Chapter-1

Introduction of Nanotechnology

1.1 Introduction

The ideas and concepts behind nanotechnology started with a talk entitled “There’s Plenty of Room at the Bottom” by Physics Nobel laureate Richard Feynman in an American Physical Society meeting at the California Institute of Technology on 29th December 1959, long before the term nanotechnology was used. In his talk, Feynman described a process in which scientist would be able to manipulate and control individual atoms and molecules [1]. Over a decade later, in 1974, Norio Taniguchi introduced the term ‘nanotechnology’ to represent extra-high precision and ultra-fine dimension and also predicted improvements in integrated circuits, optoelectronic, mechanical devices and computer memory devices [2]. This is the so-called ‘top-down approach’ of carving small things from large structures. Inspired by Feynman's concepts, K. Eric Drexler used the term ‘nanotechnology’ in his book ‘Engines of Creation: The Coming Era of nanotechnology’ published in 1986, which proposed the idea of a nanoscale and discussed the future of nanotechnology, particularly the creation of larger objects from their atomic and molecular components, so called ‘bottom-up approach’ [3]. In 1981, Binnig and Rohrer invented the scanning tunneling microscope. The first technical paper on molecular engineering with atomic precision was published in 1981, while the Bucky ball was discovered in 1985. Fullerene is a molecule that is made up of carbon, in the form of a hollow sphere, ellipsoid or tube. It was discovered by Kroto, Smalley and Curl in 1985. In 1989, scientists at the International Business Machines (IBM) Research
Center, San Jose, California, spelled out the company's logo using 35 xenon atoms. By doing so, they further demonstrated how nanoparticles can be manipulated. Many scientific and technological advances recently made depend on the properties of materials at very small scale, such technological advances are known as ‘nanotechnology’ the prefix ‘nano’ being derived from the Greek word ‘nano’ which means dwarf. One nanometer (nm) is equal to one-billionth of a meter, or about the width of six carbon atoms or ten water molecules.

Mihail (Mike) Roco of the U.S. National Nanotechnology Initiative (NNI) has described four generations of nanotechnology development. The 1st generation of nanostructures would be aerosols and polymers, ceramics. Generation 2nd incorporates bio-active and physical-chemical active structures, such as drugs and transistors, amplifiers, actuators. The 3rd generation focused on robotics and new hierarchical architectures on the nano-level. We are currently focusing on 4th generation of nanotechnology; this generation focuses on molecular level nano-devices, this type of technology is said to be made functional by 2015-2020 and incorporates technology from the other three generations. Nanotechnology is the creation and exploitation of nanomaterials with structural features in between those of atoms and their bulk materials. In other words, nanotechnology is a design and applications of nano scale materials with their fundamentally new properties and functions, when the dimension of materials is in nanoscale regime the properties of the materials are significantly different from those of atoms as well as those of bulk materials [4]. The development and practical application of nanostructures and devices depends on nanometer size. A dimension of below 100 nm is important in nanotechnology, because under this limit one observed new properties of matter, primarily the laws of quantum physics. Moreover, when the transition metal ion substitutes into host (ZnO) material then optical properties of host material can be
controlled, which makes nanomaterials ideally suitable candidates for many types of optoelectronic device applications such as light emitting diode (LED), photoconductive cells, solar cells [5-7]. When the small percent of magnetic metal ions doped in host (ZnO) material than non-magnetic host material becomes totally ferromagnetic, which makes nanomaterial ideally suitable for spintronic devices application [8-10]. The invention of super computers, cell phones, nano-devices, scanning tunneling microscope (STM) in 1981, atomic force microscopy (AFM) in 1986, and first single electron transistor in 1987 and the discovery of Carbon nanotubes in 1991 are some milestones in the developments of nanotechnology.

Currently, nanotechnology has been recognized as a revolutionary field of science and technology and has been applied in many applications, including medical applications, biomedical applications, environmental applications, healthcare and life sciences, food safety, security, energy production and conversion applications, energy storage and aerospace [11-14]. Moreover, the nanotechnology applications provide very low cost, long lifetime, fast response, easy to use for unskilled users, and high efficiency of devices and it also provides new approaches to diagnosis and treatment of diseases, effective environmental monitoring and alternative ways for substantial energy development for a better world. Therefore, we can say that, nanotechnology is applied almost in every aspect of our modern world.

1.2 Classification of nanostructures material

The first classification idea of nanostructured material was given by Gleiter in 1995 [15] and further was explained by Skorokhod in 2000 [16]. However, Gleiter and Skorokhod scheme was not fully considered because of 0–dimension, 1–dimension, 2–dimension, and 3–dimension structures such as fullerenes, nanotubes, and nanoflower were not taken
into account. Therefore, Pokropivny and Skorokhod [17, 18] reported a modified classification scheme for nanostructures materials.

According to Pokropivny et al. [17] nanostructure materials can be classified into zero-dimension (0–D), one dimension (1–D), two-dimension (2–D) and three-dimension (3–D). While zero dimension nanostructures refer to quantum dots or nanoparticles, one dimension nanostructures refer to nanorods, nanowires, nanofibres, nanotubes and nanobelts, two dimension nanomaterials represent for nanowalls, nanosheets and nanoplates and 3–D nanomaterials are nanoflower and other complex structures such as nanotetrapods. Due to the quantum confinement effects and most of the dominating properties of the nanomaterials, its density of states of the nanometer are quite different from those of the bulk materials. The density of states, which describes the electronic states versus energy in the band diagram of the Zero–dimension, One–dimension, Two–dimension and bulk materials are shown in Fig. 1.1

![Fig.1.1 Density of states D (E) in semiconductor (i) zero dimensional (0–D) nanoparticles (ii) one dimensional (1–D) nano wire (iii) two dimensional (2–D) nanoplates (iv) three dimensional (3–D) bulk nanomaterial](image-url)
1.2.1. Zero–dimension nanomaterials (0–D)

Zero-dimension nanomaterials have nano dimension is in all three directions. Metallic nanoparticles such as silver and gold as well as ZnS, CdS, ZnO quantum dots are the perfect example of this kind of nanomaterial. Most of the nanoparticles are in spherical in size and the diameter of the nanoparticles will be in the range 1–50 nm. Recently, zero–dimension nanostructures material such as uniform particle arrays (quantum dots), heterogeneous particle arrays, core–shell quantum dots, hollow spheres and nano-lenses have been synthesized by several research groups. Fig. 1.2 shows the image of zero dimension nanostructure material, which have been reported in literatures [19-22]. Moreover, zero dimension nanostructure materials, such as quantum dots has been extensively studied for light emitting diodes (LEDs), solar cells, single-electron transistors, and lasers application [23-26].

![CdSe$_{1-x}$S$_x$ Quantum dots](image1) ![CoFe$_2$O$_4$ Nanoparticles](image2)

Fig. 1.2 Zero dimensional (0–D) nanostructure material

1.2.2. One-dimension nanomaterials (1–D)

In the last decade, the 1-D nanostructure material has stimulated an increasing interest due to their importance in research and developments and has a wide range of potential
applications. The 1–D nanostructures have a dimension that is outside the nanometric size range. These 1–D nanostructures have a shape like a rod and consist of nanotubes, nanorods, nanoneedles and nanowires. It is generally accepted that 1–D nanostructures are ideal systems for exploring a large number of novel phenomena at the nanoscale and investigating the size and dimensionality dependence of functional properties. 1–D nanostructures material also plays an important role as both interconnect and the key units in fabricating electronic, optoelectronic and LEDs with nanoscale dimensions. The field of 1–D nanostructure materials such as nanotubes has attained a significant attention after the pioneering work of Iijima et al. [27]. 1–D nanostructure materials have a profound impact in nanoelectronics, nanodevices and systems, nanocomposite materials, alternative energy resources and national security [28]. Fig. 1.3 shows the 1–D nanostructure materials such as nanorods, nanotubes etc., which have been reported in literature [29-38].

![ZnO Nanorods arrays](image1.png) ![ZnO Nanotubes arrays](image2.png)

**Fig. 1.3** One dimensional (1–D) nanostructure material

### 1.2.3. Two-dimension nanomaterials (2-D)

The 2–D nanostructures have two dimensions outside of the nanometric size range. Hence, these 2–D nanostructures display plane-like structures and consist of thin films, nanosheets, nanowalls and nanolayers [39]. In recent years, synthesis of 2–D
nanostructure materials has become a focused area in materials research, owing to their many low dimensional characteristics different from the bulk properties. In addition, two dimensional nanostructures are particularly interesting not only for basic understanding of the mechanism of nanostructure growth, but also for the investigation and developing novel applications in sensors, photocatalysts, nanocontainers, nanoreactors, and templates for 2-D structures of other materials [40]. Fig. 1.4 shows the 2–D nanostructures, such as junctions (continuous islands), branched structures, nanoplates, nanosheets and nanowalls etc., which have been reported in literature by other authors [41-47].

![Fig. 1.4 Two dimensional nanostructure materials](image)

**1.2.4. Three-dimension nanomaterials (3-D)**

The 3–D nanostructures have three dimensions outside of the nanometric size range. Owing to the large specific surface area and other superior properties over their bulk counterparts arising from quantum size effect, 3–D nanostructures material have attracted considerable research interest and many 3–D nanostructures materials have been synthesized in the past 10 years. It is well known that the behaviors of nanostructures materials strongly depend on the sizes, shapes, dimensionality and
morphologies, which are thus the key factors to their ultimate performance and applications. Therefore, it is of great interest to synthesize 3–D nanostructures materials with a controlled structure and morphology. In addition, 3–D nanostructures are an important material due to its wide range of applications in the area of catalysis, magnetic material and electrode material for batteries. Moreover, the 3–D nanostructures materials have recently attracted intensive research interests because the nanostructures have higher surface area and supply enough absorption sites for all involved molecules in a small space [48]. On the other hand, such materials with porosity in three dimensions could lead to a better transport of the molecules [49, 50]. Fig.1.5 shows the typical nanostructure material such as nanotetrapods and nanoflower, which have been reported in literature by other authors [51-55]. All of the 0–D, 1–D, 2–D and 3–D nanostructures can be amorphous or nanocrystalline.

There are two approaches for synthesis of nano materials and the fabrication of nano structures. ‘Top down approach’ refers to slicing or successive cutting of a bulk material to get a nano sized particle. ‘Bottom up approach’ refers to the buildup of a material from the bottom: atom by atom, molecule by molecule or cluster by cluster. Both
approaches play an important role in modern industry and most likely in nanotechnology.

Fig. 1.6 shows the schematic of Bottom–up and Top–down synthesis approach. There are advantages and disadvantages in both approaches. Attrition or Milling is a typical Top down method in making nanoparticles, whereas the colloidal dispersion is a good example of Bottom up approach in the synthesis of nano particles [56].

![Schematic of Bottom–up and Top–down synthesis approach of nanoparticles.](image)
1.4. **Properties of nanomaterials**

Nanomaterials have properties that are different from those of bulk materials. Most nanostructure materials are crystalline in nature and they have unique properties such as surface area to volume ratio and quantum confinement.

1.4.1. **Surface area to volume ratio**

Nanomaterials have a relatively larger surface area when compared to the same volume or the mass of the material produced in a larger form. When the given volume is divided into smaller pieces the surface area increases. So the particle size decreases a greater proportion of atoms are found at the surface compared to those inside. Hence, nanoparticles have a much greater surface area as per given volume compared with larger particles. It makes the materials more chemically reactive.

1.4.2. **Quantum confinement**

In nanocrystals, the electronic energy levels are not continuous as in the bulk, but are discrete (finite density of states), because of the confinement of the electronic wave function to the physical dimensions of the particles. This phenomenon is called quantum confinement. If one length of three dimensional nanostructures is at nano-dimension, then it is called a quantum well. If two sides of three dimensional nanostructures are at nano-dimension, then it is called a quantum wire. If all three dimensional nanostructures is at nano-dimension (Nano Crystals), are referred as quantum dots.

1.4.3. **Magnetic properties**

Magnetic properties of nanoparticles are also important to fabricate spintronic devices and memory storage devices because magnetic properties depend on the size of the nanoparticles. ZnO is basically insulated and diamagnetic material, but when we go to nanoscale it becomes totally ferromagnetic. Bulk gold and platinum are non magnetic but at the nano size they act as magnetic particles [57, 58]. Au gold nanoparticles become
ferromagnetic when they are capped with the appropriate molecules such as thiol [59]. Giant magneto resistance (GMR) is a phenomenon observed in nanoscale multilayer’s consisting of strong ferromagnetic (Fe, Co, Ni) and a weaker magnetic or non magnetic buffer (Cr, Cu). It is usually employed in data storage and sensing. Magnetic nanoparticles are several applications like biomedical, refrigeration as well as high storage density magnetic memory media [60].

1.4.4. Optical properties

One of the most fascinating and useful aspects of nanomaterials is their optical properties. Applications based on optical properties of nanomaterials include light emitting diode, solar panel display, sensors, laser diodes, photo catalysis, optical detector, imaging, phosphor, photoelectron chemistry and biomedicine [61, 62]. The optical properties of nanomaterials depend on parameters such as size, shape, surface area to volume ratio and other variables, including doping and interaction with the surrounding environment. Semiconductors and many metals show large changes in optical properties such as colour, as a function of particle size [63]. Examples, colloidal suspensions of gold nanoparticles have a deep red color which becomes progressively more yellow as the particle size increases. Other properties, which may be affected by reduced dimensionality, include photo catalysis, photoconductivity, photoemission and electroluminescence.

1.4.5. Electrical properties

The electrical properties of nanomaterials vary between metallic to semiconducting materials. Electrical properties of nanostructures discuss about the fundamentals of electrical conductivity in nano tubes and nano rods, carbon nanotubes, photoconductivity of nano rods, electrical conductivity of nano composites [64]. One interesting method which can be used to demonstrate the steps in conductance is the mechanical thinning of
a nano wire and measurement of the electrical current at a constant applied voltage. The important point here is that, with decreasing diameter of the wire, the number of electron wave modes contributing to the electrical conductivity is becoming increasingly smaller by well-defined quantized steps [65-67].

1.5 Selected application of nanotechnology

1.5.1. Drug delivery

One of the application of nanotechnology in medicine currently being developed involves employing nanoparticles to deliver drugs, heat, light or other substances to specific types of cells (such as cancer cells). Particles are engineered so that they are attracted to diseased cell, which allows direct treatment of those cells. This technique reduces damage to healthy cells in the body and allows for earlier detection of disease [68, 69].

1.5.2. Therapy techniques

Researchers have developed nanosponge that absorb toxins and remove them from the bloodstream. The nanosponge is polymer nanoparticles coated with a red blood cell membrane. The red blood cell membrane allows the nanosponge to travel freely in the bloodstream and attract the toxins [70].

1.5.3. Diagnostic techniques

Researchers have developed a sensor using carbon nanotubes embedded in a gel; that can be injected under the skin to monitor the level of nitric oxide in the bloodstream. The level of nitric oxide is important because it indicates inflammation, allowing easy monitoring of inflammatory diseases [71, 72]. A method for early diagnosis of brain cancer under development uses magnetic nanoparticles and nuclear magnetic resonance (NMR) technology. The magnetic nanoparticles attach to particles in the blood stream.
called microvesicles which originate in brain cancer cells. NMR is then used to detect these microvesicle/magnetic nanoparticles clusters, allowing an early diagnosis.

1.5.4. Elimination of pollutants

Nanocrystalline materials have extremely large grain boundaries relative to their grain size. Hence, nanomaterials are very active in terms of their chemical, physical, and mechanical properties. Due to their enhanced chemical activity, nanomaterials can be used as catalysts to react with such noxious and toxic gases as carbon monoxide and nitrogen oxide in automobile catalytic converters and power generation equipment to prevent environmental pollution arising from burning gasoline and coal [73].

1.5.5. High power magnets

The strength of a magnet is measured in terms of coercivity and saturation magnetization values. These values increase with a decrease in the grain size and an increase in the specific surface area (surface area per unit volume of the grains) of the grains. It has been shown that magnets made of nanocrystalline yttrium samarium-cobalt grains possess very unusual magnetic properties due to their extremely large surface area. Typical applications for these high-power rare-earth magnets include automobile alternators, land-based power generators and motors for ships, ultra-sensitive analytical instruments, and magnetic resonance imaging (MRI) in medical diagnostics [74].

1.5.6. Cosmetics

The applications of nanotechnology and nanomaterials can be found in many cosmetic products including moisturizers, hair care products, make up and sunscreen. The two main uses for nanoparticles in cosmetic products are UV filtering and delivery of active ingredients. Titanium dioxide and zinc oxide nanoparticles are the main compounds used in these applications [75]. Some cosmetic products, such as sunscreens, use mineral-based materials and their performance depends on their particle size. In sunscreen
products, titanium dioxide and zinc oxide, in the size range of 20 nm, are used as efficient UV filters. Their main advantage is that they provide broad UV-protection and do not cause cutaneous adverse health effects. Many of the leading cosmetic companies claim their products to contain various types of nano-sized materials like fullerenes, nanotubes, liposomes, quantum dots etc.

1.5.7. Biosensors

A nanomaterial has an important role in the development of biosensors. Sensitivity and other attributes of biosensors can be improved by using nanomaterials in their construction. The functional nanoparticles (electronic, optical and magnetic) bound to biological molecules (peptides, proteins, nucleic acids) have been developed for use in bio-sensors to detect and amplify various signals. Different nanostructures include nanorods, nanofibres; nanoparticles etc. are used as biosensors [76].

1.5.8. Electronic devices

Today, multifunctional laptops and smart phone are more users friendly, faster, and have large memory capacities. Mobile phones, pocket sized memory storage devices and the widely used MP3 players, iPods are perhaps the most convincing benefits of nanomaterials. Most of them make use of magnetic materials such as ferrites [77].

1.5.9. Information storage

Since the 1940, with the sudden growth in popularity of magnetic recording $\gamma$-Fe$_2$O$_3$ in the form of small single domain particles have dominated the magnetic storage materials technology. The data storage industry is driving towards higher densities of stored ‘bits’. If a reliable data storage system based on a single 5 nm magnetic nanoparticles acting as an individual bit of information could be created, storage densities of 10 Gbit/cm$^2$ would be possible. The presence of silica was found to enhance coercivity of cobalt ferrite nanomaterials [78].
1.5.10 Catalysis

Catalysis from nanoparticles is beneficiary due to the extremely large surface to volume ratio. The potential application of nanoparticles in catalysis ranges from fuel cell to catalytic converters and photo catalytic devices. Catalysis is also important for the production of chemicals. Platinum nanoparticles are now being considered in the next generation of automotive catalytic converters because the very high surface area of nanoparticles could reduce the amount of platinum required [79].

1.6 Literature survey

A simple search in Web of Science with just the single key word “ZnO” results in 93,500,000 hits (Jun 2016) within the various research areas including physics, chemistry, nanotechnology and interdisciplinary materials science. Such a large quantity of published research papers having ZnO as the study object reflects its importance as a multifunctional versatile II–VI (ZnO) semiconducting material with a direct wide band gap (3.37 eV at RT), large excitonic binding energy (60 meV), and excellent optoelectronic and piezoelectric properties [80, 81]. A new chapter concerning the ZnO–related research area has been opened upon doping it with transition metals (3–d) like Fe, Co, Mn, Ni, Cr, or V, leading to materials with completely different behaviour towards magnetic and optical excitation. The physical, chemical and other properties of ZnO nanomaterials can be easily tailored with doping of transition metal ion into the ZnO semiconductor material as per the demand of device fabrication [82]. This new research direction is frequently entitled as diluted magnetic semiconductors (DMS) including, apart from ZnO and other semiconductors hosts. The intense interest is mainly driven by the search for new device applications in spin–based technologies (Spintronic). Having simultaneously semiconducting and magnetic properties, one can take the advantage of both the electron charge and the electron spin for information recording. On the way to
the practical use of both charge and spin of electrons, two criteria must be fulfilled. Firstly, a relatively high concentration of magnetic elements should be introduced in the semiconducting matrix, and secondly Curie temperatures ($T_C$) of ferromagnetic material greatly exceeding at room temperature or above room temperature should be obtained. Both requirements are highly demanding in terms of synthesis implying that many reports are disclosed about attempts in achieving room temperature ferromagnetism. As typical semiconductor hosts, metal oxides like ZnO, TiO$_2$, SnO$_2$, or In$_2$O$_3$ are usually considered. Unlike the diluted magnetic semiconductors based on III–V or II–VI group of elements showing ferromagnetism only at very low temperatures, some oxide-based DMSs exhibit ferromagnetism at higher temperature and even above room temperature. They are also optically transparent, making them suitable for magneto-optoelectronic applications, particularly for electrodes in solar cells [83]. Among the metal oxides, ZnO is relatively well understood from an experimental point of view, requiring an extensive systematic experimentation and data analysis. Well defined doping and defect chemistry, the potential for transparent high-temperature applications and the ability to lose or emit spontaneously at ultraviolet wavelengths make ZnO attractive for many device applications. ZnO is a semiconductor material, which contains a small amount of magnetic impurities. The main challenge for this a kind of material is to preserve their magnetic character at room temperature, that is, Curie temperature above 300 K, in order to be useful for spintronic application. Despite some initial promising results on transition metal ion doped ZnO, it is not clear if dilute magnetic semiconductor (DMS) can exhibit this required high temperature magnetism. For most of the experimental results, doubts arose about the real origin of ferromagnetism. In some cases it was demonstrated that the magnetism was due to segregation of metallic clusters while in some cases presence of intrinsic defects are responsible for room temperature
ferromagnetism [84]. Recently, Tahir et al. demonstrated that doping ZnO thin films with 3d non-magnetic ions (as Ti or V) also leads to room temperature ferromagnetic behavior [85, 86]. As typical transition metals, like Co, Mn, Ni, Fe ions has been dope into ZnO to get dilute magnetic semiconductor [87]. It was reported in literature that Co ions doped ZnO displayed paramagnetism at room temperature [88], while other cases, room temperature ferromagnetism was obtained when Co doped ZnO nanoparticles [89]. Recent research has been devoted to the synthesis of ZnO nanostructures with a Fe and Ni co-doping, which displayed room temperature ferromagnetism of nanomaterials with varying dopant concentration [90]. Among the various oxides based DMSs, ZnO doped with transition metal (Co$^{2+}$ & Mn$^{2+}$) has been the centre of interest for the fabrication of spintronic and optoelectronic devices mainly because of their abundant electron state and large solubility in the ZnO matrix. There are several reports available in the literature on optical and magnetic properties of transition and non-transition metal doped ZnO using a different synthesis method. Even though so many research papers published on metal ion-doped ZnO, many researchers are making efforts to enhance magnetic properties and control optical properties, but there is also no general agreement of researchers over which of the intrinsic or extrinsic point defects and other some parameters are responsible for the changing magnetic and optical properties of the material [91, 92]. Recently, many studies have been performed to improve the optical properties by varying the grain size or shape of the ZnO [93]. Richa Bhargava et al. [94] have studied the effect of cobalt on the thermal, structural and optical properties of ZnO nanoparticles, it has also been reported that up to 0.15 % doping of cobalt ion shows single phase and above 0.15 % doping of cobalt ion shows the secondary phase of Co$_3$O$_4$ has been detected by X-ray diffraction. Kim et al. [95] have shown the room temperature ferromagnetism in Zn$_{1-x}$Co$_x$O thin film and suggested that origin of ferromagnetism at
room temperature due to Co clusters formation. L. B. Duan et al. [96] have studied the structural and magnetic properties of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($0 \leq x \leq 0.40$) nanoparticles synthesized by auto-combustion method and have reported that the lattice parameters increase with increase in Mn concentration. It has also been reported that Mn shows the highest solubility limit of about 30 % in ZnO. M. Ebrahimizadeh Abrishami et al. [97] have successfully synthesized the undoped and Mn$^{2+}$ doped ZnO nanoparticles by using two synthesis methods like chemical co-precipitation and sol-gel auto combustion method. The effects of dopant elements on the structural, micro structural and optical properties have been discussed. Sajid Ali et al. [98] have studied the structural, optical and dielectric properties of nano crystalline Co doped ZnO nanoparticles obtained by using sol-gel auto combustion route using citric acid as a fuel. Structural studies suggest that crystal system of parent compound remains same which is hexagonal crystal system up to 10 at %. The authors also suggest that energy band gap decreases with increasing Co concentration. The dielectric study shows that dielectric constant, dielectric loss and dielectric loss tangent decreases with increases in frequency and composition. Vijayaprasath Gandhi et al. [99] have studied that effect of cobalt doping on structural, optical and magnetic properties of ZnO nanoparticles successfully synthesized by co-precipitation method and obtained some interesting result. Crystallite sizes have been calculated by XRD which is found to be decreases with the increase in cobalt content. From the vibrating sample magnetometer study shows that pure ZnO exhibits diamagnetic behavior, whereas Co doping in ZnO makes the samples ferromagnetic at room temperature, and magnetization values are found to be increased with the increase of Co concentration in ZnO. Sivagamasundari A. et al. [100] have reported that cobalt doped ZnO nanoparticles successfully synthesized by sol gel auto combustion method and obtained some interesting result. The authors also reported that with increase in the
cobalt concentration the crystallite size increases and solubility limit of cobalt also increased up to 20 %. The magnetic measurements showed that no ferromagnetism was observed only paramagnetism observed due to non availability of free carriers for long range ferromagnetic interaction. Zhang et al.,[101] have showed that ZnO nanoparticles have intrinsic ferromagnetism when doped with cobalt. Bouloudenine et al. [102] have reported the absence of ferromagnetism in cobalt doped ZnO. An enhancement of magnetism is expected when the doping of transitional metal impurity increases. Ming Wei et al. [103] and Patra et al., [104] reported that increase in impurity decreases the magnetization. Mukta V. Limaye et al. [105] presented that the origin of room temperature ferromagnetism is associated with vacancies/defects present on the surface of nanorods. Garcia et al. [106] reported that the magnetic properties of nanoparticles strongly depend on the preparation method.

### 1.7 Aim of the present work

Zinc oxide is a group II-VI semiconductor material with a direct wide band gap of 3.37 eV at room temperature and large excitonic binding energy of 60 meV, Zinc oxide is one of the most promising materials for the fabrication of optoelectronics devices operating in the blue and ultraviolet (UV) regions and gas sensing applications. It has a wide range of technological applications including transparent conducting electrodes for solar cells, flat panel displays, surface acoustic devices, chemical and biological sensors and UV lasers. In order to make suitable spintronic and optoelectronic devices, it is necessary to understand the magnetic and optical properties of ZnO nanoparticles. Many researchers are trying to maintain strong ferromagnetic properties of ZnO at room temperature and above room temperature with doping of suitable transition metal ions and using various synthesis methods etc. Recently, many studies have been performed to improve the optical properties of ZnO with doping of transition metal ions and varying the grain size.
or shape of the ZnO nanoparticles. Cobalt and Manganese doped zinc oxide is a complex material and the ferromagnetic behavior is controversial owing to the fact that the magnetism is very sensitive to the preparation conditions. According to our knowledge the structural, optical, electrical, and magnetic properties of cobalt and manganese substituted zinc oxide nanoparticles by sol-gel auto combustion method have not been studied systematically. Among the transition metals, Co$^{2+}$ and Mn$^{2+}$ are considered potential candidates for optoelectronic and spintronic device application because of its variable oxidation state, a ferromagnetic state in elemental form at room temperature and large solubility in ZnO matrix. To our knowledge, the effect of heavily doped Co$^{2+}$ and Mn$^{2+}$ ions on the structural, morphological, optical, electrical, dielectric and magnetic properties of ZnO nanoparticles has not been reported in the literature previously.

In view of the above facts, the aim of the present work is to investigate the structural, morphological, optical, electrical, dielectric and magnetic properties of Zn$_{1-x}$TM$_x$O (TM: Co$^{2+}$, Mn$^{2+}$) (0.00≤x≤0.36) system. The structural, morphological, optical, electrical, dielectric and magnetic properties of cobalt and manganese doped ZnO nanoparticles were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy with selected area diffraction pattern, UV-Vis spectroscopy, photoluminescence emission spectroscopy, two-probe resistivity measurement technique, LCR-Q meter and vibrating sample magnetometer etc. In this work, we have studied the effects Co$^{2+}$ and Mn$^{2+}$ concentration on the structural, morphological, optical, electrical, dielectric and magnetic properties of ZnO nanoparticles. It is expected that the substitution of Co$^{2+}$ and Mn$^{2+}$ ion in ZnO semiconductor nanoparticles may modify the structural, optical electric and magnetic properties, which are useful for various applications such as spintronic and optoelectronic devices.
References


[21]


[25]


[28]