1. INTRODUCTION

We briefly deal with here, in this Chapter, the background information required for the present research work.

1.1. Nanoscience and Nanotechnology

Nanoscience and Nanotechnology have added new dimensions to basic science leading to a range of new technologies.

The concept of nanotechnology is attributed to Nobel laureate Richard Feynman who first elaborated this subject to some extent in his famous 1959 lecture titled “There’s Plenty of Room at the Bottom” given in California Institute of Technology. The term nanotechnology was first used by the Japanese researcher Taniguchi in 1974 when he referred to the ability to engineer materials at the nanometer scale. The term “nanotechnology” was not always used so broadly. It was coined by K. Eric Drexler in his 1986 book, Engines of Creation, to refer to his theories for molecular manufacturing, following up on visionary ideas presented 27 years earlier by famed physicist, Richard Feynman.

If Feynman was the philosopher, then Drexler was the prophet. Feynman’s definition was expanded by Drexler in a most stimulating and lateral thinking way in his book, Engines of creation, the Coming Age of Nanotechnology. To quote Drexler (1990): ‘Nanotechnology is the principle of atom manipulation atom by atom, through control of the structure of matter at the molecular level. It entails the ability to build
molecular systems with atom by atom precision, yielding a variety of nanomachines’ [1-6].

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.

Nanotechnologies are the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale. The main idea behind this terminology was the miniaturization in the electronics industry. The prefix nano in derived from the Greek work for dwarf. Technology means the building of useful things from scientific principles. Thus nanotechnology means building useful things at the $10^{-9}$ level. One nanometer (nm) is equal to one-billionth of a metre, $10^{-9}$ m. A human hair is approximately 80,000nm wide, and a red blood cell approximately 7000nm wide. Atoms are below a nanometer in size, whereas many molecules, including some proteins, range from a nanometer upwards.

Nanomaterials are those which have structured components with at least one dimension less than 100 nm.

Nanomaterials include clusters of atoms (quantum dots, nanodots, inorganic macromolecules), grains that are less than 100 nm in size (nanocrystalline, nanophase, nanostructured materials), fibres that are less than 100 nanometres in diameter (nanorods, nanoplatelets, nanotubes, nanofibrils, quantum wires), films that are less than 100 nanometres in thickness, nanoholes and composites that are a combination of these[5].
Nanomaterials are classified as

**Nanomaterials**

1. Quantum dots
2. Nanodots
3. Inorganic macromolecules
4. Nanoparticles
5. Nanointermediates
6. Nanocomposites

The term nanomaterials covers materials in one dimension (thin films), two – dimension (nanofibers, nanowires, nanotubes, etc), and three – dimension (nanoparticles/ nanopowders, nanocapsules, fullerenes, dendrimers, precipitates, colloids, quantum dots, nanostructured materials, nanoporous materials, etc [4].

Two principal factors cause the properties of nanomaterials to differ significantly from other materials: increased relative surface area and quantum effects [5].
In conventional materials most of the atoms are not at the surface. They form part of the bulk of the material, sometimes well crystallized and well laid out and sometimes full of defects and impurities that destroy the strength of the material. In nanomaterials this bulk does not exist indeed the principle difference in dealing with nanotechnological materials is the surface-to-bulk ratio. That is, the number of atoms bordering a surface divided by the total number of atoms. Materials with this property are unique and more than anything this is the reason why nanomaterials are different [3].

The world market in these materials was estimated to be about 120 billion in 2002, and it is growing at an annual rate of 15%. NSF has predicted that by 2015 the nanotechnology will become a trillion dollar industry worldwide [4].

1.2. Importance of Nanomaterials

The nanomaterials are known for their unique mechanical, chemical, physical, thermal, electrical, optical, magnetic, biological and also specific surface area properties, which in turn define them as nanostructures, nanophotonics, nanobiomaterials, nanobioactivators, nanobiolabels, etc.

Nanomaterials and nanotechnology depend on size dependent properties. In general they can be recognized as follows:

(i) Chemical properties – reactivity, catalysis
(ii) Thermal property – melting temperature
(iii) Mechanical property – adhesion, capillary forces
(iv) Optical properties – absorption and scattering of light
(v) Electrical properties – tunneling of current
(vi) Magnetic properties – super paramagnetic effect

The particle size of the material has significant influence on its physical and chemical properties. Especially, when the particle size is reduced to nanometer scale, it behaves completely different from their bulk counterpart [7].

Unusual physico-chemical properties of nanoparticles are due to three main reasons.

1. The size of nanoparticles is comparable to the Bohr radius of the excitons. This significantly alters the optical, luminescent and redox properties of nanoparticles when compared to the bulk material.

2. As the particle size decreases, the net internal cohesive force increases, and as a consequence the surface energy that depends on the internal cohesive force should increase with decreasing particle size.

3. The natural size of the nanoparticles is comparable with the size of molecules. This determines the peculiarities of the kinetics of chemical processes on the surface of nanoparticles. In general it is easily noticeable that, the reduction in the particle size results in:

   1. Increase in surface to bulk atom ratio
   2. Increase in the surface area [7].

1.2.1. Physicochemical properties

The physical properties of nanostructured materials differ fundamentally from that of the corresponding bulk materials. This is due to the reduced dimensionality on the one hand, and to the modification of fundamental properties on the other hand as the system size approaches quantum mechanical scale. Optimization of geometry,
structure, morphology and the electronic, mechanical, and optical properties of nanometer-sized systems are of fundamental importance for the design of nanostructures with favorable properties. Essentially, the reduction in the particle size from bulk to nanosize results in an increase in the proportion of surface energy and also alters the interparticle spacing [7].

1.2.2. Electrical properties

Nanomaterials can hold considerably more energy than conventional because of their large grain boundary (surface) area. They are materials in which an optical absorption band can be introduced, or an existing band can be altered by the passage of current through these materials, or by the application of an electric field. Conventional and rechargeable batteries are used in almost all applications that require electric power. The energy density (storage capacity) of these batteries is quite low requiring frequent recharging. Nanocrystalline materials are good candidates for separator plates in batteries because they can hold considerably more energy than conventional ones. The effects of size on electric conductivity of nanostructures and nanomaterials are complex, since they are based on distinct mechanism. These mechanisms can be grouped into four categories: surface scattering including grain boundary scattering, quantized conduction including ballistic conduction coulomb charging and tunneling, widening and discrete of band gaps and change of microstructures. In addition, increased perfection such as reduced impurity, structural defects and dislocations would affect the electrical conductivity of nanostructures and nanomaterials [8].
1.2.3. Dielectric materials and properties

All insulating materials fail at some level of applied voltage, and ‘dielectric strength’ is the voltage a material can withstand before breakdown occurs. Dielectric strength is measured through the thickness of the material and is normally expressed as a voltage gradient (volts per unit length). Note that the voltage gradient at breakdown is much higher for very thin test pieces (<100µm thick) than for thicker sections. The value of dielectric strength for a specimen is also influenced by its temperature and ambient humidity, by any voids or foreign materials in the specimen, and by the conditions of test, so that it is often difficult to compare data from different sources. Test variables include electrode configuration and specimen geometry, and the frequency and rate of application of the test voltage. Dielectric materials have wide range of applications as capacitors in electronic applications or as electrical insulators [8].

1.2.4. Optical properties

Nanocrystalline systems have attracted interest for their novel optical properties which differ remarkably from bulk crystals. The factors include quantum confinement of electrical carriers within nanoparticles, efficient energy and charge transfer over nanoscale distances and in many systems a highly enhanced role of interfaces. With the growing technology of these materials it is essential to understand the detailed basis for photonic properties of nanoparticles. The linear and nonlinear optical properties of such materials can be finely tailored by controlling the crystal dimensions, and the chemistry of their surfaces, fabrication technology becomes a key factor for the applications.
1.2.4. a. Semiconductor nanoparticles

The reduction in the particle size in the case of semiconductors results in the increase in the band gap which results in the shift of the light absorption towards the high–energy region (blue shift). In addition, the band edge position of valence and the conduction bands are stabilized and destabilized respectively. This leads to an increase in the oxidation and reduction ability of the semiconductor. Certainly, the rate of recombination of photoexcited electron–hole pair is also reduced greatly.

1.2.4. b. Metal nanoparticles

When the particle size of the metal atom is reduced, the energy levels are altered like in the case of semiconductor. In bulk metal, the valence and conduction band of the metal are overlapping which results in the continuous electronic states. Whereas when the particle size is reduced, the valence and conduction band energy levels are separated to a certain extent. As a result, the movement of electron (conductivity) and the optical absorption of light are different from that of the bulk metal. It can be seen in many cases that when the particle size of the metal nanoparticle is varied, the colour of the metal nanoparticles is also changed. The origin of colour for metal nanoparticles is due to the surface plasmons. The surface plasmon is a natural oscillator of the electron gas inside a given nanosphere. If the sphere is small compared to a wavelength of light, and the light has a frequency close to that of the surface plasmons, then the surface plasmons will absorb energy. The frequency of the surface plasmons depends on the dielectric function of the nanomaterial, and the shape of the nanoparticle [7].
1.2.5. Magnetic properties

Many properties of magnetic systems are fundamentally determined by the underlying electronic structure. Magnetic behaviour, electronic transport and even structural stability are intimately related to electronic properties. Reducing the size or dimension of magnetic systems changes the electronic properties by reducing the symmetry of the system and by introducing a quantum confinement. 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 grain. In the case of nanoparticles the volume is so small, therefore the thermal energy ($k_B T$) is enough to invert the magnetization with relaxation time as low as few seconds. Thus the material losses coercivity and remanence, giving rise to the so-called superparamagnetic behaviour.

Magnetic materials are broadly classified into two main groups with either hard or soft magnetic characteristics. Soft magnetic materials can be magnetized by relatively low strength magnetic fields and when the applied field is removed, they return to a state of relatively low residual magnetism. Soft magnetic materials typically exhibit coercivity values of approximately 400 Am$^{-1}$ (5Oe) to as low as 0.16 Am$^{-1}$ (0.002Oe). Soft magnetic behaviour is important in any applications involving a change in magnetic induction. Hard magnetic materials retain a large amount of residual magnetism after exposure to magnetic field. These materials typically have coercivities, $H_c$ of 10kA/m (125Oe) to 1MA/m (12kOe). The materials at high coercivity end of this range are known as permanent magnets. These materials are used principally to supply a magnetic field [7, 8].
1.3. Methods of Preparation of Nanomaterials

A major challenge in the nanomaterials science is the accurate control of the size and shape, which in turn is directly linked with the nanomaterials processing method. On the whole there are only two approaches known for the nanomaterial fabrication: bottom-up and top-down methods.

The bottom-up approach deals with the controlled assembly of atomic and molecular aggregates into larger systems (e.g., clusters, organic lattices, supramolecular structures and synthesized macromolecules). This covers the popular synthesis methods like: chemical synthesis, self-assembly, positional assembly, etc leading to the formation of particles, molecules, cosmetics, fuel additives, crystals, films, tubes, displays, atomic or molecular devices. Bottom-up approach is known as chemical or soft methods.

The top-down approach deals with the reduction in structure sizes of microscopic elements to the nanometer scale by applying specific machining and etching techniques like: lithography, cutting, etching, grinding, etc giving rise to electronic devices, chip masks, quantum well lasers, computer chips, MEMS, precision engineered surfaces, high quality optical mirrors. The top-down approach is known as physical or hard methods [4, 8]. Table 1 gives the major methods of preparation of nanomaterials.
Table 1: Methods of preparation of nanomaterials [8]

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Physical methods (or) Top-down approach</th>
<th>Chemical methods (or) Bottom-up approach</th>
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<td>1.</td>
<td>Are discharge method</td>
<td>Solvothermal</td>
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<td>2.</td>
<td>Laser Ablation</td>
<td>Hydrothermal method</td>
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<td>3.</td>
<td>Aerosol Synthesis</td>
<td>Reverse Micellar / Microemulsion method</td>
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<tr>
<td>4.</td>
<td>Inert gas Condensation</td>
<td>Sol – gel Synthesis</td>
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<td>5.</td>
<td>High – energy Ball Milling (Mechanical alloying method)</td>
<td>Microwave method</td>
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<tr>
<td>6.</td>
<td>Chemical Vapor Deposition</td>
<td>Sonochemical process</td>
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<tr>
<td>7.</td>
<td>Plasma synthesis</td>
<td>Co – Precipitation</td>
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<tr>
<td>8.</td>
<td>Electro-deposition</td>
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Here we discuss briefly some of the methods below:

1.3.1. Arc discharge method

A common technique for the production of single walled carbon nanotubes (SWNTs) is the electric arc discharge method in which carbon is vaporized between two carbon electrodes. Small diameter, single wall nanotubes can be synthesized using a d.c. arc welder to maintain the optimal settings between two horizontal electrodes in helium or argon atmospheres. This technique involves the generation of an electric arc between two graphite electrodes of which one of them is usually filled with catalyst metal powder in a helium atmosphere. Nanotubes of dichalcogenides such as MoS$_2$, MoSe$_2$ and WS$_2$ are also obtained by this technique [8].
1.3.2. Aerosol synthesis

In this method, a liquid precursor is first prepared. The precursor can be a simple mixture solution of desired constituent elements or a colloidal dispersion. Such a liquid precursor is then mistified to make a liquid aerosol, i.e., a dispersion of uniform droplets of liquid in a gas which may simply solidify through evaporation of solvent or further react with chemicals that are present in the gas. The resulting particles are spherical and their size is determined by the size of initial droplets and concentration of solid. Aerosol can be relatively easily produced by sonication or spinning. This technique has also been used in the preparation of polymer colloids. Usually, particles formed by this technique are larger particles, with diameters ranging from \( \sim 1-20 \) micron meters [8].

1.3.3. Inert gas condensation

Gas condensation was the first technique used to synthesize nanocrystalline metals and alloys. In this technique, a metallic or inorganic material is vaporized using thermal evaporation sources such as a Joule heated refractory crucibles, electron beam evaporation devices, in an atmosphere of 1-50m bar. Gas condensation allows us to produce nanoparticles with well controlled size distributions. In this process the metal is evaporated by several methods including evaporation, sputtering, laser ablation, etc., where it subsequently nucleates and grows into nanoparticles as a result of interaction with an inert gas [8].

1.3.4. High-energy ball milling

The only top-down approach for nanoparticle synthesis has been used for the generation of magnetic, catalytic and structural nanoparticles. The technique, which is
already a commercial technology, has been considered dirty because of contamination problems from ball-milling processes. Common drawbacks include the low surface area, the highly polydisperse size distributions, and the partially amorphous state of the as-prepared powders [8].

1.3.5. Solvothermal synthesis

A solvent is mixed with certain metal precursors and the solution mixture is placed in an autoclave kept at relatively high temperature and pressure in an oven to carry out the crystal growth and assembly process. The pressure generated in the vessel due to the solvent vapour elevates the boiling point of the solvent. Typically, solvothermal methods make use of solvents such as ethanol, methanol, toluene and t-butanol. This method has been found to be a versatile method for the synthesis of variety of nanoparticles with narrow size distribution and dispersity. The technique is also widely used to the synthesis of zeolites, inorganic structures and solid materials. This method is one of the simple techniques for the preparation of nanomaterials with high yield and number of materials have been grown which are well documented [8].

1.3.6. Hydrothermal synthesis

Hydrothermal synthesis can be defined as a method of synthesis of crystals which depends on the solubility of minerals in hot water under high pressure. Possible advantages of the hydrothermal method over other types of crystal growth include the ability to create crystalline phases which are not stable at the melting point. Also, materials which have a high vapour pressure near their melting points can also be grown by the hydrothermal method. The method is also particularly suitable for the growth of large good quality crystals while maintaining good control over their
composition. Hydrothermal synthesis is commonly used to grow synthetic quartz, gems and other single crystals with commercial value. Some of the crystals which have been efficiently grown are emeralds, rubies, quartz, alexandrite and others[8].

1.3.7. Reverse micellar / micro-emulsion method

This method is exemplified by the synthesis of nanoparticles inside reverse micelles or in microemulsion. In reverse micellar synthesis, reactions proceed among the reactants that are available only inside the micelle and the particle stops growing when the reactants are consumed. When a surfactant or a block polymer, typically consists of two parts: one hydrophilic and another hydrophobic, are dissolved into solvents, they preferentially self assemble at air/aqueous solution or hydrocarbon /aqueous solution interfaces. The hydrophilic part is turned towards the aqueous solution. When the concentration of surfactants or block polymers exceeds a critical level they self assemble to form micelles. Surfactants or block polymers will reside at the interface separating hydrocarbon and aqueous solutions. A microemulsion is dispersion of fine liquid droplets of an organic solution in an aqueous solution. Such a microemulsion system can be used for the synthesis of nanoparticles. The chemical reactions can take place either at the interfaces between the organic droplets and aqueous solution when reactants are introduced separately into two non mixable solutions or inside organic droplets.

Reverse micellar method is versatile because a variety of nanomaterials (binary, ternary and quaternary oxides) of wide ranging compositions have been prepared as pure homogeneous phases [8].
1.3.8. Sol-gel synthesis

Sol-gel method involves the formation of a concentrated suspension of a metallic oxide or hydroxide (sol), which is subsequently dehydrated by evaporation or solvent extraction, resulting in a semi-rigid mass (gel).

The sol-gel method is a versatile process used in making various colloidal dispersions of inorganic and organic-inorganic hybrid materials, particularly oxides and oxide based hybrids. From such colloidal dispersions, powders, fibers and thin films can be readily prepared. Although the fabrication of different forms of final products requires some specific consideration, the fundamentals and general approaches in the synthesis of colloidal dispersion are the same. Sol gel processing has many advantages including low processing temperatures and molecular level homogeneity. Sol gel processing is particularly useful in making complex metal oxides, temperature sensitive organic-inorganic hybrid materials and thermodynamically unfavorable and metastable materials [8].

1.3.9. Laser ablation

In laser ablation, high-power laser pulses are used to evaporate matter from a target surface such that the stoichiometry of the material is preserved in the interaction. The ablation process takes place in a vacuum chamber - either in vacuum or in the presence of some background gas. This method is applicable to high melting point elements and transition metals. This method was particularly suitable to carry out in situ studies on highly toxic and radioactive materials, often in trace amounts [8].
1.3.10. Plasma synthesis method

Plasma synthesis method has been successfully used in the synthesis and preparation of advanced materials such as new ceramics, nanometric metallic powders, biomaterials and superconductors. The typical size of the nanoparticles produced by this method ranges from 20 to 100nm, depending on the quenching conditions employed.

The production of nanopowders is one the most important applications of induction plasma. The induction plasma torch possesses a high flexibility and tolerance to the processing chemistry because there are no metallic electrodes to react with the reactants, and therefore oxidizing or reducing atmospheres can be used [8].

1.4. Applications of Nanomaterials

Nanoscience and nanotechnology have already been applied in various fields such as computer electronics, communication, energy production, medicine and the food industry. Nanotechnology can solve many of the world’s current problems. For example, water shortage is a serious and growing problem. Most water is used for industry and agriculture; both of these requirements would be greatly reduced by products made by nanotechnology.

Nanotechnology also can be expanded extensively to other fields of interest due to the novel properties of nanomaterials discovered and to be discovered. For example, nanowire can be potentially used in nanophotonics, laser, nanoelectronics, solar cells, resonators and high sensitivity sensors. Nanoparticles can be potentially used in catalysts, functional coatings, nanoelectronics, energy storage, drug delivery and biomedicines. Nanostructured thin films can be used in light emitting devices, displays and high efficiency photovoltaics.
The variety of nanomaterials is great and their range of properties and possible applications appear to be enormous, from extraordinarily tiny electronic devices, including miniature batteries, to biomedical uses and as packaging films, super-absorbents, components of armour and parts of automobiles. It is clear that researchers are merely on the threshold of understanding and development and that a great deal of fundamental work remains to be done [8].

1.4.1. Nanomaterials in optical devices

Current development of optical network component devices has increased demand for various optical and opto-electronic nanomaterials for a wide range of applications such as switches, waveguides, amplifiers, Bragg gratings, splitters, isolators, circulators, lasers and detectors [8].

1.4.2. Nanomaterials as dielectric materials

Dielectric materials have wide range of applications as capacitors in electronic applications or as electrical insulators. High power transmission capacitors in the radio frequency range and in the microwave frequency range as resonant cavities. Barium titanate (BaTiO₃) is an important dielectric material used in electronic applications. BaTiO₃ is a high dielectric constant material and is widely used in the manufacture of multilayer ceramic capacitors [8].

1.4.3. Nanomaterials as catalysts

The potentials of nano-structured catalysts in various fields of catalysis viz., acid-base catalysis, photocatalysis, biocatalysis are examined to explore the opportunities for future.
1.4.4. Nanomaterials in cosmetics

Nowadays, commercial sunscreens are directly applied to the skin and usually contain an extremely high amount of active ingredients. Nanoscale zinc oxide (ZnO) and titanium dioxide (TiO\textsubscript{2}) particles are used in some sunscreen products [7].

1.4.5. Nanomaterials in food

Nanotechnology has the potential to improve food processes that use enzymes to confer nutrition and health benefits. Food preservation is also of great importance for the food industry. Food spoilages can be detected by nanosensors. Other types of nanosensors are based on microfluidics devices and can also be used to detect pathogens efficiently in real time and with high sensitivity [8].

1.4.6. Nanomaterials in health

Application of nanomaterials in health are widely used in diagnosis, therapeutic applications, surgery and artificial implants. Magnetic nanoparticles have been extensively studied for biomedical applications such as hyperthermia, magnetic resonance contrast enhancement and drug delivery [7].

1.4.7. Nanomaterials in fabric industry

The production of smart clothing is easily possible by putting a nano-coating on the fabric. Fabric industries are using embedded nanoparticles to create stain repellent khakis [8].

1.4.8. Nanomaterials in communication

Applications in communication sector are electronic communication and informatics, quantum information processing, optical communication, satellite communication, wireless communication, etc [7].
1.4.9. Nanomaterials in energy sector

The promising application fields for the energy sector are photovoltaics (solar cells), hydrogen production and conversion (fuel cells), thermoelectricity (thermoelectric devices), rechargeable batteries (for example lithium batteries), supercapacitors and hydrogen storage [7].

1.4.10. Nanomaterials for water purification and environment

Nanofiltration is a technique that has prospered over the few years. It is applied only in drinking water purification process steps such as water softening, decolouring and micro pollutant control. Viruses of dimensions 10-100nm are removed by ultrafiltration. Nanofiltration systems are applied to remove heavy metals, salt contents, particles, salt heavy metals from waste waters. It is mainly used for the removal of ions or the separation of different fluids. Magnetic nanoparticles offer an effective and reliable method to remove heavy metal contaminants from waste water by making use of magnetic separation techniques [8].

The applications of nanomaterials related to environment can be classified into three categories

(i) Pollution abatement - as catalysts for decontamination of air, water and soil.
(ii) Sensors - for monitoring and detecting pollutants in various media.
(iii) Green nanotechnology - As catalysts for improving selectivity and reducing undesirable byproducts and effluents. Controlled manufacturing for reducing solvents and starting materials [7].
1.4.11. Nanomaterials in safety, security and defence

Nanomaterials are impacting almost every aspect of security and defence to both civilian and military. Special emphasis is given to performance of nanomaterials in tagging and tracking applications (Barcoding), defense technologies for chemical and biological warfare agents, military armour technology, stealthy aircraft technology and satellites technology.

China has successfully launched the first nanotechnology based satellite, Nano-satellite I, which weighed only 25kg. There are many avenues for future research in nanomaterials from the defence perspective [7].

1.5. Present Work

Synthesis of nanometer size of semiconductor and metal particles has found great interest, in recent years, due to their size dependent optoelectronic and catalytic properties. Those properties are associated with their high surface area-to-volume ratio and quantum confinement effects. Having unusual properties these nanomaterials have found wide application in various fields such as in light emitting diodes, electrosensors, photocatalysis and so fresh [9].

The last two decades saw great interest in the physical, optical and transport properties of nanometer-sized semiconductor particles or quantum dots. The optical and electrical properties, crystallinity, melting point and phase transition temperature of nanocrystallites are significantly different from the corresponding bulk and depend on crystallite size, due to quantum confinement effect. When the dimension of the semiconductor quantum dots approaches the Bohr exciton radius, there will be large changes in their properties, this effect changes the surface to volume ratio and it also
shifts electronic energy levels towards higher energy, leading to an increase in the band gap [10].

In recent years, a lot of emphasis has been focused on the development of fast and energy efficient technique for the synthesis of engineered materials. The synthesis of binary metal chalcogenides of group II-VI semiconductors in a nano-crystalline form has been a rapidly growing area of research due to their important nonlinear optical properties, luminescent properties, quantum size effect and other important physical and chemical properties [11].

Chalcogenide nanoparticles (CdS, MnS$_2$, ZnS, PbS, MoS$_2$, WS$_2$, Ag$_2$S, CdSe, Bi$_2$S$_3$, etc) play a major role in a variety of new technologies. The intense interest in this area derives from their unique chemical and physical properties, which give rise to their potential uses in the field of nonlinear optics, luminescence electronics, catalysis, solar energy conversion, optoelectronics and so on[12].

Transition metal chalcogenides (ZnS, CdS, MnS, CdSe, CdTe, PbS, PbSe, etc) represent a class of compounds that have a wide range of applications owing to their important nonlinear properties, luminescent properties, quantum size effects and other important physical and chemical properties [12].

Transition metal dichalcogenides (MnS$_2$, NiS$_2$, CoS$_2$, FeS$_2$, MnSe$_2$, etc) crystallizing in the pyrite structure are another interesting materials from both fundamental and technological points of view. They have extensive applications in energy areas such as electrochemistry and catalysis. The large surface areas and high activity of nanomaterials will enhance their applications in these fields [12-14].
II-VI quantum dots attract more attention because of their easy synthesis in the required size range [10]. CdS is one of the II – VI semiconductors. Bulk CdS has a large and direct band gap of 2.42 and 2.56 eV at 300 and 0K respectively [15]. For nanoparticles of CdS the energy gap widens [16].

The optical band gap of CdS is around 2.40 eV and the refractive index is around 2.3 and their values are greatly dependent on the preparation technique. Pal et al [17] have observed that the bandgap and the refractive indices are related to the size of the crystallites. CdS with a direct bandgap of about 2.40 eV is a suitable window material for heterojunction solar cells [18]. There are two basic requirements for the window material: (i) low electrical resistivity and (ii) high optical transmittance. CdS in a nano-crystalline form can be prepared by a variety of methods (both physical and chemical) like sol-gel, electrostatic deposition, gas evaporation, micelles, microwave assisted method, etc.

The phases $\alpha$-MnS, $\beta$-MnS, $\gamma$-MnS and MnS$_2$ are manganese chalcogenides (manganese sulphides). MnS$_2$ is one of the transition metal dichalcogenides [14,19]. MnS$_2$ is an antiferromagnetic material at about 49K. At room temperature it is paramagnetic in nature. MnS$_2$ is a semiconductor with a band gap in the near infrared region [19]. MnS$_2$ is a magnetic semiconductor [20]. MnS$_2$ has cubic structure with pyrite type, the space group of MnS$_2$ crystal is $T_h^6$ (Pa$_3$) [21].

Pyrite type phase of MnS$_2$ (P-MnS$_2$) has an antiferromagnetic ordering of the third kind (AF$_3$) below 48K involving a doubling of the chemical cell in the direction where the moments alternate [22]. Pyrite was used as a rectifier in early radios [23]. Transition metal sulphides have been widely used for sulphur removal
(hydrodesulphurization), nitrogen removal (hydrodenitrogenation) and product quality improvement in hydroprocessing of petroleum – based feed stocks [24-27].

Many of the researchers used natural single crystals of MnS$_2$ (mineral name: Hauerite) for the studies. Van der Heide et al [28] reported that they have not been able to prepare a good sample of MnS$_2$. A few of the researchers prepared MnS$_2$ nanocrystals.

For more information regarding CdS, and MnS$_2$ the readers are requested to go through Chapter 2 in this thesis.

A nanocomposite is a multiphased solid material where one of the phases has one, two or three dimensions of less than 100 nanometers (nm), or structures having nano-scale repeat distances between the different phases that make up the material. The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ markedly from that of the component materials. Some examples of nanocomposites are Fe/MgO nanocomposite used as catalysts and in magnetic devices. SiO$_2$/Co composite is used as optical fibre. WO$_3$-SnO$_2$ and TiO$_2$ – SnO$_2$ are used in humidity sensor. CdS / dendrimer nanocomposite may be useful for fabricating novel optical sensor, microelectronic devices and fingerprint detection. CdS:Mn and CdS:Ag nanocomposites are used in optoelectronic device fabrication. Cd$_{1-x}$Mn$_x$S and Zn$_{1-x}$Mn$_x$S nanocomposites are extensively studied due to their application in the field of diluted magnetic semiconductors (DMS). It has unique magneto-optical properties [29-32].
By combining transition metal chalcogenide (sulphide) and transition metal dichalcogenide (disulphide) semiconductor quantum dots of multiphased nanocomposites can be synthesized.

Doping is important for semiconductors, which plays a critical role in tuning their optical and electrical properties for the potential applications in wavelength-controlled lasers, biotechnology and solar cells. In particular, photoluminescence emission and excitation wavelength of nanocrystals may be tuned by dopants [33].

A mixed crystal can be obtained by crystallizing together two isomorphous crystals like NaCl and KCl. Isomorphism is not the only condition for the formation of mixed crystal. The lattice constants of the component crystals should be comparable. That is, when two substances A and B have closely similar structures (isomorphic structures) with not much different cell dimensions, it is found that the atoms of one can replace those of the other indiscriminately in the lattice, resulting in a mixed crystal AB [34]. The sizes of the atoms or ions and their electronic configurations are the important considerations. Any proportion of these two substances A and B may be contained in the crystal AB with cell dimensions intermediate between those two compounds.

CdS and MnS crystals are isomorphous to each other (may be at high and ambient temperatures) and their lattice constants are comparable, the difference is very small. So, based on this condition, it may be possible for us to get mixed crystals (solid solutions) of the form \( \text{Cd}_{1-x} \text{Mn}_x \text{S} \).
In the present study, we aimed at preparing new nanocomposites by the way of microwave assisted solvothermal method [35-37]. We will be getting hexagonal phase for the CdS. As two phases are possible for manganese sulphides depending on the precursors, rate of reaction, solvent, temperature, etc we will be getting as the product one or two phases in manganese sulphides.

In our laboratory, previous experience has shown that it is possible for us to get Cd (OH)$_2$ nanoparticles in the ambient conditions while performing a reaction between cadmium acetate and urea with ethylene glycol as the solvent using this simple solvothermal method [38]. However, ZnO nanoparticles is formed directly in the ambient conditions by a reaction between zinc acetate and urea eventhough Zn (OH)$_2$ is expected to form at the first instant. It is understood that special annealing in this case is not necessary [37]. Similarly, it is possible for us to get by this method the ZnS, CdS and PbS nanoparticles from their metal acetates and thiourea directly in the ambient conditions without any special annealing [37, 39-48].

The stoichiometric composition of copper sulphide exists in five significant forms such as chlacocite (Cu$_2$S), djurleite (Cu$_{1.9}$S), digenite (Cu$_{1.8}$S or Cu$_9$S$_5$), anilite (Cu$_{1.75}$S or Cu$_7$S$_4$) and covellite (CuS) [49-52]. It has been observed that by performing a reaction between copper acetate and thiourea with ethylene glycol as the solvent in the ambient conditions using a domestic microwave oven the digenite (Cu$_9$S$_5$) is formed [53].

In a preliminary experiment made by us we were able to prepare CdS [54] and MnS$_2$ [55-57] nanocomposites instead of the other phases of manganese sulphide ($\alpha$ - MnS, $\beta$ - MnS, $\gamma$ - MnS) in the ambient conditions using cadmium acetate and
thiourea, manganese acetate and thiourea respectively for CdS and MnS₂ with ethylene glycol as the solvent. This, in addition to the importance of these CdS and MnS₂, prompted us to consider nanocomposites of these sulphides for our present study.

Transparent conducting oxides (TCOs) are the metal oxides having good optical transparency and high electrical conductivity. ZnO, SnO₂, CdO and In₂O₃ are not isomorphous to each other. However phase-segregated binary systems have been successfully formed and found to be good TCOs with increased conductivity without degrading the transparency. The phase-segregated binary systems include ZnO-SnO₂, CdO-SnO₂ and ZnO-In₂O₃ [58, 59].

CdS and MnS₂ are not isomorphous systems, it may not be possible for us to get lattice mixing sufficiently for the formation of solid solutions using these systems. However, for the formation of mixed nanocrystals in the present study, reactants (cadmium acetate, manganese acetate and thiourea and urea for doping) in suitable proportions were used and the end members as they were. So, new nanocomposites are expected to be formed with (CdS)₁₋ₓ(MnS₂)ₓ (where x = 0.0, 0.25, 0.50, 0.75 and 1.0).

Several reports are available on pure and doped CdS nanoparticles and some reports are available on pure and doped MnS₂ nanoparticles. However, there is no report available on the two component CdS-MnS₂ nanocomposites. This has prompted the candidate interested on this two component undoped and doped nanocomposite material.
In the present work (CdS)\(_{1-x}\) (MnS\(_2\))\(_x\) and 2.5 and 5.0wt.% O\(^2-\) doped (CdS)\(_{1-x}\) (MnS\(_2\))\(_x\) (where \(x = 0.0, 0.25, 0.50, 0.75\) and 1.0) nanocomposites were prepared successfully by the microwave assisted solvothermal method and characterized. Manganese acetate tetrahydrate, cadmium acetate dihydrate and thiourea were used as the precursors. Urea was used as the dopant. Ethylene glycol was used as the solvent. The product masses were measured and the yield percentages were estimated.

X-ray diffraction data were collected from powder samples of as-prepared nanocrystals using an automated X-ray diffractometer for all the 15 samples. The reflections were indexed and lattice parameters were determined. Also the sizes of the samples were calculated by using the Debye - Scherrer method. The scanning electron microscope (SEM) pictures were taken for all the 15 samples to determine the surface morphology of the samples. The Energy dispersive analysis of X-ray (EDX) spectra for pure and doped CdS were recorded. The inductively coupled plasma-optical emission spectroscopic (ICP-OES) data were obtained to determine the chemical compositions of all the 15 samples.

Thermogravimetric analysis and differential thermal analysis (TGA and DTA) were done for the 5 undoped samples to understand the thermal properties.

The DC and AC electrical measurements were carried out for all the 15 samples. The DC electrical conductivity was measured in the temperature range of 35-150°C. The electrical bandgap energy value was calculated. Capacitances (\(C_p\)) and dielectric loss tangents (\(\tan \delta\)) were measured using an LCR meter (impedance analyzer) with different frequencies, viz. 100Hz, 1 kHz, 10 kHz, 100 kHz and 1 MHz at various temperatures ranging from 35 to 150°C. Dielectric constants, dielectric loss factors and AC electrical conductivities were determined for all the 15 samples.
Complex impedances were measured using an LCR impedance analyzer at different frequencies ranging from 20Hz to 1MHz at three different temperatures, viz. 313, 323 and 333K for all the 5 undoped samples prepared.

Ultraviolet - visible - Near Infrared (UV-Vis-NIR) and photoluminescence (PL) spectral studies have been carried out for all the 15 samples. The magnetic measurements like vibrating sample magnetometer (VSM) and electron paramagnetic resonance (EPR) were carried out for all the 15 samples.

We provide in this thesis a report of our present work. The thesis is divided into ten chapters with a list of literature cited (REFERENCES). A brief resume of the candidate, Publications by the candidate and Tables of AC electrical measurements are provided at the end of the thesis in the APPENDIXES section. We have already introduced the topic of the present research work in this (first) chapter. Chapter 2 gives a brief review of studies made on CdS and MnS$_2$ nanocrystals in the recent past. Preparation of nanocrystals are dealt with in Chapter 3. Structural, morphological properties and chemical composition are dealt with in Chapter 4. Thermal characterization by thermogravimetric and differential thermal analysis (TG and DTA) measurements are dealt with in Chapter 5. The DC and AC electrical and impedance measurements are dealt with in Chapter 6. The optical measurements like UV-Vis-NIR and PL are dealt with in Chapter 7. Chapter 8 deals with the magnetic measurements by VSM and EPR. Chapter 9 contains the summary and conclusion. Chapter 10 contains suggestions for future scope in the same area of research. The literature cited have been listed, finally in the ‘References’ section. Appendixes carrying a brief resume of the candidate, list of publications made by the candidate and table of AC electrical measurements are added at the end.