and the growth mechanism of different nanostructures have been given in details. Section 5.2 includes with the synthesis of manganese oxide NPs in CTAB liquid media. In this section optical and magnetic properties have been investigated and study show that manganese oxide shows antiferromagnetic character. Sections 5.3 deals with synthesis of manganese NPs in SDS liquid media and optical and magnetic properties have been investigated. Current voltage characteristics have been also investigated of MnO (OH) NPs which is final product.
Chapter 6 includes the biological application of as synthesized magnetic NPs and contains three sections. In this chapter we have shown that toxicity of Iron and cobalt NPs depend on their concentration. Here it is shown that the smaller NPs have more effect than larger particles and cobalt oxide is more effective than pure cobalt NPs toward chromosome distortion. Iron NPs can produce chromosomal abnormality in Sesbania pea it may be due DNA breakage induce mutation effect.

Section 6.1 includes study of morphological effect of iron oxide NPs on Sesbania cannabina seed. Section 6.2 deals with toxic and mutation effect of Co$_3$O$_4$\textsuperscript{4}Co NPs on Sesbania cannabina seed. Section 6.3 deals with bio-hydrogen evaluation from Rhodobacter spheroid and E. coli bacteria using iron sulfate NPs.

Chapter 7 deals with synthesis of Li doped ZnO NPs using co-precipitation method and study of optical and magnetic properties. In this study we have shown that optical band gap of ZnO can be tuned using doping concentration of Li ions. It is also shown that ferromagnetism can be induced by doping of Li, although pure ZnO diamagnetic. Chapter 8 includes conclusion and future scope of the thesis.
Chapter-1

Introduction

Bibliography


