

INTRODUCTION TO NANOMATERIALS

SAMPLE

CHAPTER 4: SEMICONDUCTING NANOMATERIALS

4.1. Introduction

The range of nano-scale starts from 1 nm (nanometer) and reaches 100 nm, broadly classifying roughly around 100 to almost 10 million atoms. Though the lower and upper boundaries are not well defined but are selected in a way that on the top end, it excludes micrometer-scale objects, and on the bottom end, it excludes individual atoms (Ahn et al., 2006; Huang et al., 2017). This state of matter can be regarded as an intermediate state, lying somewhere between the molecular or atomic regime and the bulk phase. In nano-sized systems, we can control material properties by tuning their size. The optical and electronic properties of semiconductors and metals in the nano-scale regime, strongly depend on their crystallite size (Yao & Yu, 2008; Kim et al., 2012). The credit for the advancement of size-dependent fundamental properties should be given to aspects such as the increased surface area, and especially quantum effects, as with decreasing size, it becomes increasingly important. This change, especially for semiconductors, is quite impressive. For instance, the bandgap of CdSe nanocrystals can be tuned simply by altering their size, this gap can be tuned between 1.7 and 3 eV. Thus, the material becomes able to emit and absorb across the entire spectrum. The fact that in a single chemical composition material, the properties can be varied so remarkably is fascinating and in addition, this can be done by simply altering parameters of bulk material such as its size (Li & Zhang, 2009; Zhao & Burda, 2012).

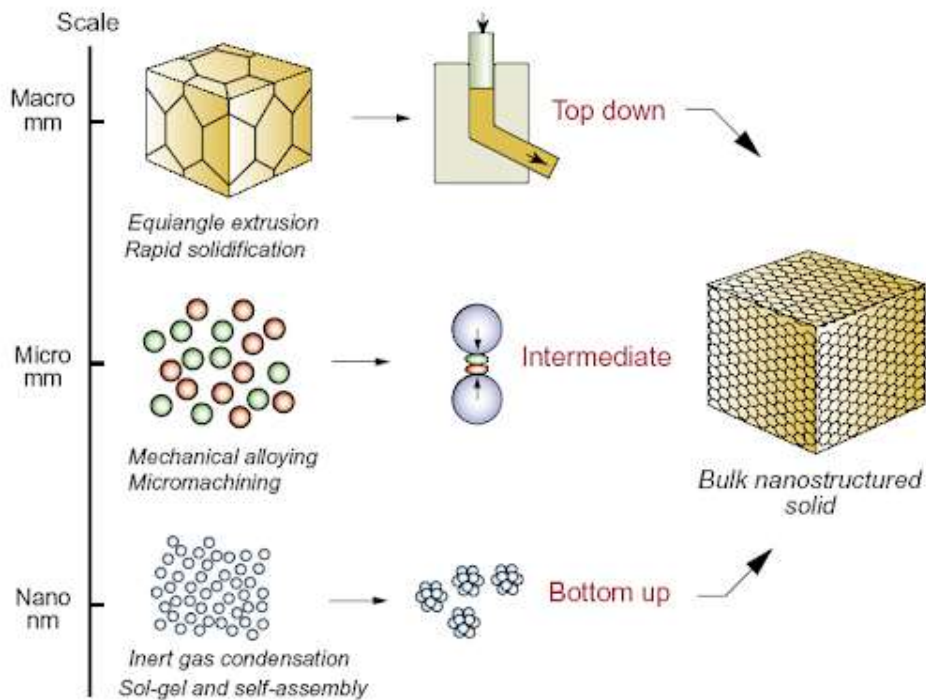


Figure 4.1. Semiconducting nanomaterials along with their synthesis

A semiconducting crystallite is only a few nanometers and it has size-specific electronic and optical behavior and is usually referred to as a quantum dot (QD) or a semiconductor nanocrystal (NC). A semiconductor nanocrystal is such promising technological material, as we can exploit its ability for controlling electronic and optical properties for various applications, such as single-molecule transistors, light-emitting diodes, solar cells, and bio-labels (Barber & Freestone, 1990; José-Yacamán et al., 1996).

4.2. Doping Semiconductor Nanocrystals

The doping or introducing trace intentional impurities is primarily for controlling the semiconducting material's behavior. Dopants can strongly modify the electronic, optical, and magnetic properties of bulk semiconductors. A dopant having an extra valence electron in contrast to the host atom, it is substituting for, may donate that valence electron to the semiconductor for transporting electronic charge (Einstein, 1905; Gans, 1912). Similarly, a hole can be donated by an impurity atom (that has a vacancy) to the SC. The ability to control the number of carriers precisely in the SC, through the method of doping, has accelerated the advancement in SC-based optoelectronic and electronic technology. Doped SCs has the advantage that the device engineer is provided with a versatile range of mobilities, to make sure that the materials contain the properties that fulfill the specific requirements (Kim et al., 2013). Thus, the versatility of nanocrystals can be extended by adding dopants. In SC NCs substantially, the range of properties can be expanded by doping; hence a plethora of applications are opened which ranges from bio-imaging and solar cell to wavelength tuned lasers (Guyot-Sionnest et al., 1999; Murray et al., 2000).

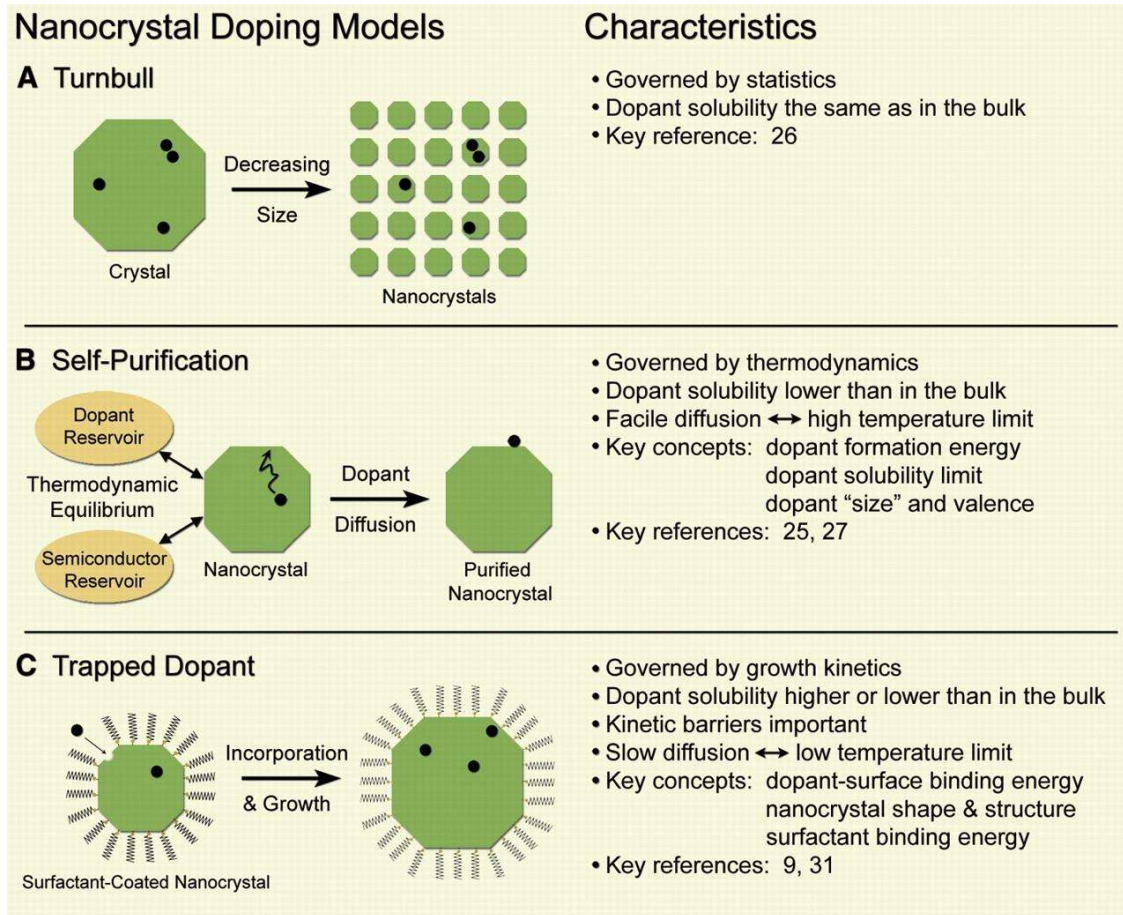


Figure 4.2. Semiconductor doping models

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The bulk-doping field is in use for decades. In 1994, Bhargava et al. strengthened the concept of nanocrystal doping when in zinc selenide manganese-doped NCs, interesting luminescent properties were observed. Since then, rare earth elements and transition metals have doped several II-VI SC NCs. However, SC NCs are still not doped with electronic dopants, which are regarded as highly advantageous (Turkevich et al., 1954; Stetsyk et al., 2015).

4.3. Issues and Challenges in Doping Nanocrystals

The most potential class of nanotechnology is represented by NCs. In the last twenty years, their intrinsic properties are ruled out. Dopant's addition in NCs extends its possible applications and also their properties. However, several challenges are faced while incorporating the dopants efficiently and successfully into NCs (Eric, 1992). The major drawback is that there exists no reliable or specific synthetic technique that ensures the incorporation of controlled dopant. NCs have high surface-to-volume ratios due to which a large portion of the dopant population is at the surface. At the surface sites, dopants may be considerably different from the ones in the NC cores. Inside the NC, dopant atoms

are not uniformly distributed throughout the NC. Furthermore, doped NC's ensemble will always possess a statistical distribution per NC of dopants. This inhomogeneity might adversely affect the doped material's targeted properties.

Moreover, how can we ensure that the nanocrystals are successfully doped? An intrinsic problem in doping NCs is that only a tiny amount of the final product is the impurity, thus, the doped nanocrystal cannot be distinguished from its analog (pure), if microscopy (Transmission Electron Microscopy and Scanning Electron Microscopy) and X-ray crystallographic techniques are used.

Therefore, it is difficult to experimentally probe these materials. Doping SC NCs have been highly unsuccessful because of these challenges. Nevertheless, if someone figures out the issue of incorporating dopants inside an NC, introducing extra charge carriers, even then, there exists a high probability that he might face some additional problems. NCs having an extra electron possess the ability to behave as a reducing (oxidizing) agent. At the surface, this results in a redox reaction, which might consume the available charge carrier, rendering it unavailable for conduction. A strong proclivity, either for *n*-type (extra electrons) doping or *p*-type (extra holes) doping, is exhibited by a wide bandgap II-VI semiconductors (ZnSe, ZnTe, CdS, CdSe). This results in restricting their usage in practical applications i.e. lasers and light-emitting diodes. One requires a deep knowledge of the doping mechanism for circumventing the mentioned problems and for achieving successful doping in them (Klimov et al., 2007).

The aim of this chapter is to develop a better understanding of the fundamental science behind the process of doping, to develop new techniques that can incorporate the dopant molecules into the nanocrystals, through means of appropriate spectroscopic techniques for verifying the presence of dopants. Finally, the location of the dopants is characterized by them. Not exclusively, but largely, the focus of this thesis is on the doping of IV-VI (PbSe) and II-VI (CdSe) colloidal SC NCs, as these are usually thoroughly and widely studied NC-systems. Furthermore, these NCs possess a massive potential for applications in solar cells, field-effect transistors, and light-emitting diodes.

So far, any evidence for electronically doped NCs has not been presented. We are hopeful that through electronically doping NCs, we will be able to complete the set of electronic, magnetic, and optical properties for SC NCs. This thesis gives us an exciting opportunity for researching and further enhancing the knowledge of doping SC NCs. Electronic doping may also give a niche that may open new pathways for further research, it may set a foundation for creating novel materials that may possess important applications.

4.4. Phase Transitions in NCs

This thesis aims to acquire the knowledge about the effect of dopant atoms (focusing more on silver) on the properties of the lead and cadmium chalcogenide NCs; we have also focused on observing the

effects of these atoms on the spectrum's other end *i.e.*, in the high limit of doping, where usually the silver chalcogenides are available, though minute amounts of cadmium and lead atoms are also found there in form of impurities. A very few reports about the study of silver chalcogenide NCs are available. Therefore, a lack of knowledge about them motivated us to study their properties in detail.

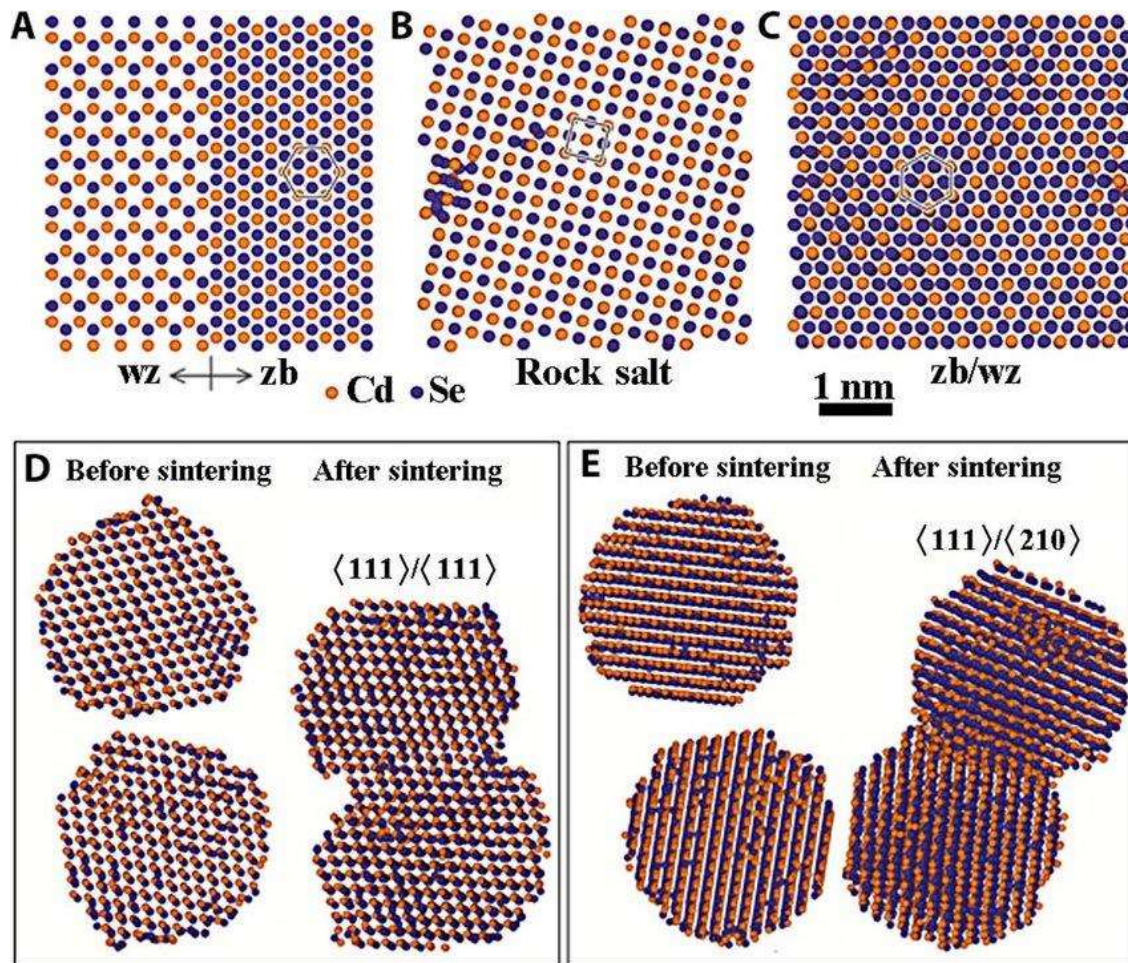


Figure 4.3. NCs phase consolidation and transition. (A) The initial configuration is shown. (B) Intermediate configuration at ~5 GPa pressure is shown. (C) The final configuration after releasing the pressure is shown. Sintering's two MD simulation cases showing (D) the $\langle 111 \rangle / \langle 111 \rangle$ interface formation and (E) the $\langle 111 \rangle / \langle 210 \rangle$ interface formation

[https://www.researchgate.net/figure/MD-simulation-of-pressure-induced-nanocrystal-phase-transition-and-consolidation-A_fig4_316750709]

We know that NC's material properties can be tuned by adding impurities and by changing their size, apart from this, another way to change their properties is by varying their temperature and tapping into new phases of crystals of the same material, exhibiting different properties. The silver chalcogenide is one of these systems, it exhibits rich phase behavior. Silver chalcogenides, as a bulk material, belongs to a class of semiconductor that has numerous intriguing properties. They have high ionic and electronic

mobility and are mixed conductors: in them, both silver ions and electrons can move easily within the semiconductor. A reversible phase transition is experienced by them [for example, water experiences phase transitions from ice (in solid form) to water (in liquid form) to water vapor (in gas form)] from α -phase (that is a low-temperature phase) to β -phase (that is a high-temperature phase) and between these phases, temperature ranges varies from 135-180 °C (it depends on what is being used i.e. silver telluride, silver sulfide, or silver selenide). In its electronic properties, a strong change is observed while these transitions are taking place.

Though these materials are being widely studied in the bulk, at the nano-scale, only a few studies have been carried out. Shrinking of the material's size to the nanoscale results in metastable crystal phases, which are absent in bulk crystals. It is possible to expand the range of structures by varying the temperature and size of the material, and hence, one can derive novel properties.

Though nanotechnology has recently caught the eye of many but the nanostructures are not new. Even in the Roman era, nanometer-sized structures and devices existed.

The Purple of Cassius comprised of a mixture of Au nanocrystals and tin oxide and the Lycurgus cup, having Ag and Au nanocrystals in its walls, serve as two classic examples. At medieval cathedrals, metal NCs in the glass windows and Maya blue, with oxide and metal NCs, demonstrate the usage of nanoparticles for ages. Though at that point, any clear knowledge about the nanoscale phenomena was not available.

In the 17th century, despite the early work, systematic studies about these materials were not really carried out until the 1800s. In 1857, Michael Faraday finally realized that the color of church windows is due to the role of metal particles, later it was followed by Einstein (1905) and then, several theories for the NC's properties were proposed by them. However, until the 20th century, the science of colloidal nanoparticles was fairly neglected. In 1915, Ostwald named his book "The World of Neglected Dimensions". This book was on colloids. In 1960, at the American Physical Society, Feynman's lecture entitled "There is Plenty of Room at the Bottom," resulted in reviving the interest to generate the nanoparticles of various materials. Though in metal nanoparticles, unique properties were identified but until the early 1980s, similar properties were not identified in SC NCs. Then, in the energy of the Highest Occupied Molecular Orbital (HOMO) – Lowest Unoccupied Molecular Orbital (LUMO) transition, a size-dependent shift in SC NCs was observed by Klimov et al. (2007). This breakthrough resulted in rapid advancements and generated a renewed interest in SC NCs. Instrumentation advancements have aided in this progress, as they facilitate in characterizing these NCs. Today, we can study and prepare the NCs of SCs, metals, and other substances. Rapid advances in both theoretical and experimental methods have helped in developing a better understanding of their properties.

4.5. Physics of SC NCs

4.5.1. Surface

NCs have such a small dimension that in contrast to the bulk, the total atoms are present in a considerably high fraction on their surfaces. An essential role to determine the nanocrystal's exhibited properties is played by the surface of the nanocrystals. Typically, attaching long-chained molecules passivate the surface. However, because of incomplete passivation, a lot of dangling bonds are present. Therefore, the surface is chemically accessible and dynamic, having sufficiently mobile surface atoms. Lack of knowledge about the surface has impeded this study. Surface affects many crucial properties of the NCs, for example, energy relaxation, carrier trapping, and fluorescence quantum yields (Link et al., 2004). Hence, for these colloidal NCs, achieving surface control is important, since the surface is responsible for governing many versatile properties (Mocatta et al., 2011; Sahu et al., 2012).

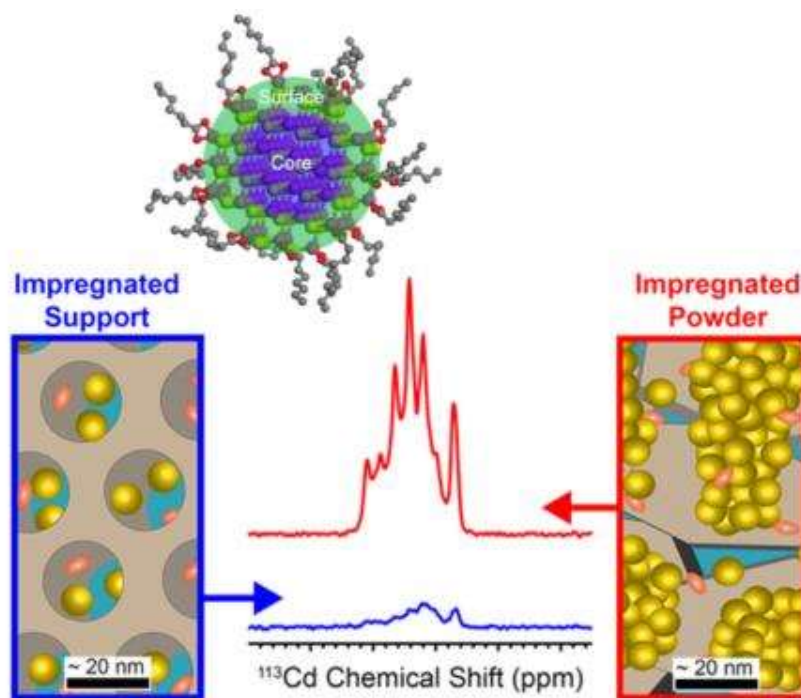


Figure 4.4. The surface structure of SC NCs

[<https://www.ameslab.gov/dmse/research-highlights/surface-structure-semiconductor-nanoparticles-revealed>]

4.5.2. Strong Quantum Confinement Effect

The gap separating the valence energy and the conduction bands is characteristic of SC materials. It is fixed in bulk SCs. It can be either indirect or direct. When from the valence band, the electron is directly promoted to the conduction band, a photon can be absorbed by direct-gap SCs; resulting in exciton or

the creation of an electron-hole pair. For absorbing or emitting light, the assistance of a phonon is required by the indirect-gap SCs. However, if the SC material's size decreases to an extent where the excitons, the holes, and the electrons start feeling the particle's physical boundary, the material starts adjusting its energy levels, exhibiting the quantum confinement phenomenon (Pandey et al., 2012; Wills et al., 2012).

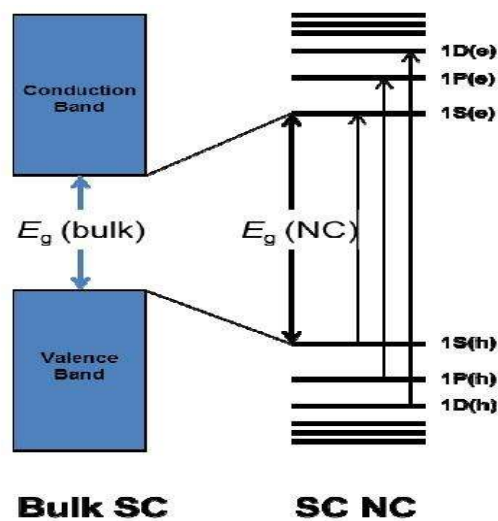


Figure 4.5. Comparison of the electronic states of bulk SCs and NCs. E_g (bulk) represents bandgap.

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In bulk SC, the valence and conduction bands collapse to discrete states (atomic-like) in SC NCs (1D, 1P, 1S, etc.). The “e” refers to electron states and “h” refers to hole states. Particles exhibiting quantum confinement are termed QDs (quantum dots). Into discrete energy levels, a collapse of the continuous conduction and valence bands of the material, and an increase in bandgap are the most common features of quantum confinement. This produces sharp features in the QD's absorption spectra. These features are different from the one in bulk SCs, in them, a continuous absorption spectrum occurs. These produced features may result in an indirect-gap material that at the nano-scale, converts to a direct -gap material (Yoffe, 2001; Swihart, 2003).

By varying the QD's size, we can only have the exciton (electron-hole pair) or the hole or the electron confined. The regime where all these three are confined is considered as the strong confinement regime. If the exciton is only confined, the regime is considered the weak confinement regime (Geyer et al., 2010; Brovelli et al., 2012).

We can treat the hole and electron as independent carriers in the strong confinement regime. Through the means of the effective mass approximation, if this system has to be modeled, we assume valence bands to have bulk effective masses for the hole and electron. Hydrogenic wave functions can describe

the hole and electron in the NC by simply using a particle in a sphere model. We can approximate the bandgap of the semiconductors NC as a size function, by solving the equation of the Schrodinger (Coulomb interaction of the electron-hole is included) as:

$$E_{bandgap}^{NC}(R) = E_{bandgap}^{bulk} + \frac{\hbar^2 \pi^2}{2R^2} \left[\frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{1.8e^2}{4\pi\epsilon\epsilon_0 R}$$

where the NC's radius is denoted by R , the Planck's constant is denoted by \hbar , the bulk bandgap is denoted by E , the material's dielectric constant is denoted by ϵ , the vacuum permittivity is denoted by ϵ_0 , the electron's effective mass is denoted by m_e , and the hole's effective mass is denoted by m_h .

4.6. Synthesis of Nanocrystals

A close interplay among biology, chemistry, physics, and materials science characterizes the nano-science. A versatile set of synthetic techniques are being extensively used and developed for nano-scale materials, these techniques vividly demonstrate this close interplay. We can group these various techniques into two schemes – the bottom-up and the top-down approaches. In the top-down approach, bulk materials are taken and are broken down into the smallest of the particles. While the bottom-up approach is initiated by taking the respective atoms and then the nanoparticle is progressively build-up by them (Manzoor et al., 2003; Orlinkii et al., 2004). The top-down approach can be categorized into physical methods, while the bottom-up approach can be categorized into chemical methods. Large quantities of nanoparticles are produced by physical methods. Chemical synthesis techniques can be easily altered for producing different materials, these techniques give higher quality nanocrystals, and a much better reaction control is offered by them (Petroff & Medeiros-Ribeiro, 1996; Bimberg et al., 1998).

4.6.1. Physical Methods

The physical method has a characteristic feature of high energy input; it is used for the evaporation of the bulk solid material that results in the formation of a supersaturated vapor. The nucleation of nanoparticles occurs, owing to the supersaturation. Controlling the distribution and the particle size is extremely hard, it is because of the extremely fast growth (Bryan & Gamelin, 2005). Some common examples of physical processes are VLS (vapor-liquid-solid) approaches, MOCVD (metal organic-chemical-vapor-deposition), and MBE (molecular beam epitaxy).

4.6.2. Chemical Methods

As compared to the physical methods, chemical methods usually take place under much milder conditions. These methods emphasize on developing different means for the production of NCs that in solvents, are then dispersed. They are usually called colloidal NCs. I have focused on these colloidal

NCs in my entire work. Any chemical reaction resulting in the colloidal NC's formation contains three main steps that are nucleation, growth, and termination. Mostly, a mixture containing the NC constituents (precursors which contain the elements involved in forming the NC), the solvent (for manipulating the precursor concentrations and for controlling the growth temperature), and capping agents (to attain colloidal stability) are taken in starting. From the same mixture, we can obtain the NCs of different dimensions through the manipulation of relative rates of steps that are tailored by changing precursor temperature and concentrations (Radovanovic & Gamelin, 2001; 2002).

During colloidal NC's growth, Ostwald ripening, which is a growth mechanism, is an essential process that must be considered. In this process, the small particles having high surface energy dissolve, releasing ions or monomers (larger particles consume these released materials). However, synthesized NC's size distribution is defocused during the early growth period and as a result, the ultimate size distribution is severely limited. This scenario can be avoided by adding reaction precursors continuously during the growth period. This adding ensures that the depletion of monomer concentrations never occurs (Mikulec et al., 2000; Stowell et al., 2003).

The essential factors in determining the success and quality of nanocrystal synthetic procedure are the surface passivation, crystallinity, obtained NC's size distribution, and dispersity in various nonpolar or polar solvents. As the properties of nanoparticles strongly depend on their size, desirably, we can have the nanoparticles of almost the same size, so that we can study and distinguish the properties arising because of the quantum size effects. In its strictest sense, the definition of monodispersity requires indistinguishable or identical particles, but still, colloidal NC samples (having standard deviation and size of 5 % in diameter) are regarded as fairly monodisperse. Chemically produced NCs can be dispersed either in organic solvents that are sterically stabilized or in aqueous media that is electrostatically or sterically stabilized (Suyver et al., 2000; Knox et al., 2006).

NCs that are stabilized sterically, can re-disperse. By this, we mean that in the solvents, the NCs can be dispersed, filtered, and precipitated. Moreover, these NCs can disperse in a vast range of concentrations. In this thesis, mostly, we have used NCs that are sterically stabilized (Wang et al., 1991; Counio et al., 1996).

Following the studies of La Mer and Dinegar, in the early 1990s, a high-temperature nanocrystal synthesis method was pioneered by Murray et al. (2000). This method yielded fairly monodisperse NCs. These yielded NCs had high crystallinity. In this technique, the target NC's organometallic precursors are rapidly injected into a coordinating solvent at a high temperature.

Therefore, it is commonly termed as the hot-injection method. The injection was necessary for separating it from the process of growth and for achieving a discrete nucleation event. Immediately after injecting it, the concentration of precursor is raised above the limit of solubility, resulting in a nucleation

burst. The precursor concentration is decreased below the threshold by the nucleation event, and due to it, the nucleation is suppressed (Bhargava et al., 1994).

The remaining precursors are added to the existing nuclei, which continue the growth process. The concentration of monomers is relatively high in this growth regime and due to this, in contrast to larger particles, small particles grow faster. Consequently, the size distribution is focused on. When the monomer concentration gets depleted, Ostwald ripening proceeds the growth process. In the case of fast nucleation, the precursor's concentration quickly falls below the threshold concentration, then, we can separate the nucleation from growth. This separation is imperative for monodispersity, as the nucleating particles will grow simultaneously at similar rates, in due course, they end up the same size (Chan & Nie, 1998; Norris et al., 2001).

For producing colloidal NCs of high quality, the size dispersion and sizes of these NCs have to be precisely controlled. The key variables are precursor concentrations, temperature, and growth time. Usually, larger particle size is implied by longer reaction times. The two factors that have a major impact on NC's size are growth temperatures and injection (Sooklal et al., 1996).

Lower injection temperatures result in a smaller nuclei number and hence, it results in yielding particles of large size having similar precursor concentrations. In the reaction solution, if a sufficiently high concentration of precursor is present, larger particles, in contrast to the lower growth temperature, are generated by higher growth temperatures after the same growth period.

In growth and nucleation, a pivotal role is played by the surfactant and precursor concentrations. A high precursor concentration results in generating a huge number of nuclei, contrary to it, lower precursor concentrations results in fewer nuclei. The resulting particle size is heavily dependent on the interplay between the consumed precursors (in the nucleation) and the left ones (for growth). There might be an adverse effect of the surfactants on NC's growth. A higher surfactant concentration may lead to lower growth rates. Thus, the generated NCs will be smaller. In case when the surfactant is stuck to the NC strongly, NC growth will be hindered, and if it is a weakly coordinating surfactant, uncontrolled growth is observed that results in agglomerates that are not dispersible in solvents (Erwin et al., 2005; Du et al., 2008).

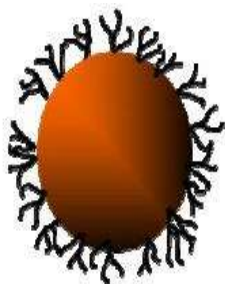


Figure 4.6. Cartoon showing a colloidal nanocrystal that is surrounded by the ligands

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The examples of coordinating solvents or surfactants used in synthesizing high-temperature NC are alkyl thiols (dodecanethiol), fatty acids (such as oleic acid), alkylphosphines (such as tributyl phosphine, tri-octyl phosphine, diphenylphosphine), alkylamines (such as octadecyl amine, hexadecyl amine, oleyl amine), alkylphosphine oxides (such as tri-octyl phosphine oxide), and alkyl phosphonic acids (such as dodecylphosphonic acid). A lyophilic polar head group, attached to the NC's surface atoms and an exposed lyophobic tail is contained by them. These surfactant molecules create an organic capping shell in the surrounding of the NC core and act as ligands (Figure 2.2). In common nonpolar solvents, the NCs are rendered soluble by the lyophobic tail; these solvents include toluene, hexane, chloroform, carbon tetrachloride, and octane. The ligands also play a part in preventing the aggregation of individual NCs (they keep them separated). These ligands can reversibly detach or attach from the surface of NC, explaining the fact that in the growth period, even if ligands are in the solution, the nuclei of NC can grow. Ligand exchanges post-synthesis is also permitted by exposing the NC to a different desired surfactant (Coe et al., 2002). Furthermore, these ligands also serve in the passivation of the surface trap sites (that is a result of dangling or uncoordinated bonds). Therefore, high photoluminescence (PL) yield is exhibited by the NCs having high crystallinity and well-passivated surfaces, for instance, higher quantum efficiencies (Colvin et al., 1994). Photons and / or phonons can be scattered by the defects in the crystal, thus, crystallinity is important. Nevertheless, an insulating potential barrier is provided by the ligand shell for charging transport between NCs. Consequently, on electrical properties, it has an adverse effect (Dabbousi et al., 1995; Zhang et al., 2006). For the syntheses of NC, the prominent chemical methods employed are high-temperature injection, reverse-micelle, and reduction. The techniques of reverse-micelle and reduction use less toxic reagents and are simpler. There are numerous benefits of high-temperature injection. It generates monodisperse particles that have fewer trap states, and stable dispersions are formed by them. The high-temperature route, though difficult it is, yields higher quality material that can serve better in fundamental studies. As the properties of nanoparticle highly depend on their size, characterization is made difficult by the polydisperse samples (Shim & Guyot-Sionnest, 2000; 2001; Ipe et al., 2005).

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