

CHAPTER 3

SYNTHESIS OF SEMICONDUCTOR NANOMATERIALS

3.1. Introduction:

Synthesis technique of nanoparticles is of great importance as the size, shape and their properties mainly depend on the preparation process and preparation parameters [1-8]. During the last few decades various synthesis methods have been reported for the preparation of doped nanoparticles and are still evolving. Semiconductor nanostructures are normally synthesized by either physical, chemical or solution based chemistry method. A variety of techniques like spray pyrolysis, thermal decomposition, molecular beam epitaxy, vapour phase epitaxy, electro chemical deposition, photo chemical deposition, Rf sputtering, sol-gel, chemical vapour deposition, laser ablation etc. have been widely used in the synthesis of II-VI semiconductor nanostructure. Chemical synthesis is one of the processes which permit the manipulation of matter at the molecular level. Chemical methods are promising in terms of cost reduction and ability to produce large amounts of particles. Usually the nanoparticles are being capped by different organic molecules since this is an easy way of stabilizing them to avoid agglomeration.

Semiconductor nanocrystals are normally doped in order to achieve two different properties i.e. luminescence and magnetism. Generally the doping of bulk semiconductor is carried out by high temperature thermal diffusion or molecular deposition techniques including chemical vapour deposition, atomic layer epitaxy, gas phase deposition, vacuum evaporation etc. But in this work, doping is carried out at room temperature by chemical method. Doping through chemical method has some new difficulties that are not encountered in the case of bulk material. For example, the dopant ions used in the reaction may preferably precipitate when it is in a stable phase prior to the incorporation into the host lattice. These may tend to diffuse on to the nanoparticles surface or the surrounding matrix because the impurity ions are always only a few lattice

constant away from the surface. Thus the preparation of effectively doped semiconductor nanocrystals and their applications in the nanotechnology frontier still remain a challenging task.

3.2. Synthesis Approaches for Nanomaterials Preparation:

There are two general approaches for the synthesis of nanomaterials. They are:

- (a) Top-down approach
- (b) Bottom-up approach

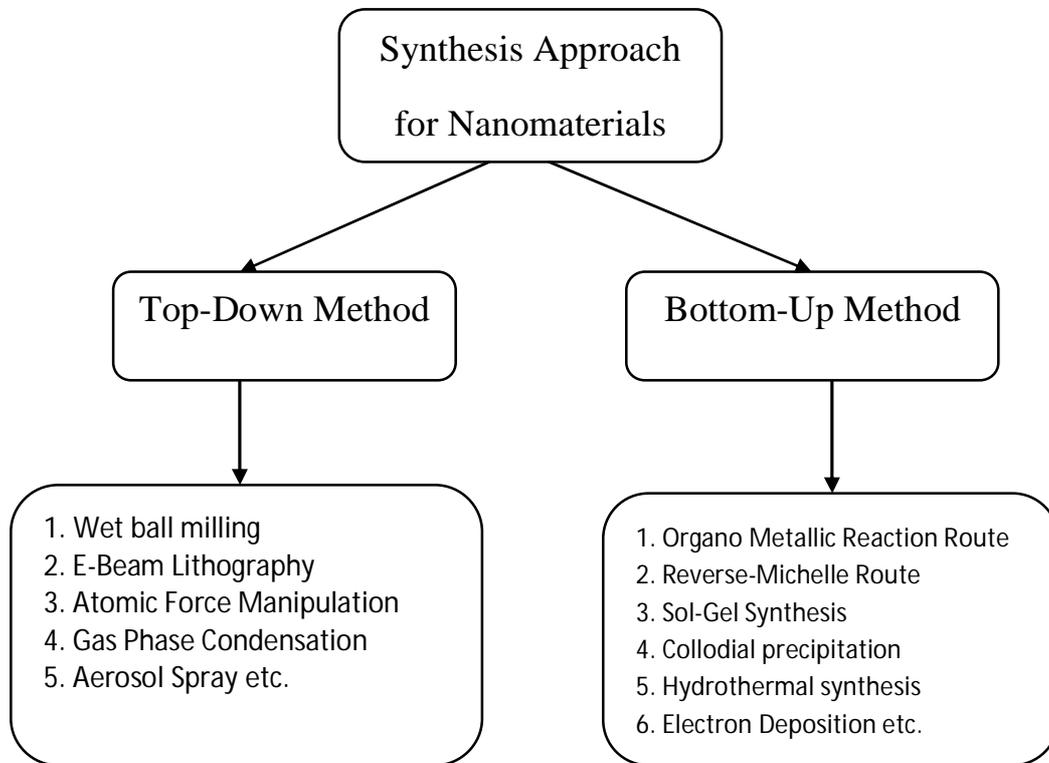


Figure 3.1: Block diagram of different nanomaterials strategies

3.2.1. Top-down Approach:

Top-down approach involves the breaking down of the bulk material into nano-sized structures or particles. Top-down approaches are extension of those that have been used for producing micron sized particles. Top-down approaches are inherently simpler

and depend either on removal or division of bulk material or on miniaturization of bulk fabrication processes to produce the desired structure with appropriate properties. Examples of such techniques are high-energy wet ball milling, electron beam lithography, atomic force manipulation, gas-phase condensation, aerosol spray etc. The biggest problem with the top-down approach is the imperfection of surface structure. For example, nanowires made by lithography are not smooth and may contain a lot of impurities and structural defects on its surface. Figure 3.1 shows the block diagram representing various nanomaterials synthesis.

3.2.2. Bottom-up Approach:

The alternative approach which has the potential of creating less waste and hence more economical is the 'bottom-up'. Bottom-up approach refers to building up of a material from the bottom atom by atom, molecule by molecule or cluster by cluster. Many of these techniques are still under development or are just beginning to be used for commercial production of nanopowders. Organometallic chemical route, reverse-micelle route, sol-gel synthesis, colloidal precipitation, hydrothermal synthesis, electrodeposition etc. are some of the well known bottom-up techniques reported for the preparation of luminescent nanoparticles. Figure 3.2 shows the schematic representation of 'bottom-up' and 'top-down' synthesis process.

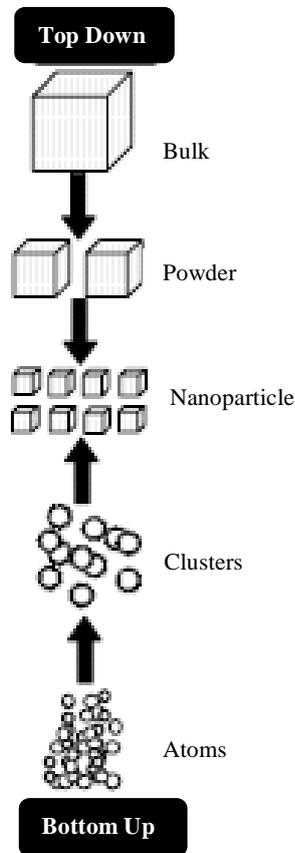


Figure 3.2: Schematic representation of top down and bottom up synthesis approach

3.3. Different Synthesis Methods for Preparing Nanomaterials:

For the synthesis of nanomaterials many experimental processes have been developed which can be broadly classified into:

- (i) Physical method
- (ii) Chemical method and
- (iii) Solution based Chemistry.

3.3.1. Physical Method:

Physical methods usually involve deposition on to appropriate substrate of the desired material from a source that is evaporated by heat or other type of energy such as

light. In these processes, vapour is created in a physical manner and hence it is also referred as physical vapour deposition method. The three most important physical vapour deposition methods are (i) Sputtering (ii) Pulsed Laser Deposition and (iii) Thermal Evaporation.

(i) Sputtering:

Sputtering is a physical vapour deposition process whereby atoms in a solid target material are ejected into the gas phase due to bombardment of the material by energetic ions. It is commonly used for thin film deposition [9, 10]. The sputtering process involves the creation of gas plasma usually an inert gas such as Argon (Ar) by applying voltage between a cathode and anode. The target holder is used as cathode and anode is the substrate holder. Source material is subjected to intense bombardment by ions. By momentum transfer, particles are ejected from the surface of the cathode and then they diffuse away from it, depositing a thin film of the material of the substrate. Thus compared with other deposition techniques, the sputtering process produces films with high purity and better controlled composition. It also provides films with greater extensive strength and homogeneity and hence permits better control of film thickness [11-13].

For nanostructured materials, sputtering becomes a useful tool as the material composition, thickness, homogeneity, deposition time, substrate temperature etc. can easily be controlled by the process. Specially, deposition time and substrate temperature are the most useful parameters to deposit nanostructured materials on various substrates. Low deposition time is necessary to prevent the deposition of large number of particles to retain their nanostructure and decrease the probability of the particles to agglomerate into bigger cluster. On the other hand, low substrate temperature also prevents the agglomeration of the particles to remain in nanocrystalline form.

(ii) Pulsed Laser Deposition:

Pulsed Laser Deposition (PLD) is another deposition technique used for nanomaterials synthesis as well as thin film deposition. In this deposition technique, a high power pulsed laser beam is focused inside a vacuum chamber to strike a target of the desired material and composition to vapourize the target and deposit materials on a substrate. The deposition generally takes place in ultra high vacuum or in the presence of some background gas of certain pressure. Argon (Ar) are used at some desired pressure to control the deposition rate as well as the film composition whereas reactive gas like oxygen or nitrogen are sometimes used to deposit oxide or nitride materials. PLD has been used to form nanowires and nanoribbons as well as multi-component thin films [14-16]. PLD can be performed in several different types of chamber which mainly consists of a vacuum chamber, a place for the target material, the deposition substrate and a window through which the laser beam can be transmitted. This technique offers many potential applications from integrated circuits and optoelectronics to micro mechanics and medical implants [17].

(iii) Thermal Evaporation:

Thermal evaporation is one of the most common forms used for synthesis of semiconductor nanoparticles. During this process, the substrate and source materials are placed inside a vacuum chamber. This vacuum can reach pressure as low as 10^{-9} Torr. A heating source is used to heat the source material to its vapour point or above. Upon evaporation, the vapour source will deposit along the substrate in the cooler area of the vacuum chamber. The main difference in the types of thermal evaporation techniques lies with the type of heating used to vaporize the source material. Some examples of heating sources are electron beam, radio frequency (RF) induction and resistive heating. Electron beam evaporation is based in the heat produced by high-energy electron beam bombardment on the material to be deposited. The electron beam is generated by an electron gun, which uses thermionic emission of electrons produced by an incandescent

filament. Emitted electrons are accelerated towards an anode by a high difference of potential. The crucible itself or a near perforated disc can act as the anode. A magnetic field is often applied to bend the electron trajectory, allowing the electron gun to be positioned below the evaporation line. As electrons can be focalized, it is possible to obtain a much localized heating on the material to evaporate with a high density of evaporation power. In comparison, RF induction uses an alternating current through an induction coil to heat the source material. The current produces a magnetic field which induces eddy currents in the source material. This provides localized heating without any physical contact between the coil and the source material. Resistive heating provides heat by sending an electrical current through a resistive coil and is a non-localized heat source as it heats the area around it as well. Therefore, it is commonly used for furnace applications. Resistive sources of heating are the most commonly used for thermal evaporation and have created a variety of nanostructures [18-21].

3.3.2. Chemical Method:

Semiconductor nanostructures are mostly synthesized by chemical method. In a typical chemical synthesis, reactants are mixed in an appropriate solvent to produce the nanostructured product of interest. The result of the synthesis depends strongly on a number of factors such as concentration, temperature, mixing rate or pH if in aqueous solution [22-29]. The advantage of chemical method is versatility in designing and synthesizing new materials that can be refined into a final product. The primary advantage that a chemical process over other methods is good chemical homogeneity, as chemical synthesis offers mixing at the molecular level. Molecular chemistry can be designed to prepare new materials by understanding how matter is assembled on an atomic or molecular level and the consequent effects on the desired material macroscopic properties. A basic understanding on the principles of crystal chemistry, thermodynamics and phase equilibrium and reaction kinetics is important to take advantage of many benefits that chemical processing has to offer.

Nanostructured materials are also prepared by chemical vapour deposition (CVD) or chemical vapour condensation. In these processes, a chemical precursor is converted to the gas phase and it then undergoes decomposition at either low or atmospheric pressure to generate the nanostructured particles. These products are then subjected to transport in a carrier gas and collected on a cold substrate, from where they are scraped and collected. The CVC method can be used to produce a variety of powders and fibres of metals, compounds or composites. The CVD method has been used to synthesize several ceramic metals, intermetallic and composite materials. Semiconductor clusters have traditionally been prepared by use of colloids, micelles, polymers, crystalline hosts and glasses [30]. The clusters prepared by these methods have poorly defined surfaces and a broad size distribution, which is determined to the properties of semiconductor materials.

3.3.3. Solution Based Chemistry:

Solution based chemistry is an important precursor which is subsequently converted to the nano phase particles by non-liquid phase chemical reactions. Some of the importance methods for solution based chemistry are (i) Chemical co-precipitation method (ii) Sol-gel method and (iii) Hydrothermal method

(i) Chemical Co-precipitation Method:

Novel route for the synthesis of semiconductor nanoparticle are an integral aspect of material science. The chemical co-precipitation method is a common technique for the synthesis of semiconductor nanoparticle and in the past few decades, this process is a fast developing area in the field of nanoparticle research. Chemical precipitation is the formation of solid in a solution when aqueous solutions of anion (-vely charged ions) and cations (+vely charged ions) combine to form a compound that is insoluble in water. The insoluble solid is called the precipitate and the remaining liquid is called the supernate. Precipitation reaction occur when a cation and an anion of two aqueous solution react to form an ionic insoluble solid known as precipitate in the solution where

the reaction is taking place. However based on the solubility rules, not all aqueous reactions form precipitate. Therefore, one must first consult the solubility rules before they can determine if a precipitate will form and make a net ionic equation. In this work, we have synthesized CdS:Mn and ZnS:Mn by chemical co-precipitation reaction from homogenous solutions of cadmium, zinc and manganese salts. The reaction proceeds with the nucleation of CdS and ZnS crystals which are immediately passivated by the anion in the solution. This in turn attracts cations i.e. cadmium, zinc and manganese which contributes to growth of crystal. These CdS:Mn and ZnS:Mn nanoparticles are stabilized using polyvinyl alcohol as capping agent.

The main objectives for adopting chemical co-precipitation method in our work are as follows:

- (i) Simple to fabricate.
- (ii) Require inexpensive and simple instruments.
- (iii) Relatively shorter synthesis time.
- (iv) Possibility for large scale production.
- (v) Possibility for surface passivation with less difficulty.
- (vi) Feasible to synthesize metals, alloy, insulator, semiconductors and even compound nanoparticles.
- (vii) Possibility to dope large number of materials at room temperature.

(ii) Sol-gel Method:

Sol-gel is a wet chemical based self-assembly process for nanomaterials formation. It incorporates the creation of inorganic networks through the formation of a colloidal suspension in a liquid (sol) and gelation of the solution to form a network in a continuous liquid phase (gel). The precursors used for synthesizing the colloids generally consists of metallic ions and ligands, which are elements surrounded by various reactive species. In general, sol-gel formation occurs in four steps:

- (i) Hydrolysis and alcoholysis
- (ii) Water and alcohol condensation and polymerization
- (iii) Growth of particles
- (iv) Agglomeration of particles followed by the formation of networks throughout the liquid medium resulting in thick gel.

In general, all the above steps are dependent on several initial conditions such as pH value of the sol, temperature of the reaction, reagent concentrations, time of reaction, nature and concentration of the catalysts. By controlling these parameters, it is possible to vary the structural, electrical and optical properties of the sol-gel derived inorganic network over a wide range. Once the gel is formed, there are several ways to convert this gel to the desired solid form. Depending on the deposition and drying processes or condition, this gel can be converted into various forms such as aerogel, xerogel, gelled spheres, nano-powders, nanostructured layers etc. The important applications for sol-gel are the formation of nano-wires, nano-rods via porous matrix, such as alumina template, porous silicon, etc.

(iii) Hydrothermal Method:

Hydrothermal synthesis included the various techniques of crystallizing substances from high temperature (150 °C-700 °C) and high pressure water solutions. This method harnesses the solubility in water of almost all the inorganic substance under these conditions and the crystallisation of the dissolved material from the fluid. The crystal growth is performed in an autoclave made of steel or titanium alloys with a hot and a cold end which maintain a temperature gradient in the reaction chamber. The growth principle is simple, the reaction chamber is filled with water and reagents which is due to temperature gradient in the hotter part of the autoclave. The reagents are dissolved while in the cooler part there is the nucleation and consequent crystal growth. Usually, these kinds of synthesis need few hours to several days to be completed.

With this technique it has been possible to produce nanoparticles which are not possible at room temperature because of the peculiar structural properties that reagents and water can have at high temperature and pressure condition. Tuning of parameters such as reaction time, temperature, pressure, reagents type and concentration allows the synthesis of different kinds of nanoparticles with different size and shape and a good size distribution.

3.4. Size Controlled Preparation of Nanomaterials:

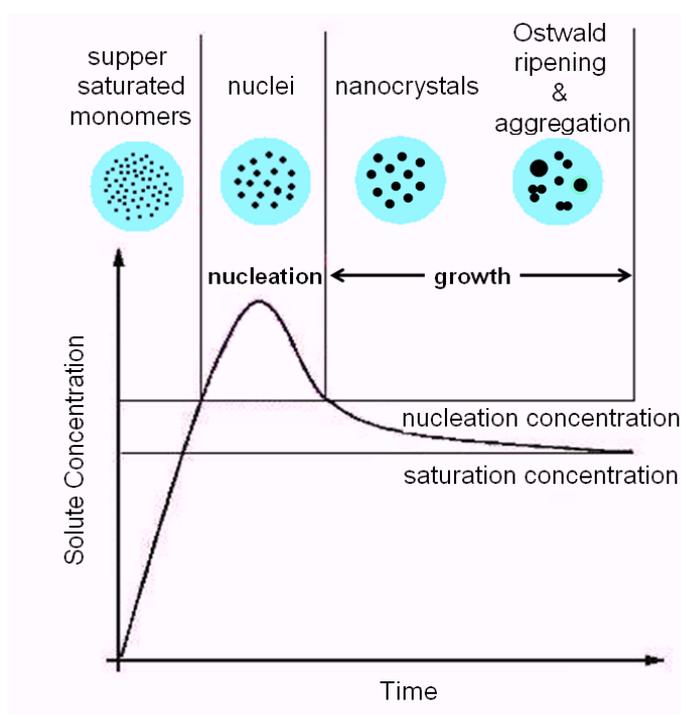


Figure 3.3: The LaMer and Dinegar plot: Schematic illustration of nucleation and growth process during the preparation of nanoparticles

In order to control the size and size distribution of prepared nanoparticles, we need to understand the nucleation and growth process of the particles. The LaMer and Dinegar plot shown in figure 3.3 illustrates the production of monodispersed colloids which requires a fast nucleation followed by slower controlled growth of the existing nuclei [31]. Generally the synthesis of nanoparticles can be divided into three steps that is (i) Nucleation (ii) Nanoparticles growth and (iii) Nanoparticles ripening.

In the nucleation stage, fast nucleation can be achieved by using rapid injection of precursors into a vigorously stirred flask containing a hot coordinating solvent. Large amount of tiny seeds i.e. monomers are formed spontaneously as a result of the fast reaction at high temperature. As the reaction continues, the monomer concentration increases and rises above the supersaturation concentration, eventually reaching a critical concentration at which nucleation occurs and many nuclei formed in a short period. Then the supersaturation is relieved and as long as the monomer concentration stays lower than the super saturation concentration, no further nucleation takes place. After that the reaction enters the nanoparticle growth stage. During this stage, the particles continue to grow by molecular addition. Size-focussing can occur when the nanocrystals present in the solution are all slightly larger than the critical size i.e. the particle size at which atomic attachment and detachment are at equilibrium. Smaller particles grow faster than the larger ones. The desired size and narrow size distribution can be achieved by stopping the reaction at suitable time during size focussing process. On the other hand size-defocusing occurs when the reactant concentration is too low to support the nanoparticles growth. This process is usually known as ‘Ostwald ripening’ which is derived from the name of the German physical chemist who first described it. In this stage, larger particles continue to grow at the consumption of the smaller ones. As a result, the average nanoparticle size increases over time, accompanied by an undesirable broad size distribution [32-34]. In such case, size refocusing can be achieved by injection of additional monomer at the growth temperature, which shifts the critical size back to a small value. By doing this, the narrow size distribution of the nanoparticles can be resumed [34]. Nanoparticles can also grow by aggregation with other particles. In order to control such a secondary growth, suitable surface protecting reagents must be added e.g. organic ligands, inorganic capping materials, inorganic matrix or polymers [33]. The surface protecting reagents can provide a steric barrier to counteract the Van der Waals attractions between nanoparticles, so as to prevent nanoparticle aggregation. They can also affect the reactivity and stability of the seeds (monomers) as well as the nanoparticle produced.

3.5. Role of Capping Agent and Polyvinyl Alcohol (PVA):

Semiconductor nanoparticles are themselves highly unstable in the absence of capping agent and hence they agglomerate very rapidly [35]. For this reason, capping of nanoparticles is necessary to provide chemical passivation and also to improve the surface state which has substantial influence on the optical and electronic properties of nanoparticles. These optoelectronic properties include changes in emission colour of semiconductor with size, improved solubility of semiconductor in solvents and improved catalytic properties etc. [36]. This is generally understood as the presence of surface trap states arising from surface non-stoichiometry unsaturated bonds etc. These surface states trap electrons and holes and degrade the optical properties of the materials. The control of the surface is a key to prepare high quantum yields nanoparticles. Both the organic materials and inorganic materials have been used for surface control. Thus, the surface control process is called surface passivation or capping. It is made through bonding the surface atoms to another material of a much large band gap, eliminating all the energy levels inside the gap. The ideal termination naturally removed the reconstructions, strains and produces an abrupt jump in the chemical potential for electrons and holes at the interface. Furthermore, capping of semiconductor materials especially during synthesis controls particle agglomeration and passivate the semiconductor surface against surface defect [37, 38]. This capping agent molecule binds to the surface of the particle by stabilizing the nuclei and larger nanoparticles against aggregation, hence controlling the growth of nanoparticles [39].

The choice of capping agent depends on the material of the nanoparticle core, particle size and the solvent during synthesis. Capping agents with strong binding molecule form dense layer on the particle surface that stabilizes nanoparticles better, while weak binding molecule results to fast particle growth leading to large nanoparticle size and aggregation [40]. Therefore, the choice of a suitable capping agent, the dynamic of binding and unbinding and its concentration becomes the pre-requisite for particle size

regime, stabilization against aggregation and high quantum yield during synthesis of nanoparticles.

In the past few years, various materials that provide distinct cavities have been used to synthesize semiconductor nanoparticles, for example zeolite, micelles, molecular siever, mesoporous solids or polymers to restrict the growth [41-46]. Among them using polymer as a capping agent for controlling the growth of the particle is a very promising scheme for nanoparticle preparation.

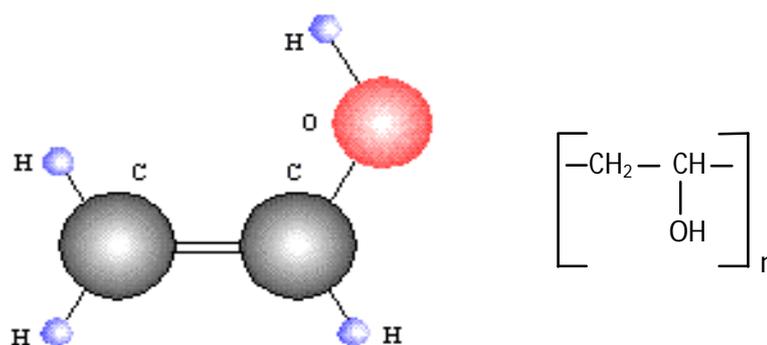


Figure 3.4: Structure of Polyvinyl Alcohol

Polyvinyl alcohol (PVA) has excellent emulsifying and adhesive properties. Because of its high viscosity of the polymer solution, it would be helpful in controlling the growth of the nanoparticles. The repeat structure unit of polyvinyl alcohol has ligands that permit metal ion coordination and has similar capabilities of complexing along the polymer chain. Figure 3.4 shows the structure for polyvinyl alcohol. These properties automatically generate a regular structure so that the semiconductor nanocrystals formed by the chemical methods are of similar dimension and evenly distributed. Polyvinyl alcohol is not electrolyte sensitive and the sample can be obtained in both liquid and solid form. Because of these manifold advantages, we have selected PVA as a capping agent for the synthesis of CdS and ZnS nanoparticles doped with varying concentration of Mn^{2+} in our experiment.

3.6. Doped Semiconductor Nanomaterials:

The technique of incorporation of atomic impurities in semiconductor is known as doping. The incorporation of impurities into semiconductor lattices can affect the electronic as well as the magnetic and optical properties of the semiconductor. So, doping is a powerful and effective way to alter the properties of semiconductors. The ability to use atomic impurities in nanoparticles therefore extends the already exciting size-dependent properties. These dopants often function as emissive traps with trap energy levels between the valence and conduction band of the host crystals. Doping is essential also in the semiconductor industry because most semiconductors are essentially insulators without doping at room temperature. For doped semiconductor, the conductivity can be increased by adding a small amount of another material in it. So similar to bulk materials, doping has been used for semiconductor nanomaterials [47, 48]. There are some unique challenges with doping nanomaterials. For example, when the size is very small, one dopant ion per nanostructure can make a major difference in the properties of the nanostructure. The addition of the dopant can introduce electronic and structural defects into the pristine nanomaterials that can be advantageous or deteriorous. Thus, it is therefore critical to attempt to dope the nanostructures uniformly that is same number of dopant ion per nanostructures. There are further complications to this issue beyond just the number of dopants. For example, the location of the dopant on the surface versus the interior affects the optical or electrical properties differently. Another issue is the interaction among the dopants when the dopant concentration per particle is high e.g. two or more dopants in close proximity. This will remain a challenging and interesting issue for years to come, particularly when spatial features become smaller and the importance of the dopant becomes more critical. Almost all studies of doped semiconductor nanostructures have been performed on ensemble average samples i.e. the sample contains particles with a distribution of dopant per particle.

For instance, doping of a semiconductor with magnetic impurities produces a dilute magnetic semiconductor (DMS) which is one of the exciting developments in

semiconductor science and technology [49]. The magnetic impurity can generate a huge Zeeman splitting, over two orders of magnitude larger than the splitting of normal semiconductors, giving rise to potential applications in optical and spin-based electronics [50]. Furthermore, doping with conventional impurities allows control of the number of carriers (electrons and holes) in semiconductors. For example, an impurity with one fewer valence electron than the host atom can provide its extra hole to the semiconductor, resulting in ‘p-type’ doping. In contrast, an impurity with one more valence electron can donate an electron to give ‘n-type’ doping. These types of doping have built the foundation for p-n based semiconductor devices, such as computer chips [51].

In this work, we will discuss about the complexity and uniqueness of CdS and ZnS nanoparticles doped with different concentrations of Mn^{2+} . Because the incorporation of Mn^{2+} ions into cadmium or zinc (Cd^{2+} or Zn^{2+}) lattices are easier due to their similar chemical properties (e.g. ionic radius, valence band). Mn^{2+} has $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5$ electronic configuration and hence Mn^{2+} ions used in many luminescent materials has a d^5 configuration. The Mn^{2+} ions exhibit a broad emission peak whose position depend strongly on the host lattice due to changes in crystal field strength with host lattice. The emission colour can vary from green to deep red, corresponding to ${}^4\text{T}_1$ - ${}^6\text{A}_1$ transition [52]. Since this transition is spin allowed, the typical luminescent relaxation of this emission is of the order of milliseconds [53, 54]. Bulk ZnS:Mn has been widely used as a phosphor [55] particularly in alternating current thin film electron luminescent devices [56-58]. Mn^{2+} d-electron states acts as a luminescence centres while interacting strongly with s-p electronic states of ZnS host lattice into which external electronic excitation of the Mn^{2+} semiconductor host (CdS, ZnS) have been suggested. In one mechanism, a hole trapped by the Mn^{2+} ion is recombined with an electron, leading to Mn^{2+} in an excited state [59, 60]. Since a large portion of the atoms in nanocrystals is located on or near the surface, the surface properties should have significant effects on their structural and optical properties [61].

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