CHAPTER 1

INTRODUCTION

1.1. Nanostructured Materials

The study of nanomaterials has extended the frontiers of science and has justified the existence of a new domain of research called nanoscience. Research in nanoscience coupled with nanotechnology has stimulated the growth of conventional scientific disciplines. Nanoscience includes the physical, chemical and biological aspects of nanoentities (molecules and structures with at least one dimension between 1 and 100 nm). Nanotechnology is the application of the principles of nanoscience into useful deliverables. This includes the application of nanostructures/nanomaterials into useful nanoscale devices and components. Further, by tailoring (or manipulating) the concepts of nanoscience, nanotechnology aims at improving the lifestyle of the human race.

The word ‘nano’ derives from the Greek word ‘nanos’, which means dwarf or extremely small. The prefix ‘nano’ in word of nanotechnology means a billionth (1×10^{-9}) [1]. Manipulating the shape of a nanomaterial leads to an even higher degree of material property customization. Anisotropic structures such as sheets, tubes and wires can be assembled with different properties from isotropic spheres of the same material. The near-perfect conduction of metallic carbon nanotubes as compared to other carbon allotropes is an example. The applications employing nanotechnological design principles include nanoscale medicine capsules that can actively seek out and target pathogens and metal oxide nanoparticle paints that use sunlight to break down air pollution.

Nanotechnology is an engineering of functional systems at the molecular level, covers a broad range of topics and is focused on controlling and exploiting the structure of matter on a large scale below 100 nanometers. It is an interdisciplinary science, with applications in biology, chemistry, material physics and electronics. Changing the size of a material from bulk to nanoscale results in profound changes in material properties and behavior. Mechanical properties of nanoscale materials are often orders of magnitudes higher than their bulk counterparts, because the probability of harmful material defects decreases. This lower defects lead to superior electrical and magnetic properties.

Nano science and nanotechnology are recent revolutionary development in science and engineering that are evolving at a very fast pace [2]. The idea of nanotechnology was introduced in 1959, when Richard Feynman, a physicist at Caltech, gave a talk called, "There's plenty of room at the bottom" [3]. In his work Richard Feyman described the idea of creating things out of tiny pieces instead of making things smaller as so far at that time [4]. Norio Taniguchi was the man who first used the term 'nanotechnology' (Professor of Tokyo Science University) in 1974. He started his research on the mainly free abrasive mechanisms of high precision machining of hard and brittle materials. Kim Eric Dexler is known as the father of nanotechnology. He is the man behind to theorize nanotechnology in depth and popularized the subject. He is an American engineer best known for popularizing the potential of molecular nanotechnology from the year 1970 to 1980. In 1979, Eric Drexler encountered Feynman's talk on atomic manipulation and "Nano-factories." The Caltech physicist's ideas inspired Drexler to put these concepts into motion [3].

1.1.1. Classification of Nanostructured materials

The classification is based on the number of dimensions, which are not confined to the nanoscale range (<100 nm) (Figure 1.1).

(1) zero-dimensional (0-D) - All dimensions at the nanoscale

(2) one-dimensional (1-D) - Two dimensions at the nanoscale
One dimension at the macroscale

(3) two-dimensional (2-D) - One dimension at the nanoscale
Two dimensions at the macroscale

(4) three-dimensional (3-D) - No dimensions at the nanoscale
Three dimensions at the macroscale

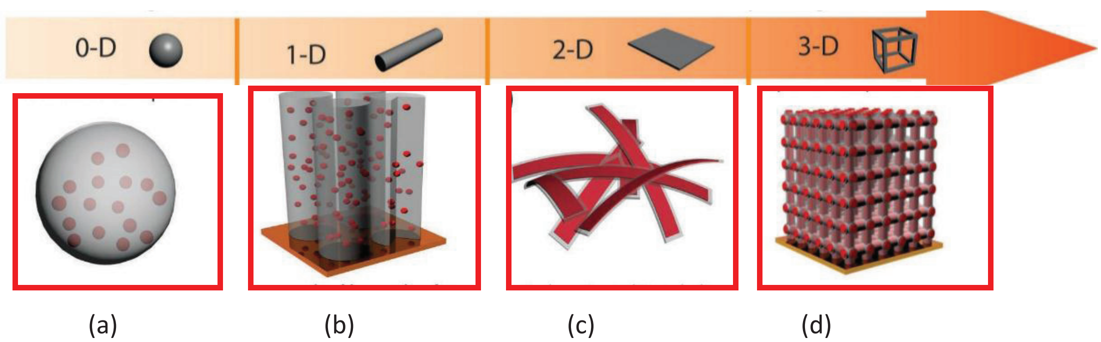

Figure 1.1. (a) 0-D [nanoparticles] (b) 1-D [nanotubes, wires and rods] (c) 2-D [nanofilms, nanocoatings] (d) 3-D [Bulk nanomaterials]

The first generation involves the simple components of NPs, nanotubes, nanolayers and nanocoatings. The second generation involves active nanostructures that change their properties (morphology, shape, magnetic, biological, etc.) during the operation. Examples are targeted drugs and chemicals, energy storage devices, transistors and so on. The third generation includes nanosystems that might self-assemble or self-organise. Examples are artificial organs and electronic devices. The fourth generation includes molecular nanosystems, where each molecule in the nanosystem has a specific structure and plays a different role. Now we will come to the fifth generation [5]. It is shown in Figure 1.2.

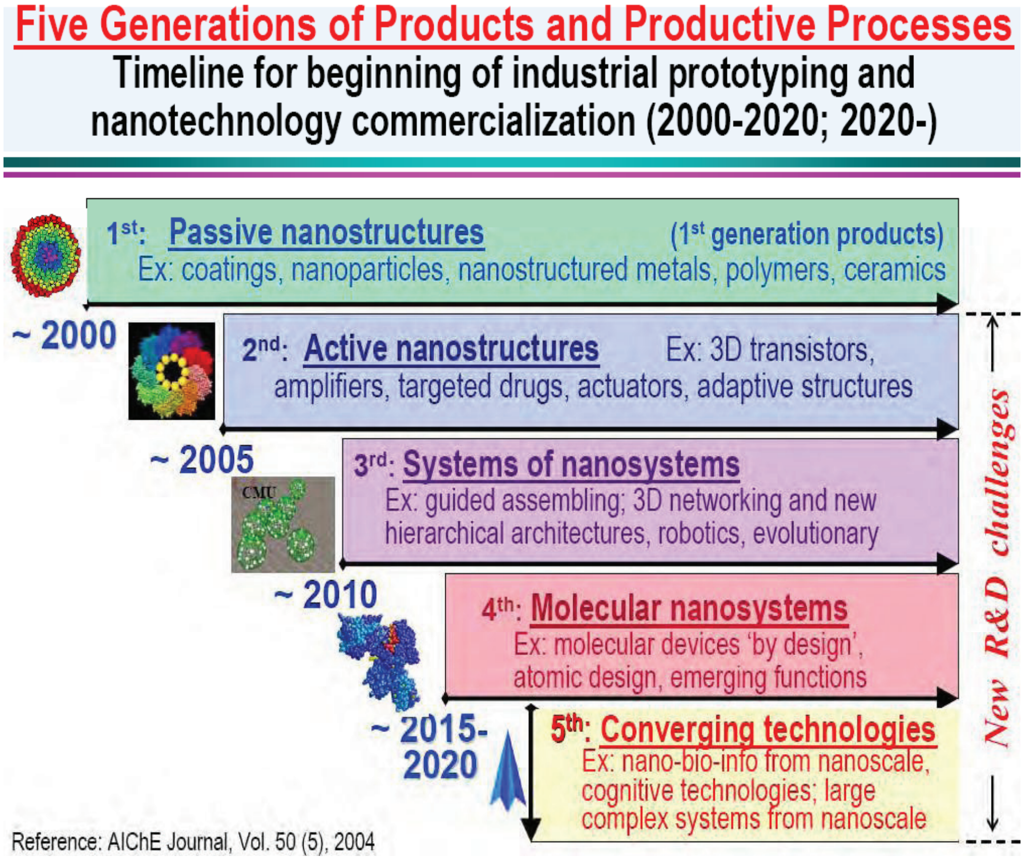

Figure 1.2. Different generations of nanostructures

Synthesis of nanomaterials with controlled morphology, size, chemical composition, crystal structure and in large quantity is a challenge in nanotechnological applications. The various geometrical morphologies of nanomaterials such as nano tubes [6,7], cages [8], cylindrical wires [9,10], rods [11], biaxial cables [12], ribbons or belts [13] and sheets [14] have been produced with the peculiar properties.

Many benefits of nanotechnology depend on the fact that it is possible to tailor the structures of materials at extremely small scales to achieve specific properties, thus greatly extending the materials science toolkit. Using nanotechnology, materials can effectively be made stronger, lighter, more durable, more reactive, better electrical conductors. Many everyday commercial products are currently found in the market and in daily use that rely on nanoscale materials and processes.

1.1.2. Applications of nanostructured materials

- Nanoscale additives to or surface treatments of fabrics can provide lightweight ballistic energy deflection in personal body armour and can help them resist wrinkling, staining and bacterial growth.
- Clear nanoscale films on eyeglasses, computer and camera displays, windows, and other surfaces can make them water and residue-repellent, antireflective, self-cleaning, resistant to ultraviolet or infrared light, antimicrobial, scratch-resistant, or electrically conductive.
- Nanoscale materials are beginning to enable washable, durable "smart fabrics" equipped with flexible nanoscale sensors and electronics with capabilities for health monitoring, solar energy capture and energy harvesting through movement.
- Nanoscale polymer composite materials are being used in baseball bats, tennis rackets, bicycles, motorcycle helmets, automobile parts, luggage, and power tool housings, making them lightweight, stiff, durable and flexible.
- Carbon nanotube sheets are now being produced for use in next-generation air vehicles. For example, the combination of light weight and conductivity

makes them ideal for applications such as electromagnetic shielding and thermal management.

- Nano-engineered materials in automotive products include high-power rechargeable battery systems, thermoelectric materials for temperature control, tires with lower rolling resistance, high-efficiency and low-cost sensors, thin-film smart solar panels and fuel additives for cleaner exhaust and extended range.
- They also make superior household products such as degreasers and stain removers; environmental sensors, air purifiers and filters, antibacterial cleansers, specialized paints and sealing products, such as self-cleaning house paints that resist dirt and marks.
- Nanostructured ceramic coatings exhibit much greater toughness than conventional wear-resistant coatings for machine parts.
- Nanoparticles are used increasingly in catalysis to boost chemical reactions. This reduces the quantity of catalytic materials necessary to produce desired results, saving money and reducing pollutants. Two big applications of NPs are in petroleum refining and in automotive catalytic converters.
- Using magnetic random access memory (MRAM), computers will be able to "boot" almost instantly. MRAM is enabled by nanometer-scale magnetic tunnel junctions and can quickly and effectively save data during the system shutdown or enable resume-play features.
- Ultra-high definition displays and televisions are now popular, because they use quantum dots to produce more vibrant colours while being more energy efficient.

- Flexible electronics have been developed using, for example, semiconductor nanomembranes for applications in smartphone and e-reader displays. Other nanomaterials like graphene and cellulosic nanomaterials are being used for various types of flexible electronics to enable wearable and "tattoo" sensors.
- Nanomedicine, the application of nanotechnology in medicine, draws on the natural scale of biological phenomena to produce precise solutions for disease prevention, diagnosis and treatment.
- Commercial applications have adapted gold nanoparticles as probes for the detection of targeted sequences of nucleic acids and gold nanoparticles are also being clinically investigated as potential treatments for cancer and other diseases.
- Nanotechnology researchers are working on a number of different therapeutics where the nanoparticle can encapsulate or otherwise help to deliver medication directly to cancer cells and minimize the risk of damage to healthy tissue. This has the potential to change the way doctors treat cancer and dramatically reduce the toxic effects of chemotherapy.
- Nanotechnology is also being applied to oil and gas extraction. For example, the use of nanotechnology enabled gas lift valves in offshore operations or the use of nanoparticles to detect microscopic down-well oil pipeline fractures.
- Researchers are investigating carbon nanotube "scrubbers" and membranes to separate carbon dioxide from power plant exhaust.

- Researchers are developing wires containing carbon nanotubes that will have much lower resistance than the high-tension wires currently used in the electric grid, thus reducing transmission power loss.
- Nanotechnology can be incorporated into solar panels to convert sunlight to electricity more efficiently, promising inexpensive solar power in the future. Nanostructured solar cells could be cheaper to manufacture and easier to install, since they can use print-like manufacturing processes and can be made in flexible rolls rather than discrete panels. New solar panel films incorporate nanoparticles to create lightweight and flexible solar cells.
- An epoxy containing carbon nanotubes is being used to make windmill blades that are longer, stronger and lighter-weight than other blades to increase the amount of electricity generated by windmills.
- Nanoparticles are being developed to clean industrial water pollutants in ground water through chemical reactions that render the pollutants harmless. This process would cost less than methods that require pumping the water out of the ground for treatment.
- Researchers have also placed magnetic water-repellent nanoparticles in oil spills and used magnets to mechanically remove the oil from the water.
- Nanotechnology-enabled sensors and solutions are now able to detect and identify chemical or biological agents in the air and soil with much higher sensitivity than ever before.
- The use of nanotechnology-enabled lightweight, high-strength materials would apply to almost any transportation vehicle. For example, it has been estimated that reducing the weight of a commercial jet aircraft by 20 percent

could reduce its fuel consumption by as much as 15 percent. The analysis performed by NASA has indicated that the development and use of advanced nanomaterials with twice the strength of conventional composites would reduce the gross weight of the launch vehicle by as much as 63 percent.

- Nanotechnology may be used in agriculture and food production in the form of nano sensors for monitoring crop growth and pest control by early identification of plant diseases.
- Nano crystals, nano emulsions, solid lipid nanoparticles are used in cosmetic applications .

1.1.3. Nanoparticles

Particle whose size range of 1-100 nm is called a nanoparticle, whether it is dispersed in gaseous, liquid or solid medium. There are number of atoms or molecules bonded together and intermediate in size between individual atoms and aggregate large enough to be called as bulk material [15].

Properties of Nanoparticles

a) Physically, materials can be characterized by some critical length, a thermal diffusion length or a scattering length [15].
b) Nanoparticles can be built by assembling individual atoms or subdividing bulk materials [15].
c) The size of the nanoparticles is less than the wavelength of light [16].
d) Their critical characteristics are high surface-to-volume ratio [16].
e) Vander wall forces or magnetic forces play more important role than gravitational forces [16].

After some time the particles undergo aggregation. The degree of aggregation depends on the nature of the particles and the conditions during their synthesis. Some organic surfactants are used during the synthesis to avoid aggregation of the particles and to reduce the size of the particles. Use of surfactants will help in tailoring the size and shape of the nanoparticles and to hinder the aggregation.

The experimental methods to synthesize nanoparticles such as chemical precipitation [17], microwave technique [18], combustion route [19], sol–gel [20], solvothermal [21], hydrothermal [22], sonochemical [23] and mechanochemical [24] have been reported with different sizes and shapes. The structural, optical, magnetic and biological properties of metal oxide nanoparticles are of meticulous interest for practical applications.

1.2. Metal oxide nanostructures

Metal oxide nanoparticles represent a field of materials physics which attracts considerable interest due to the potential technological applications of these compounds. The implications of these materials in fields such as medicine, information technology, catalysis, energy storage and sensing have driven much research in developing synthetic pathways to such nanostructures [25]. Semiconductor nanoparticles exhibit exciting size-tunable optical, magnetic, chemical and electronic properties with practical applications in a wide spectrum of fields including catalysis, photonics, photovoltaics, electronics, biological imaging and data storage. Colloidal approaches provide quantum dots of excellent quality due to the control in their size, shape, structure and composition of the material. Metal oxides play a very important role in many areas of chemistry, physics and materials science [26]. The metal elements are able to form a large diversity of oxide compounds [27]. These can adopt a vast number of structural geometries with an electronic structure that can exhibit metallic, semiconductor or insulator character. In technological applications, oxides are used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion and as catalysts. In the emerging field of nanotechnology, a goal is to make nanostructures or nanoarrays with special properties with respect to those of bulk or single particle species [28]. Oxide nanoparticles can exhibit unique physical and chemical properties due to their limited size and a high density of corner or edge surface sites. Particle size is expected to influence the following important groups of basic properties in any material.

1.2.1. Structural Properties

The first one comprises the structural characteristics, namely the lattice symmetry and cell parameters [29]. Bulk oxides are usually robust and stable systems with well-defined crystallographic structures. However, the growing importance of surface free energy and stress with decreasing particle size must be considered: changes in thermodynamic stability associate with size can induce modification of cell parameters and structural transformations [30] and in extreme cases the nanoparticle can disappear due to interactions with its surrounding environment and high surface free energy [31]. In order to display mechanical or structural stability, the nanoparticle must have low surface free energy. As a consequence of this requirement, phases that have a low stability in bulk materials can become very stable in nanostructures. As the particle size decreases, the increasing number of surface and interface atoms generates stress/strain and related structural perturbations [32]. Beyond this "intrinsic" strain, there may be also "extrinsic" strain associated with a particular synthesis method which may be partially relieved by annealing or calcination. Non-stoichiometry is also a common phenomenon. On the other hand, interactions with the substrate on which the nanoparticles are supported can complicate the situation and induce structural perturbations [33].

1.2.2. Electronic properties

The second important effect of size is related to the electronic properties of the oxide. In any material, the nanostruture produces quantum size or confinement effects which essentially arise from the presence of discrete, atom-like electronic states. The electronic effects of quantum confinement experimentally probed on oxides are related to the energy shift of exciton levels and optical bandgap [34]. Theoretical studies for oxides show a redistribution of charge when going from large periodic structures to small clusters or aggregates which must be roughly considered to be relatively small for ionic solids while significantly larger for covalent ones [35]. The degree of ionicity or covalency in a metal oxygen bond strongly depends on size in systems with partial ionic or covalent character [36].

1.2.3. Optical Properties

The studies on the optical properties of nanocrystalline semiconductors have been done widely in recent years because of their enhanced properties which are used in practical applications. As the particle size is decreased, the band gap is increased thereby modifying the optical and electrical properties of the material and it will formulate the material appropriate for new applications and devices. In nano particles, the effect of reduction in size on the electronic structure has tremendous changes on the energies of highest occupied molecular orbital (valence band) and the lowest unoccupied molecular orbital (conduction band). The emission and absorption of optical energy occur when the transition of the electrons takes place between highest occupied molecular orbital (valence band) and the lowest unoccupied molecular orbital (conduction band). The intrinsic color of nanoparticles changes with size because of surface plasmon resonance. Such nanoparticles are useful for molecular sensing, diagnostics and imaging applications. Iwakoshi observed that the bulk gold particles appear yellow in color. But gold nano particles appear in red color [37]. Also the ZnS bulk semiconductor with energy gap of 3.5eV is white in colour. As particle size is reduced, the energy gap increases and it becomes yellowish. Since the size of the particles is reduced, the electrons are not free to move compared to bulk materials. Due to this restriction of the particles it reacts differently with light. The most important optical feature is the reduction of its size from macro scale to nano scale, resulting in the increase of the band gap and blue shift in emission and absorption spectra [38] (shift towards shorter- wavelength end of the optical spectrum). The doping of magnetic ions like transition metals may change the absorption properties of the host material as the band gap energy may shift to either lower wavelength (blue shift) or higher wavelength (red Shift) or no appropriate change in their position. On the other hand, the band gap of semiconductors and the optical property of the materials could be changed by varying pore size in the nano crystalline state for small particle sizes.

1.2.4. Magnetic properties

Reducing the size of the magnetic systems changes the electronic properties by reducing the symmetry of the system and by introducing a quantum confinement [39]. The strength of a magnet is measured in terms of coercivity and saturation magnetization value. These values increase with decrease in the grain size and an increase in specific surface area (surface area per unit volume) of the grain. Nanoparticles exhibit magnetic properties that are different from bulk materials. These are due to the following reasons:

- As the size of the system reaches the typical lengths of few nanometers, it is expected that the response of the system depends on the boundary conditions determined by the particle size and therefore to be different from bulk materials.
- Because of the large ratio of surface to volume atoms in NPs, the surface energy becomes important when compared with volume energy, and therefore, the equilibrium situation can be different for bulk materials. In the case of NPs, the volume is so small, therefore the thermal energy (K_BT) is enough to invert the magnetization with relaxation times as low as few seconds. Thus, the material looses coercivity and remanence, giving rise to the so-called super paramagnetic behavior.

Non-magnetic semiconductor is doped with transition metal ions to achieve magnetism. It was found that the transition metal cation impurity is of dilute concentration. Due to this reason such materials are called as diluted magnetic semiconductors (DMSs). Since ferromagnetism in DMS is related to the carriers in the semiconductors, ferromagnetic order can be disturbed thus gives rise to new possibilities such as optical manipulation of magnetic behaviour of DMS [40] or gate controlled ferromagnetism [41]. Oxide based diluted magnetic semiconductors play a very essential role in materials science and chemistry because they are used in storage devices, optoelectronics, nanoelectronics and photonic devices. The impurity doping [42], coating with surfactants [43], and annealing [44] will improve the properties of nanostructures. Recently, oxide based diluted magnetic semiconductors (DMS) such as transition-metal-doped semiconductors with room-temperature ferromagnetism (RTFM) have been investigated for their superior applications in spintronic devices. Transition-metal-doped semiconductors have involved a lot of attention due to their potential applications, such as UV detectors, field-effect transistors, short wavelength lasers, high sensitive chemical sensors, and nonlinear varistors [45-47].

1.3. Tin oxide (SnO_2) Nanoparticles: A brief review

Recent research, on tin oxide semiconductor has been growing due to the wide range of its applications including field effect transistors, transparent electrodes in photoelectric conversion devices, liquid crystal displays, catalysts for oxidation of organics, heat mirrors, photovoltaic devices, photo sensors, optoelectronic devices, electrochromic displays, antimicrobial agent, antistatic coating, planar wave guides, lithium-ion batteries, solar cells, gas sensors etc., [48-53] due to its good optical properties, good chemical and mechanical stability [54-57]. The success in many of its technological applications depends on the crystalline SnO_2 with a uniform nanosize pore structure [58]. The progress in research towards tin oxide nanomaterials with high sensitivity, excellent selectivity, quick response and recovery behavior to gases has increased. Tin oxide is one of the most important materials due to its high degree of transparency in the visible spectrum, high reflectivity in infra-red range, low electrical resistance, high electrical conductivity, strong physical and chemical interaction with adsorbed species, low operating temperature, strong thermal stability in air up to 5000 °C, high band gap and when suitably doped, can be used both as a *p*-type and *n*-type semiconductor. The carrier concentration of n-type tin oxide semiconductor is very high (up to 6×10^{20} cm^{-3}) [59]. Tin occurs in two oxidation states +2 and +4, therefore two types of oxides are possible i.e. stannous oxide (SnO) and stannic oxide (SnO_2). Among these two oxides, SnO_2 is more stable than SnO.

1.3.1. Crystal Structure of SnO_2

SnO_2 is a wide band-gap metal oxide semiconductor in which inherent oxygen vacancies act as n-type dopants [60,61]. It belongs to a class of materials that combines high electrical conductivity with optical transparency and thus constitutes an important component for optoelectronic applications [54]. The study of SnO_2 is motivated by its applications as a solid state gas sensor material, oxidation catalyst, and transparent conductor [62-66]. The key for understanding many aspects of SnO_2 surface properties is the dual valency of Sn. The dual valency facilitates a reversible transformation of the surface composition from stoichiometric surfaces with Sn^{4+} surface cations into the reduced surface with Sn^{2+} surface cations depending on the oxygen chemical potential of the system [67]. SnO_2 has the rutile type tetragonal structure belonging to the $P4_2/mnm$ space group (Figure 1.3). The lattice parameters are a = b = 4.7382 Å and c = 3.1871 Å, and the band-gap energy is in the ultraviolet range between 3.5 and 3.8 eV as estimated from experimental results and theoretical calculations [68]. The unit cell of SnO_2 contains two Sn and four O atoms. Each Sn atom is at a centre of six O atoms placed approximately at the corners of the regular octahedron, while each oxygen atom is surrounded by three Sn atoms at the corners of an equilateral triangle. SnO_2 shows interest because it is a naturally non-stoichiometric prototypical transparent conducting oxide.

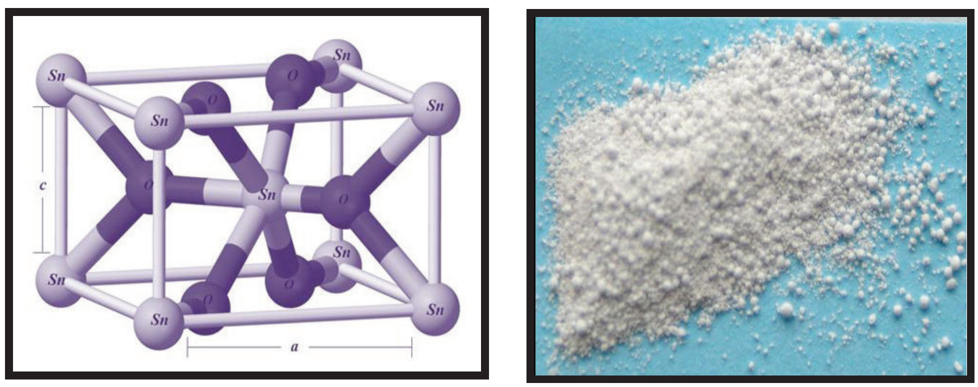

Figure 1.3. Schematic diagram of rutile type tetragonal structure and powder form of SnO_2 nanoparticle.

1.3.2. Properties of SnO_2

Table 1.1 shows the general properties of SnO_2. Tin (IV) oxide adopts the tetragonal rutile structure (cassiterite in its mineral form) with the (110) surface being the most stable one [69]. The presence of oxygen deficiency in the nominally pure material induces n-type conductivity attributable to the appearance of shallow donor levels at energy 0.03 and 0.15 eV below the conduction band [70]. The surface properties play a major role in the achievement of nanostructured configurations in the tin oxide particles [71]. Such properties are closely related to strong variations of the surface electrical conductivity with deviation from stoichiometry [70]. In fact, non-stoichiometric surface layers of about 1 nm thick (with crystalline stoichiometric cores) are proposed to be present in SnO_2 nanoparticles from Raman results [69]. On the other hand, the variation observed in the electrical conductivity with oxygen pressure ($P^{-1/4}$ dependence) is compatible with singly ionized oxygen vacancies as the main structural defect in SnO_2 nanoparticles [72].

Properties	**Data**
Chemical formula	SnO_2
Molar mass	150.71 g mol^{-1}
Melting point	1630 °C
Boiling point	1900 °C
Density	6.95 g cm^{-3}
Appearance	White or light grey powder
Odor	Odorless
Solubility in water	Insoluble
Solubility	Soluble in hot concentrated alkalis Concentrated acids, Insoluble in alcohol
Magnetic susceptibility (χ)	4.1×10^{-5} cm^3 mol^{-1}
Refractive index	2.006
Crystal structure	Rutile tetragonal
Electronic configuration	Tin [Kr] $4d^{10}$ $5s^2$ $5p^2$ Oxygen [He] $2s^2$ $2p^4$

Table 1.1. Properties of SnO_2

The addition of dopants in the parent system is one of the most significant methods to modify the characteristics of the materials. The dopants increase the surface area of SnO_2, by reducing the grain size and crystallinity. Band gap and the properties of nanomaterials can be improved by impurity doping. Doping introduces impurities into an extremely pure semiconductor for the purpose of modulating its electrical properties. The large direct bandgap and a high exciton binding energy (130meV) of SnO_2 are favourable for room-temperature UV applications. The structural defects and impurities in the nanostructures are detected using the optical band gap measurement and photoluminescence techniques. The research on optical studies on wide band gap semiconducting materials have been done. But there have been only rare investigations of SnO_2 optical properties. This is due to the even-parity symmetry of the conduction-band minimum and the valence-band maximum in SnO_2, which bans the band-edge radiative transition. Transition metal (TM) doping has been proposed to introduce magnetic functionality in conventional semiconductors [73,74]. The oxide based DMS material SnO_2 exhibits remarkable behaviour because of the native oxygen vacancies, high carrier density, transparency, high chemical and thermal stabilities. Spintronics involves the study of control and manipulation of spin degrees of freedom in solid state systems [75,76]. It could make integrated use of both charge and spin of the electrons. The ferromagnetism of DMSs is used in the field of spintronics, nanoelectronics, nanophotonics, magnetoelectronics and microwave devices. Nanometric size can organize on the various physical properties of not only the host semiconductor but also the DMS material derived from them. Undoped tin oxide nanoparticles exhibit RTFM, while their corresponding bulk sample is diamagnetic [77]. From the magnetic properties of the transition metal doped tin oxide nanostructure, we can understand that the magnetic nature is contributed by lattice defects. Defects can be introduced in the metal oxide crystals by doping [57, 78] or by varying the oxygen stoichiometry [79] which leads to the modification in the electronic band structure of the material.

The principle of DMS is the small concentration of magnetically active atoms like Ni, Mn, Co and Cu which are distributed at the cation sites of the host semiconductor and hence it possesses both semiconducting and ferromagnetic properties. When the crystallite size of some of the DMS materials is reduced to below 20 nm, they are found to exhibit better ferromagnetic properties when compared to those having microcrystalline particles (>100 nm) [80]. When the tin oxide is doped with transition metal ions (Mn, Fe, Ni, Co, etc), it becomes a good ferromagnetic semiconductors with electronic structure which has metallic, semiconductor or insulator character [27]. Many research groups have reported the magnetic properties in Ni, Fe, Mn and Co doped SnO_2 [77, 81-83]. The bandgap energy is decreased in Ni doped SnO_2 samples when Ni concentration is increased and a higher saturation magnetization is exhibited by low concentration Ni doped tin oxide nanoparticles [81].

Mn doped tin oxide exhibits room temperature ferromagnetism because of oxygen vacancy, transparency and larger carrier density. An attractive strong correlation is also found in the experimental results of the PL with the RTFM, which indicates that the oxygen deficiency related structural defects are responsible for the RTFM. Some experimental results reveal that the surface states of the nanostructures play a vital role on the observed ferromagnetism [84,85]. Ogale et al. reported room-temperature ferromagnetism in pulsed laser deposited SnO_2:Co (5 and 27%) thin films [86]. Fitzgerald et al. found ferromagnetism in Co - doped SnO_2 thin films of Co contents ranging from 0.1 to 15% [87]. Nevertheless, ferromagnetism is much more difficult to find in polycrystalline samples. Punnoose et al. detected room-temperature ferromagnetism in Co -doped SnO_2 powders prepared in 350-600°C range only in samples containing less than 1% of Co. For higher concentrations, ferromagnetism gets vanished and the samples show a paramagnetic behaviour [88].

Three types of magnetic semiconductors are

- magnetic semiconductor in which the magnetic elements are present
- dilute magnetic semiconductor, an alloy between nonmagnetic semiconductor and magnetic element
- non magnetic semiconductor which contains no magnetic ions

The exclusive characteristics of DMS are

(i) the existence of a magnetic phenomenon in host with simple band and crystallographic structures

(ii) possibility of control of charge carrier, impurities and magnetic ion concentration

(iii) excellent optical and transport properties [89,90].

Nowadays, these characteristics are used in device application and have made DMS as an interesting research field. SnO_2 nanoparticles have been successfully doped with rare earth ions (Tb^{3+}, Eu^{3+}, and Ce^{3+}) [91] and transition metal ion (Cu^{2+}) [92]. N.V. Hieu et al reports the effective dopants such as Zn, La, Pt, and Pd with SnO_2 nanoparticles for improving the sensor response or reaction speed and other characteristics of SnO_2 nanomaterials [93]. The optical properties including absorption and luminescence are enhanced and the growth of crystallites is inhibited by the dopant cobalt (Co) [42]. Moreover, 'Co' has corrosive resistance in nature, ferromagnetic and is a reasonable conductor of heat and electricity. Since ionic radius and valence of Co^{2+} (0.58A°) is smaller than that of Sn^{4+} (0.69 A°), Co ions can be expected to get substituted at Sn^{4+} site in the SnO_2 system [94]. Cu is very effective as a dopant in low concentration. The ionic radii of Sn^{4+} are 0.069 nm and that for Cu^{2+} is 0.073nm. Since the radii are comparable to each other, doping of Cu in SnO_2 occurs without any major alteration in the crystal structure. Cu doped SnO_2 can potentially be used as an opto-electronic device due to its optical properties.

SnO_2 nanoparticles have been synthesized using different methods such as hydrothermal method [95,96], solvothermal method [97], gel-combustion [98], sol–gel method [99], microwave-assisted synthesis method [100,101], chemical vapour deposition [102], R.F magnetron Co-sputtering [103], laser pulse evaporation [104,105] and spray pyrolysis [106,107]. These nanoparticles can be scaled to various sizes depending on the synthesis process.

The nanoparticles of metal oxides have been synthesized and are found a good inhibitor of different bacterial strains [108,109]. The antibacterial activity of nanoparticles is dependent on the bacterial strain. The gram positive and gram negative bacteria have differences in their cell wall. Electrostatic interactions are directly responsible for the connection of nanoparticles to bacteria. These interactions modify the integrity of cell membrane of bacteria and toxic free radicals are released which encourage oxidative stress on bacteria [109]. The assessment of antimicrobial and antioxidant activity of metal oxide nanoparticles has become one of the major studies in pharmaceutical science. Antibacterial agents are of great attention in several industries such as hospital implants, medicine, food disinfection [110,111]. Metal oxide nanostructures are considered as most promising antibacterial agents due to their high thermal stability, photo catalytic and antimicrobial properties [108,112]. The inorganic metal oxides such as TiO_2, ZnO, and SnO_2 doped with transition metal ions develop more attention in antimicrobial applications because such materials can attain effective disinfection without the formation of any harmful by-products. Antimicrobial activity of nanoparticles has largely been studied with human pathogenic bacteria such as *Escherichia coli, Pseudomonas aeruginosa* and *Staphylococcus aureus* [113].

Bactericidal activity of nanoparticles depends on size, stability, and concentration in the growth medium. While growing in medium altered with nanoparticles, the bacterial population growth can be inhibited due to the interactions of nanoparticle. Usually, the cell size of bacteria is in the micrometer range, and the pores formed in its outer cellular membranes are in the nanometer range. Since the size of the nanoparticles is smaller than bacterial pores, they can cross the cell membrane. There is another challenge in preparing metal oxide nanomaterials which is stable to restrict bacterial growth appreciably.

In the present work, the antibacterial activities of Mn-doped tin oxide nanoparticles and Co doped tin oxide nanoparticles were determined against gram-positive and gram-negative bacterial strains. *Bacillus subtilis* strains were used as gram-positive test organisms and *Escherichia coli* and *Pseudomonas aeruginosa* were gram-negative test organisms. The objective of this study is to evaluate the anti-bacterial effects of nanoparticles against various strains. Tin oxide is chosen because it has various applications regarding biomedicine due to its different properties and good catalytic activities in different reactions.

1.3.3. Applications of SnO_2 NPs

- Due to fine magnetic properties of transition metal doped tin oxide nanoparticles, they are used in magnetic data storage and magnetic resonance imaging.
- SnO_2 NPs, as one of the most important semiconductor oxides, has been used as photocatalyst for photodegradation of organic compounds.
- SnO_2 NPs are also used as catalysts, energy-saving coatings and anti-static coatings, in the making of optoelectronic devices and resistors.
- SnO_2 layers have been used as transparent and electrically conducting coatings on glass. These films have a high mechanical and chemical stability. Due to the mechanical stability of the SnO_2 they are used in hot end coatings on bottles.
- SnO_2 NPs have very good transparent mirror properties. Due to this property they are used as electrodes and anti-reflection coatings in solar cells, as heat shields in electronic devices, in thermal insulation, in solar head collectors, in photovoltaic cells, in double glazing lamps.
- SnO_2 NPs are widely used in smoke sensors, humidity sensors, gas sensors etc., due to their semiconductor properties.

- SnO_2 NPs are used in transparent ovens and in liquid crystal displays due to the transparent electrical conduction property.
- SnO_2 NPs show prominent antimicrobial properties and they act as antibacterial and antifungal agent.

1.4. Objectives of the Present Research Work

Recently, the development of semiconducting materials with novel, exclusive optical and magnetic property seems to be the versatile and appropriate materials for electronic, spintronic, optoelectronic and magneto-optical devices. The aim of our research work is to present a systematic study of structural, optical and magnetic properties of DMS materials based on wide band gap semiconductor stannic oxide (SnO_2), that have a potential application in technology. The better understanding of its structural properties with varying particle size, optical and magnetic behavior with different doping concentrations may help us to explore the materials capabilities in the futuristic applications. SnO_2 is one of the most promising candidates for DMS material which shows RTFM. Hence this research work is focused on SnO_2 semiconducting nanoparticles with transition metal doped elements.

Our investigation will be under taken with the following objectives:

- to synthesize the pure SnO_2 and transition metal (Ni, Mn, Co and Cu) doped SnO_2 nano particles using microwave assisted solvothermal method.
- to study the structural and morphological properties of tin oxide and transition metal (Ni, Mn, Co and Cu) doped tin oxide nanoparticles with the help of X-ray diffraction (XRD), Fourier Transform Infrared Spectroscopy

(FTIR), Scanning Electron Microscope (SEM), Energy Dispersive X-ray Analysis (EDAX), Transmission Electron Microscope (TEM) and Selective Area Electron Diffraction (SAED) techniques.

- to examine the optical properties of prepared samples using UV-Visible spectroscopy and Photoluminescence spectroscopy techniques.
- to detect the room temperature ferro magnetism (RTFM) in pure SnO_2 and transition metal (Ni, Mn, Co and Cu) doped SnO_2 nano particles by vibration sample magnetometer (VSM).
- to observe the antibacterial application of synthesized nanoparticles Mn doped SnO_2 and Co doped SnO_2 against Gram Positive and Gram Negative bacteria.