Chapter 1

Introduction
Nano-science and technology is considered as the fast growing and alluring field in research community. It comprises of different areas of science and technology and poses challenging problems to conquer. Initial period of this field focused mainly on synthesis and preparation of nanomaterials. Semiconductor nanocrystals (NCs) attracted attention of not only early researchers but current crop of scientific community also due to their astonishing optical [1–3], electrical [4,5] and magnetic [6,7] properties. These properties, as found out by many, could be utilized for some very interesting applications.

In the past three decades, the focus of the major research was the size dependent optical properties of semiconductor NCs. Tremendous amount of work has been carried out, both theoretically [8–12] as well as experimentally [13–17] to probe the electronic structure of the semiconductor NCs. Though these NCs exhibit interesting optical properties, because of smaller sizes the surface becomes larger and the volume smaller. Thus the surface to volume ratio is high in these NCs, making these NCs vulnerable to surface defects, which hinders their optical properties. To overcome this difficulty, the surface of the NCs was coated with another semiconductor material. The first reported system was CdSe/ZnS [18]. These heterostructured NCs were termed as core-shell NCs. Cladding a shell of another material, preferably with higher band gap than core, improved the photoluminescence (PL) efficiency, prevented oxidation of the core surface, enhanced the stability against photo-bleaching and eliminated the possibility of degradation of the surface [19]. There are mainly two types of core-shell NCs [19,20], (i) Type I, with smaller band gap material at the core and coated with higher band gap material, whereas (ii) Type II with either the valence band edge or the conduction band edge of shell in the band gap of the core material. By confining both or either of the charge carriers, optical properties are greatly modified. When electron and hole, both are confined inside the core, higher luminescence yield was observed. Whereas, with either electron or hole confined in the core leads to better photovoltaic applications. Albeit with better optical results, due to lattice strain at the interface, these heterostructures are prone to interfacial defects and strain induced effects [21,22]. It is possible to tune the optical properties with induced strain [20]. To avoid the formation of strain and the defects, lattice constants are adjusted by synthesizing alloy NCs or compositionally graded NCs [23–25]. By tuning the composition and using the reactivity of certain chemicals, graded NCs can be prepared [26,27]. The composition varies slowly from core to
shell in graded core-shell NCs. Moreover, as the exciton is more confined inside the core region, these NCs possess high luminescence efficiency, better crystallinity, and improved stability etc.

Another class of material that is being studied for their opto-electronic properties is metal-semiconductor nano-heterostructures. Metal-semiconductor nanostructures are widely studied for plasmon enhanced spectroscopy, biotechnology, photocatalytic and solar cell applications. Gold (Au)-semiconductor heterostructure is the most exploited nano-heterostructure system. Au-based systems improve charge separation as well as enhance light absorption in semiconductors. Both these phenomenon can be utilized for superior photocatalytic activity as well as higher light harvesting efficiencies of semiconductors. Varied luminescence properties of Au-semiconductor systems have been observed. Many reports claim quenching of luminescence whereas there are some studies which show enhancement in the PL. The reduction in PL is due to the charge transfer from semiconductor to metal nanostructure. The enhancement in PL is attributed to number of factors such as increased light absorption/emission due to spectral overlap between exciton and plasmon resonance bands, separation between metal and semiconductor, spontaneous emission, surface plasmon induced energy transfer mechanism. It is still an open and debatable problem as which mechanism is responsible for the enhancement of PL in metal-semiconductor nano-heterostructures. Understanding of electronic structure of NCs is very important to gain control and engineer the optical properties.

1.1 Quantum size effects:

In case of semiconductor NCs, the electronic and optical properties are governed by size dependence [1,12]. This size dependence arises due to quantum confinement of charge carriers, viz. electron and hole. When semiconductors are excited with energy higher than the forbidden gap of that material, a bound electron-hole pair is created in small size nanocrystals. The bound electron-hole pair is known as exciton. The radius of this bound electron-hole pair is known as Bohr exciton radius ($a_B$) which forms due to Coulombic attraction between electron and hole.

$$a_B = \frac{4\pi\hbar^2 \varepsilon}{e^2 \left(\frac{1}{m_e} + \frac{1}{m_h}\right)}$$ 1.1
where, \( \varepsilon \) is the dielectric constant of the material, \( m^* \) and \( m^* \) are the effective masses of electron and hole respectively. Depending on the size of the NC \( a \) with respect to the Bohr exciton radius, the confinement can be divided in to three regions [28]. In the weak confinement region, \( a >> a_B \), the optical properties are governed by the exciton centre of mass [12]. In the intermediate confinement regime, \( a \sim a_B \), the exciton Bohr radius lies between the individual Bohr radii of electron and hole. The region where the size \( a << a_B \) is the strong confinement regime. In this regime, the optical properties of the material are dominated by the confinement effects of electron and hole. In case of semiconductor NCs with sizes smaller than the excitonic Bohr radius of that material, the electron and hole sees ‘Particle in a box potential’ in all three dimensions, collapsing the bulk band structure in discreet atomic-like energy levels. In this model [16], an arbitrary charge carrier of mass \( m_0 \) is considered inside a spherical potential well of width \( a \):

\[
V(r) = \begin{cases} 
0, & r < a \\
\infty, & r > a 
\end{cases} 
\]  

By solving Schrödinger’s equation with this potential, one can get,

\[
\Psi_{n,l,m}(r, \theta, \phi) = C \frac{j_l(k_n r) y_l^m(\theta, \phi)}{r} 
\]  

where, \( C \): normalization constant,

\( y_l^m(\theta, \phi) \): spherical harmonic,

\( j_l(k_n r) \): \( l \)th order spherical Bessel function

The energy eigen value in this case can be given by,

\[
E_{n,l} = \frac{\hbar^2 k^2_{n,l}}{2 m_0} 
\]  

Under several approximations one can reduce the nanocrystal problem to the particle in a sphere format [16]. One of the models is effective mass approximation (EMA) [8–10]. Efros and Efros developed the model to explain the optical properties of QDs [8]. The model developed by Efros and Efros assumes parabolic bands, infinite potential wells at the crystallite surface and excludes Coulomb interaction between the charge carriers. In EMA, the highest valence band and the lowest conduction band are taken to be parabolic at their extrema, i.e. near \( k = 0 \). Here one treats an electron in the conduction band as a particle with effective mass \( m^* \) obtained from the bulk band-edge dispersion, confined to move inside the crystallite [8–10]. The model predicts size dependent contribution to energy gap which is proportional to...
1/R², R being the radius of spherical particle. The relation between energy gap and particle size given by EMA is:

\[ E^* = E_{\text{bulk}} + \frac{\hbar^2}{2R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - \frac{1.8e^2}{\varepsilon R} - 0.248E_{\text{RY}}^* \]  

Here, the first term is the bulk band gap of the material. The second term gives the confinement energy by considering effective masses of electron and hole system. The relation clearly shows that energy gap depends inversely on R², the radius of the particle. Third term gives decrease in energy due to Coulomb interaction between electron and hole having 1/R dependence. Last term gives spatial correlation between electron and hole and is size independent. On theoretical front this is widely used method for calculating electronic states.

EMA fails to explain the electron energy level structure of small quantum particles. To obtain realistic picture the valence band mixing as well as non-parabolicity of bands also needs to be considered. For a quantitative description of the quantum size effects one has to go beyond EMA. For past three decades, electron energy structure of quantum dots is being examined with empirical tight binding formulations [29,30], empirical pseudo-potential method [31], LMTO formulations [32] aside from the first principle studies.

### 1.2 Core-shell nanocrystals:

The optical properties of semiconductor NCs have been the main focus of the research in nanoscience and nanotechnology since the last three decades. Highly luminescent and crystalline NCs are the crucial requirements for applications such as light emitting diodes, lasers, biological markers, photovoltaics etc. While preparing these technologically important NCs, one has to take into account the surface to volume ratio of these smaller particles. As size of the particle is reduced, its surface area decreases and the ratio of surface to volume increase. Chemically prepared semiconductor NCs have dangling bonds on the surface which may trap the charge carriers, reducing the photoluminescence quantum efficiency (PQE) of the NCs. Subsequently, quantum dots are electronically as well as chemically passivated by organic capping molecules. However, even though the NCs are capped with organic layer on the surface, photogenerated charge carriers may still get trapped inside the surface traps or the organic ligands. These traps act as non-radiative de-excitation channels reducing the PQE. To improve the luminescence yield, it was proposed that
the surface of the NC be coated with another semiconductor to form core-shell (CS) NCs. Core-shell NCs are anticipated to attain higher photoluminescence (PL) yield and chemical robustness. Uniform growth of inorganic semiconductor layer on core semiconductor NC has not only improved [33,34,18,35] the PL efficiency but also allowed [3,20,36–38] manipulation of the discrete energy levels in multishell NCs called as wave function engineering. Core-shell materials are broadly divided into two types, based on their bulk band-alignment; (i) Type-I and (ii) Type-II CS structures. In case of NCs same band alignment is considered. Following part as well as next section discusses different types of core-shell NCs (such as Type-I, Type-II, graded core-shell), synthesis methods to prepare these NCs, and their optical properties.

In Type-I CS structures, the band-gap of the core lies in between that of the shell material. In short, the shell material has higher band-gap than that of the core material. In this structure, both electron and hole are confined within the core region. In case of Type-II CS, both conduction band and valence band of core are lower (or higher) than the shell. Thus in this case either of the charge carriers is confined in the core region while the other resides in the shell. Emission wavelength which is not obtainable in single component nanocrystal can be observed in the Type II CSNCs. On the other hand, passivation is substantially improved in Type-I CS NC, which in turn improves the optical properties. Due to cladding by shell on core surface, the surface dangling bonds get satisfied, the surface is protected from inevitable oxidation, and the density of surface defects is kept to minimum [19,39]. Type-I CS NCs are mainly synthesized to improve the photoluminescence quantum yield stability against photo-degradation. CdSe/ZnS CS NCs [40] is the first Type I structure prepared. It was grown by using organometallic precursors of zinc and sulphur at high temperature. Incidentally, this is the most studied Type-I CS system. Later, Dabbousi et al. [18] reported detailed characterizations on same system with varying core sizes. Lad et al. [3] adopted this method to synthesize ZnSe/ZnS CS NCs with varying sizes and shell thickness. Precursors with low reactivity [41] lead to formation of blue light emitting CdSe/ZnS CS NCs, which showed PL quantum yield of 60%.

Due to the band alignment, it is possible to tune the emission energy [20] of these CS NCs. Moreover, this band alignment allows one to separate the charge carriers, which is a very useful for solar cell applications and in photocatalysis.
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Figure 1.1 Schematic showing energy level arrangement of different types of semiconductor core-shell NCs [19].

Lattice mismatched epitaxial shell formation can generate the interfacial defect levels which adversely affect the PL quantum yield. Reports on the strain induced modulations [20,42,43,21] on the optical properties of semiconductor NCs are conflicting. A forbidden gap is found to blue shift due to induced strain in NCs [44,45]. On the other hand in case of CdSe/CdTe, on generation of strain, reduction in the forbidden gap [46] is observed. Strain induced switchover of direct to indirect [47] as well as indirect to direct [48] bandgap is documented. Due to strain, band alignment of Type I to Type II core-shell structures, which is characterized by spatial separation of electron and hole is reported [20]. Similarly, change in band alignment from Type II to Type I is also observed [49]. Diverse strain-induced results dictate a need to probe implications of strain on the electronic and optical properties in further details. Core/shell and alloyed NCs are naturally suitable candidates for studying strain induced effects [50].

Figure 1.2 Schematic of strain formation after ZnS shell cladding on CdS nanocrystal
Effect of strain on CdSe based core/shell NCs is addressed in the literature [34,51–53]. The optical properties of CdSe/CdS quantum dots, tetrapods and nanorods are studied [51] by applying hydrostatic pressure. The emission and absorption features are observed to blue-shift or even split in two distinct peaks on strain generation. Similar results are observed [52] by forming thicker shells of CdS on CdSe (enhancing strain on CdSe NCs). Despite these reports, effect of strain on NCs is not comprehended well and the understanding is still in a rudimentary state.

Further, strain induced behaviour of other semiconductor nanostructures is still an open question. In an isolated report, strain induced effects are manifested [54] as the distinct polarization properties of CdS nanowires due to anisotropic response of A, B, and C excitons.

As a manifestation of strain, switching of ground state from heavy hole to light hole is observed [55] in case of self-assembled GaAs quantum dots. It may be worthwhile to note here that a size dependent changeover in hierarchy of $S$- and $P$-orbital hole levels is predicted [56] in CdS theoretically and later reconfirmed [57] experimentally. Strain can also be effectively used [58] to tune the emission wavelength of Mn related transitions in Mn-doped ZnSe-CdSe-ZnSe NCs.

### 1.3 Graded and alloy NCs:

Luminescence behavior can be tuned over a wide range of energies without any perturbation by the surface defects by making alloy NCs [59,23,60]. For example, smaller sized CdSe NCs emit in blue region but emission from the surface defects also arises [61,62]. When $\text{Cd}_{1-x}\text{Zn}_x\text{Se}$ alloy is formed by diffusing Zn ions into CdSe, blue emission can be achieved. Similarly in case of CdS, defects are prominent for almost all the sizes. The defects can be minimized by making an alloy of CdS with Se or with Zn [63,64]. In this way alloy NCs can be utilized for band gap tuning without changing the size of the NCs. The alloyed NCs show interesting properties that are not observed in the binary semiconductor materials.

High temperature colloidal methods are widely employed to synthesize alloyed NCs with small size dispersion. Alloy $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$ NCs were prepared by changing the molar ratio of Zn and Cd in hot solutions [23]. These NCs are highly monodisperse. Synthesis of $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$ NCs [65,66] from ZnSe is also feasible. By exploiting different reactivity of precursors in the reaction and reaction time, $\text{Cd}_{1-$}
\( \text{Zn}_x\text{Se} \) alloy NCs were synthesized [27] which show high luminescence efficiency and very narrow Stoke’s shift. Very broad emission peaks were observed by \( \text{Zn}_{1-x}\text{Cd}_x\text{S} \) NCs prepared by chemical reduction method [67]. Sadhu et al. [63] prepared \( \text{Cd}_{1-x}\text{Zn}_x\text{S} \) NCs by wet chemical organometallic route and correlated its lattice constants and relaxation dynamics with a stochastic model. Similarly, \( \text{CdS}_x\text{Se}_{1-x} \) [68], \( \text{CdSe}_x\text{Te}_{1-x} \) [69], and \( \text{CdS}_x\text{Te}_{1-x} \) [24] NCs were prepared by wet chemical route. These alloy NCs are classified in two sub-types: (i) homogeneous alloy NCs and (ii) graded NCs (Figure 1.3). In graded NCs, composition of constituent elements is varied along the radius. Graded NCs are different than core-shell NCs where a shell of different material is coated on top of a core semiconductor. The interfacial strain observed in case of core-shell NCs is eliminated by matching the lattice constants of the materials in consideration.

![Figure 1.3 Schematic representation of different types of compositional NCs](image)

The concentration of one material decreases from shell to core while that of the other material increases from core to shell. This allows one to have better crystallinity and thus higher PL efficiency. In synthesizing graded NCs various methods are used. By playing with the reactivity of the precursors, graded NCs can be prepared [27,26,70,71]. In such reactions, one precursor is more reactive than the others and thus grows faster to form core of the NC whereas the slowly reacting precursor forms the shell. Core-shell NCs can be annealed for long duration [26] in a chemical bath so that the shell precursors diffuse inside the core to form graded interface. Synthesis of homogeneous alloy of CdTeSe and graded structure of CdTe-CdSe NCs were reported by changing the concentration of Cd [69]. By controlling concentration of precursors, composition as well as morphology of graded NCs can be controlled [68]. Graded \( \text{Cd}_{1-x}\text{Zn}_x\text{S} \) QDs were prepared [72] by exchanging Cd ions with Zn ions in aqueous solution. Synthesis of gradiently alloyed \( \text{Cd}_{1-x}\text{Zn}_x\text{S} \) QDs [73]
was demonstrated using non-injection one pot method, with high quantum yield and narrow emission line width (FWHM).

In most of the highly luminescent NCs, the luminescence line width (FWHM) is observed to be small at room temperature [18,23,27,26,74]. The narrow linewidth is attributed to homogeneous and inhomogeneous broadening, quantum confinement effects, narrow size distribution. The inhomogeneous broadening arises due to fluctuations in size, shape, composition etc. whereas; homogeneous broadening arises due to scattering of excitons with optical and acoustic phonons. The exciton-acoustic phonon coupling can be determined from optical measurements such as spectral hole burning [75], temperature dependent PL spectroscopy [76,77], femtosecond photon echo experiments [78,79], Raman spectroscopy and pump probe measurements [80]. Exciton–phonon studies are important to study energy relaxation pathways and thermal transport processes. Coupling to acoustic phonons gives information related to homogeneous line width and contributes to resonant Stoke's shift. Coupling to LO-phonon modes has been observed to relax selection rules, yielding phonon-assisted transitions from dark states [81].

In longitudinal optical (LO)-phonon spectra of CdSe/CdS core/shell NCs, studied by resonance Raman spectroscopy, a shoulder at low frequency is visible which is termed as a surface optical phonon (SO) [82]. The intensity of SO-phonon is correlated with surface properties of core-shell NCs. LO-modes are sharp and involve motions of atoms in the interior of the NC, whereas the modes at lower frequency involve motions of atoms equally distributed throughout the NC [82]. Wu et al. [83] studied SO-phonon peak as a function of size in case of CdS QDs and found out that with decrease in size, the SO-phonon peak intensity increases. Moreover, on ligand exchange, SO-phonon peak intensity does change.

Exciton-phonon coupling in case of semiconductor NCs has been studied for a long time. For CdSe NCs with radius < 70 Å, the exciton-phonon coupling increases with decrease in size, due to the enhanced participation of high energy phonons [84]. CdSe NCs with size > 70 Å, the value of the exciton-phonon coupling increases with increase in size. This happens because, in this regime, the contribution from Coulomb interaction is increased with the size and the quantum confinement effect has reduced with the size [84]. Increased coupling [76] between exciton-acoustic phonon with decrease in size of CdSe NCs due to the quantum confinement effect was also reported. In addition to that difference between first three excited states was shown to
have a value equal to $4E_{\text{LO}}$, implicating the fact that thermal escape is due to scattering with 4-LO phonons. Recently, it was reported [77] that the exciton-phonon coupling increases with decreasing size of CdTe QDs leading to broadening of photoluminescence linewidth. Theoretical calculations [85] predict with smaller particles, total exciton–phonon coupling increases as inherent phenomenon. In case of epitaxially grown CdSe/ZnCdSe quantum structures, the confinement imposes increased interaction with acoustic phonons and reduced exciton-LO-phonon coupling [86]. For CdSe and CdSeS NCs, it was observed [87] that acoustic phonon contributes for broadening of the FWHM up to 130 K and above that temperature, LO-phonon-exciton interaction dominates. On the other hand, recent communication [88] states that the decreased exciton-phonon coupling with increase in CdSe core size is not due to the quantum confinement effect but its rather a surface related phenomenon; presence of trapped charges enhances the LO-phonon coupling and thus the linewidth in NCs. Kaniyankandy et al. [89] have carried out temperature dependent PL studies on CdSe-CdTe graded NCs indicating enhanced charge separation in graded structures than abrupt core/shell interface.

1.4 Metal-semiconductor nano-heterostructures (NHs):

The advantages of nano-materials are not only limited to tunable optical properties of single component but also in combination of two or more components into hybrid structures. Hybrid nanostructures consisting of metal and semiconductor components are deserving candidates for numerous applications. This is a reason, why these materials have attracted a wide attention in the recent times. The different yet extraordinary optical properties shown by these materials are due to co-existence and interactions of excitons and surface plasmons (SP). Optical excitations in semiconductor NCs are the transitions in the discrete electronic levels between conduction and valence bands. These transitions lead to the formation of exciton, bound electron-hole pair. Surface plasmons, the equivalents in metal nanostructures, are defined as the collective oscillations of conduction band electrons. In metals, conduction electrons are delocalized. Oscillating electric fields associated with the incident electromagnetic waves can delocalize the electrons and force them to move away from the metal. The free electrons are pulled back due to the Coulombic attraction coming from the cations of the crystals. The resonance condition is reached
when the frequency of the incident light is coupled to the natural frequency of the electron oscillation in the metal. Two types of SPs can be generated: Propagating Surface Plasmon Resonance (PSPR) and Localized Surface Plasmon Resonance (LSPR).

PSPR are characteristics of smooth metal surfaces. Positive and negative charges are generated as the electron waves propagate along the metal surface with excitation of incident light. LSPR are generated in metal particles which have smaller sizes than the wavelength of incident light. Induced oscillations of the free electrons by the incident electromagnetic waves are confined to the volume of the metal particles. The separation of the charges creates a dipole whose direction can be changed with an electric field. When the natural dipole frequency coincides with that of the incident electromagnetic waves, these waves are strongly absorbed, which is known as LSPR. LSPR depends strongly on size and shape of the metal particles and the dielectric constant of the local environment. Figure 1.4 depicts the difference between PSPR and LSPR.

![Figure 1.4](image)

**Figure 1.4** Graphics describing (a) Propagating Surface Plasmon Resonance (PSPR) and (b) Localized Surface Plasmon Resonance (LSPR) [90].

Thanks to tremendous progress in the fabrication/synthesis of the nanoscale metal as well as semiconductor materials; a variety of shape, size and combinations can be successfully prepared [39,91–95]. This set the stage for the preparation methods of hybrid structures such as metal-semiconductor NHs. Largely for metal synthesis, gold and silver are more preferred as the SPs generated in these NCs are in visible region, although other metals offer interesting properties as well. The colloidal synthesis route is favoured over epitaxial one for having better tunability of optical properties, strong NC non-linearity, and compatibility with self-assembly techniques [96].
In the hybrid structures, the optical tunability can be achieved by changing the LSPR of the metal NCs. In case of Au/Cu$_2$O nanostructure systematic change in the LSPR of Au can be obtained by varying the shell thickness. In general, the metal-semiconductor nanostructures red shift the LSPR of metal NCs due to the large dielectric constant of semiconductors. Interaction of electromagnetic field in metal-semiconductor nano-hetero-structure is broadly divided into two regimes, weak coupling and strong coupling. In weak coupling regime, exciton wave functions and plasmon electromagnetic modes are often unperturbed. The exciton-plasmon interaction is then explained from the coupling of the exciton dipole and the electromagnetic field of surface plasmon [96]. The enhanced absorption cross-sections, increased radiative emission rates and exciton-plasmon energy transfers fall in to the weak coupling regime. In strong coupling regime, resonant exciton-plasmon interaction modifies the exciton wave functions and surface plasmon modes, changing the surface plasmon and exciton resonance energies. Another interaction mechanism in these metal-semiconductor nano-hetero-structures is the plasmon induced charge transfer from the excited metal surface; viz. plasmon induced hot electron transfer mechanism [97]. Plasmon decays into hot electron-hole pair at metal surface, followed by electron transfer from metal to semiconductor which is a hot electron transfer. However the efficiency of such charge transfer is very low. On the contrary, the surface plasmon can also decay [97] by creating an electron in the conduction band of the nearby semiconductor and hole in the metal NC. Here the metal plasmon acts as a light absorber and the mixing of metal and semiconductor levels lead to new plasmon decay pathway [97].

Preferential growth of gold on tips of CdSe [98,99] and CdS [100] nanorods is a prime example of surface growth. Gold (Au) is deposited at the tip of the rod due to the increased adsorption coefficient of gold ions on the tips. The reactivity of the tips is governed by the fact that the chemical potential of the surface is inversely proportional to the NC radius [16]. Thus, smaller NCs have higher reactivity than larger NCs as the radius of curvature is higher. In another method [101], gold and silver were selectively grown on the surface of PbS NCs by aqueous method at room temperature. Mokari et al. [102] reported a preferential growth of Au on the surface of InAs. However, with increase in Au concentration, gold diffuses inside the crystal and forms core-shell NHs with InAs NCs. Similar core-shell NHs are also reported by other researchers but using different materials and synthesis methods [103–107].
When metal and semiconductor are in close proximity, interactions between excitons and SPs take place causing variation in the properties of the semiconductor material and making it useful for light emission or photocatalytic activity. Moreover, the plasmonic properties of metal structures are also altered as the SPs are dielectric function dependent phenomenon. Normally, with hybridization of the metal NCs with semiconductors, LSPR of metal NCs red shifts because of the higher dielectric constants of the semiconductors [104,105,108]. Complex interactions of excitons and SPs are responsible for the optical properties of gold tipped CdSe and CdS nanorods [98,99,109]. These interactions can cause enhancement [110–117] or quenching [98,104,118,119] in PL of metal-semiconductor NHs. For instance, Au-PbS nanostructures showed red shift in optical absorption as well as enhancement in the absorption than bare Au nanostructures. Enhanced absorption in Au-PbS nanostructures is attributed to the generation of strong local electric field [105]. Lin et al. [103] have proposed a carrier transfer induced photoluminescence mechanism in case of CdS-Au nanostructures and FePt-CdS nanostructures. SP induced electrons in Au nanoparticles transfer to conduction band of CdS and enhances the band-edge as well as defect level emission. Enhancement in PL can be attributed to increase in the local charge density due to the presence of metal NCs; hot electron transfer [97,109], increased probability of the spontaneous emission [112,117,120,121]. Enhancement in band-edge PL intensity and suppression of defect intensity was observed in case of Au/ZnO nanorods [112] and attributed to coupling between excitons and surface plasmons which enhances the spontaneous emission rate. A large increase in PL intensity was observed in case of InGaN films when coated with silver [120] due to resonant surface plasmon excitation. The excitonic emission for InGaN was at 470 nm whereas the surface plasmon energy for Ag in this particular case was at 400 nm. This helps in coupling of surface plasmon with exciton energy, enhancing the emission intensity. Reboud et al. [122] showed that PL intensity increased for a particular concentration of Au in CdSe/ZnS NCs. The life time was observed to decrease from 9.2 ns to 7.9 ns. Authors claim that the reduced decay is in agreement with the enhanced PL intensity, which shows that additional decay path has to be considered to account the increased PL intensity. Whereas, in case of Au-CdSe NHs [123], PL was observed to increase for a particular concentration of Au, which is due to the spontaneous emission. The surface plasmons can also observed to excite electrons in CdSe NCs and thereby PL efficiency. With higher concentration of Au, quenching in
PL is seen. This is due to the transfer of electron from conduction band of CdSe to the Fermi level of Au.

Hybrid nanostructures comprising of gold (Au) core and CdSe shells with a spacer layer of SiO$_2$ were synthesized chemically [124]. These structures showed quenching as well as enhancement in photoluminescence (PL) intensity. The enhancement in PL intensity is due to the modified electric field in the proximity of metal surface, modulating both the incident and radiated field. The inference was understood from the changes in absorption cross-section and spacer layer thickness. Similar results were reported by Naiki et al. [125]. The enhancement in PL of Ag/SiO$_2$ structure was attributed to the electromagnetic field effect of localized surface plasmon. PL quenching also observed in these structures due to the small distance in the Ag nanoparticles and SiO$_2$ quantum dots. In case of chemically prepared Au-CdS core-shell NCs, PL intensity quenches [104] due to the electron transfer from CdS to Au. Moreover photoinduced charge transfer property was investigated in these NCs and it was shown that charge is transferred from CdS to Au. Whereas, an enhancement in PL is reported in Au-CdS core-shell NCs due to charge transfer [103] as well. It was understood on the basis of energy level diagram of Au and CdS NCs. The Fermi energy level is higher in case of Au than that of CdS. Thus CdS energy levels bend downwards in order to match the Fermi levels of the combined Au-CdS NC. This enables charges to transfer from Au to CdS. In another report on Au-CdS core-shell NCs [106], on the basis of reduced radiative lifetime of the carriers, the electron transfer from CdS to Au is conjectured. A new material [107] was developed wherein Au/CdSe core-shell NCs were attached to another core-shell of CdSe/CdS NCs. In these structures, energy transfer from Au to CdSe takes place which leads to increased production of excitons in CdSe which increases PL intensity. The increase in PL is understood from photoluminescence excitation spectra of CdSe and Au-CdSe nanostructures.

1.5 Motivation:

Study of optical properties of semiconductor NCs is very important considering their potential for numerous applications. The core-shell NCs provide us an opportunity to study highly luminescent NCs with varying sizes and shell thickness. As the core surface is coated with another semiconductor, the surface traps
are minimum and yield higher PQE than core NCs. Albeit with better PQE, the interfacial defects are dominant due to strain generated by shell formation. In case of CdS, the ground hole energy levels are found to interchange the hierarchy with size. The same phenomenon is reported by tight binding calculations. It is interesting to study the effects of induced strain, because of the shell formation, on the ground hole energy levels experimentally by temperature dependent PL and time resolved PL spectroscopy.

Graded core-shell NCs reveal higher PL efficiency. Effect of interfacial defects are also minimal and hence exhibit narrow emission line width, which can be understood from the exciton-phonon coupling. This effect has been studied by many researchers. However, there has been little or no reports on the narrow emission line width due to exciton-phonon coupling observed in graded core-shell NCs. With change in the size and composition gradient, the exciton-phonon coupling can be enhanced or decreased. Due to slowly changing confinement potential, the electron and hole wave function confinement changes and so does the overlap. It is exciting to find out how the exciton-phonon coupling affects the line width with different graded structures and sizes.

Hybrid nanostructures with two or more components are interesting candidates for nano-technological applications. If these hybrid structures involve a semiconductor NC and a metal NC, then the optical and electrical properties are altered drastically than the individual counterparts. Interaction of surface plasmon with exciton has many interesting facets and can be utilized for numerous applications. The enhancement in PL efficiency in case of metal-semiconductor nanoheterostructures is a controversial topic. Underlying phenomena depend on the morphology of the system, distance between metal and semiconductor nanocrystal and spectral overlap of exciton and plasmon. If one studies a particular metal-semiconductor system with different morphology and coupling mechanism such as core-shell NHs or coupled NHs, then the physical understanding of this phenomenon can be understood better.
References:

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