IV.1.1 Introduction

Colloidal nanocrystals have attracted a great deal of attention in recent times for their discernible role in fundamental studies and technical applications mainly due to their size dependent properties and flexible processing chemistry.\textsuperscript{1,2} The shape and size of the nanocrystals control their widely varying electrical and optical properties.\textsuperscript{3,4} The ability to systematically and precisely manipulate the shapes of the nanocrystals remain an important goal of modern day material chemists.\textsuperscript{5} Size and shape are physical attributes of critical importance as they directly influence the solid state phenomena that are unique to the nanoscale. Rod or wire shaped semiconductor nanocrystals possess clearly different optical properties in comparison to their dot shaped analogues.\textsuperscript{6,7} The formation of high-quality semiconductor nanocrystal, with well-controlled size and shape as well as well-confined surface passivation, can be achieved by controlling the thermodynamics and kinetics during the nucleation and growth of nanocrystals (NCs).\textsuperscript{8,9} Various methods of synthesis of nanoparticles with a series of anisotropic structures like nanorods, bipods, nanocubes and nanowires have been well established by various groups,\textsuperscript{10–19} but only a few reports are found to produce CdS NCs and metal nanoparticles of different shapes using the same basic technique and the same set of starting reagents.\textsuperscript{20–23} Several groups have also studied the photo excitation dynamics of nanocrystals by using time resolved photoluminescence technique.\textsuperscript{24,25} In this thesis, CdS nanorods and nanospheres were synthesized with the same basic
technique and starting materials at room temperature and also were analysed in
detail by using time resolved emission studies.

**IV.1.2 Abstract**

Shape tuning of CdS nanocrystals by controlled growth and
stabilization by using tetraoctyl ammonium bromide ligand in non-aqueous
medium is comprehensively investigated in this chapter. CdS nanorods and
nanospheres were synthesized by manipulating the addition rate of the
sulphide precursor. Higher addition rate (10 mL/min) of the precursor
yields nanorods while lower addition rate (1 mL/min) of the precursor
yields nanospheres. An addition rate of (7 mL/min) which is in between the
above mentioned two addition rate yields a mixture of nanorods and
nanospheres. The present investigation further reveals that an optimum
concentration of stabilizing agent plays a paramount role in deciding the
shape of the nanocrystal. The mole ratio of the precursor does not play any
significant role in the shape tuning. The band edge and trap state emission
of the NCs synthesized were analysed by time-resolved emission studies.

**IV.1.3 Materials used**

Chemicals obtained from the following sources were of highest purity
grade commercially available and were used as received without any further
purification unless otherwise stated. Cadmium bromide tetrahydrate
(CdBr₂.4H₂O) and Sodium sulfide nonahydrate (Na₂S.9H₂O) were purchased
from Sigma-Aldrich chemicals. Tetraoctyl ammonium bromide (TOAB) was purchased from Lancaster chemicals. Toluene of HPLC grade and Sodium sulphate of analytical grade were purchased from SRL chemicals.

**IV.1.4 Synthesis of tetraoctyl ammonium bromide stabilized CdS quantum dots by phase transfer method**

In this chapter, a novel procedure is adopted for the synthesis of tetraoctyl ammonium bromide stabilized CdS nanocrystals at room temperature. Here in, the tetraoctyl ammonium bromide acts as a phase transfer catalyst and also performs the role of stabilizing agent. The synthesis procedure is explained below in detail.

**Step1: Preparation of tetraoctyl ammonium bromide stabilized cadmium precursor**

85 mg (2.5 mM) of CdBr$_2$.4H$_2$O was dissolved in 100 ml of argon saturated distilled water. 548 mg (10 mM) of TOAB was dissolved in argon saturated toluene. Both the solutions were deaerated for 10 minutes and then subsequently mixed together and stirred for 1 hour in a three necked round bottomed flask with simultaneous argon purging. The organic layer was then separated and treated as the precursor for cadmium ions.

The precursor solution was later divided into four equal portions of 25 mL (2.5 mM) to prepare CdS quantum dots with varying precursor ratio.
Step2: Preparation of sulfide ion precursor solution

60 mg (25 mM) of Na₂S.9H₂O was weighed and made up to 10 mL with triply distilled water which was saturated with argon. This solution was treated as the bulk. From the bulk solution, two precursor solutions each of 10 mL of identical concentration, 6.3 (mM) were prepared such that the mole ratio of cadmium to sulfide becomes 1:1 and later they were labeled as S1, S2.

Step3: Preparation of CdS nanocrystals

25 mL (2.5 mM) of argon saturated Cd²⁺ precursor solution was taken in a round bottomed flask and 10 mL of argon saturated solution (S1) was taken in a pressure-equalizing dropping funnel and was added to the Cd²⁺@TOAB solution at a uniform rate of 10 mL/min with simultaneous stirring. The addition rate was maintained uniform throughout the addition process. After 1 hour of stirring under inert atmosphere, the yellow organic layer which was obtained was separated from the aqueous phase. The organic layer was then treated with a pinch of sodium sulfate to dehydrate the solution. The solvent was then removed using rotary evaporator at 60 °C. The yellow solid of TOAB stabilized CdS nanocrystals obtained was stored under vacuum in inert conditions. Similar procedure was followed to prepare CdS nanocrystals with a lower addition rate of 1ml/min sulphide precursor (S2). The nanocrystals obtained were stored in vacuum. The particles were redispersed in non-polar solvents such as toluene and were used for further investigations. Some of the studies in this present investigation were also carried out with the freshly prepared nanocrystals. In this method of synthesis, TOAB acts as a phase
transfer catalyst for cadmium ions initially and subsequently it also performs the role of a stabilizer for the CdS nanocrystals formed.

**IV.1.5 Absorption studies of 1:1 CdS 1 and CdS 2**

The CdS NCs synthesized with a precursor ratio of 1:1 using higher (10 mL/min) and lower (1 mL/min) addition rate of the sulphide precursor were labeled as CdS 1 and CdS 2 respectively. The absorption spectrum was recorded for these two samples of CdS and is presented in Figure IV.1.1. Absorption in the UV region with a typical exciton peak around 370 nm was observed. This exciton peak confirms the formation of a nanoparticle. The absorption spectrum shows a gradual shift in the exciton peak towards the red region as the addition rate of the precursor was reduced from 10 mL/min (CdS 1) to 1 mL/min (CdS 2). The respective absorption band edge shifts from 375 to 400 nm and the observed band edge shift are attributed to the change in size or shape of the NC formed. As the size of the nanoparticles increases, the absorption band edge shifts to the longer wavelength.

**IV.1.6 Emission studies of 1:1 CdS 1 and CdS 2**

Emission spectra were recorded for CdS 1 and CdS 2 and are presented in Figure IV.1.2. The observed emission of CdS 1 was broad from 400 nm to 700 nm and the FWHM was approximately 200 nm and the peak maximum was observed at 530 nm. The emission spectrum of CdS 2 also showed a broad band with a FWHM of 210 nm and a peak maximum at 550 nm. When
compared to the emission spectrum of CdS 1, the peak maximum of CdS 2 is shifted by 20 nm to the red region and this observation is similar to that of the observed absorption spectrum. The emission of CdS 1 and CdS 2 can be attributed to a combination of band edge and the trap state emission due to its higher FWHM. It is also observed that the absorption and emission maximum shifts to longer wavelength region with the decrease in the addition rate of the sulphide precursor. This observation is attributed to the change in size or shape of the NCs.

IV.1.7 X-ray diffraction and Energy dispersive X-ray analysis of 1:1 CdS 1 and CdS 2

X-ray diffraction studies were carried out to determine the crystal structural pattern of the CdS 1 and CdS 2 NCs. X-ray diffractogram of 1:1 CdS 1 and CdS 2 are given in Figure IV.1.3 & Figure IV.1.4, which shows 2θ values of 24.89 {100}, 26.15 {002} and 27.25 {101}. The samples CdS 1 and CdS 2 showed similar XRD spectrum and their corresponding d-spacing values are close to 3.57, 3.40 and 3.05 Å respectively. These 2θ values and d-spacing values match very well with the hexagonal pattern of the bulk CdS particles obtained from the literature (JCPDS card No. 06-0314). The other intense peaks observed in the X-ray diffractogram are attributed to the presence of the stabilizer TOAB whose d-spacing values are tabulated in Table IV.1.1. The rest of the unassigned peaks in the 2θ range from 30° to 45° may be attributed to the unreacted Cd^{2+} ions (JCPDS card No.05-0674). The EDAX spectrum
presented in Figure IV.1.5 shows the co-existence of Cd and S atoms in the CdS NCs which is in clear agreement with other spectral studies. The S and Cd atom peaks were observed between 2.3 to 4 eV.

IV.1.8 HRTEM studies of 1:1 CdS 1 and CdS 2

HRTEM images of 1:1 CdS 1 and CdS 2 NCs are given in Figure IV.1.6 & Figure IV.1.7 respectively. These figures clearly reveal the effective change in the morphology with respect to the addition rate of the precursor solution. The images a and b of Figure IV.1.6 corresponding to 1:1 CdS 1, show nanorods of aspect ratio ~5. The presence of lattice fringes in Figure IV.1.6b clearly reveals the crystalline nature of the nanorods formed. The SAED pattern of the corresponding TEM images as shown in Figure IV.1.6c also reveals the crystalline nature of the nanorods formed. TEM studies form an important evidence to confirm the shape tuning of CdS NCs synthesized by the present synthetic method. The higher sulphide addition rate produces nanorods (CdS 1). The TEM images of CdS 2 show a sphere shaped morphology. Figure IV.1.7b shows the lattice fringes of the nanospheres and image Figure IV.1.7c shows its corresponding SAED pattern confirming the crystalline nature of the nanospheres formed. It is evident from the TEM images that lower addition rate of the sulphide precursor results in the formation of nanospheres. A schematic representation (Scheme IV.1.1) has been put forth to explain the mechanism of nucleation and growth of CdS nanorods and nanospheres. The scheme shows a detailed description of the nucleation and growth of the
particles, when higher and lower addition rate of the sulphide precursor is employed.

**IV.1.9 Mechanism of shape tuning of CdS nanorods and nanospheres**

Various approaches were invoked by researchers to explain the shape evolution mechanism\(^{23}\) viz. the classical model given by Gibbs-Currie-Wulf theorem, orient attachment model, surfactant template model, the selective adsorption model and effective monomer concentration model. For the present investigation, the effective monomer concentration model is found to be more applicable. The reason to invoke this model is explained henceforth. In this model, the shape evolution is explained by manipulating the free energy of the crystallographic faces of the nuclei formed by controlling the precursor concentration either by varying the addition rate or by multiple injections. The shape evolution may be accounted as follows; At lower S\(^{2-}\) addition rate, where the resulting concentration of the S\(^{2-}\) precursor is lower at a single instant, the diffusional flux of the S\(^{2-}\) anion towards the growing crystal face is reduced and the nuclei tend towards the spherical morphology, which is thermodynamically more favorable. On the other hand, when the rate of addition of S\(^{2-}\) is higher, the concentration of the S\(^{2-}\) precursor at a single instant is higher, which facilitates the unidirectional growth along the c-axis leading to the formation of nanorods. The primarily addressed parameter, which controls the morphology of the nanoparticles, is the crystallographic face of the initial nuclei formed, which acts as a seed
for further crystal growth.

To confirm that the shape tuning is only due to the precursor addition rate and not due to the bulk precursor concentration, CdS NCs were synthesized by varying the precursor concentration. Effect of various reaction conditions such as temperature, precursor concentration, growth time, co-surfactants etc in generating a series of anisotropic nanostructures like nanorods, bipods, tripods, nanocubes, nanowires and nanoplatelets have been well explored earlier by various groups.\textsuperscript{10-20}

**IV.1.10 Absorption and emission studies of 1:2 CdS 1 and CdS 2**

To ascertain that the addition rate of the sulphide precursor is the only deciding factor in the observed morphology of the NCs formed, CdS NCs were also synthesized using higher sulphide precursor ratio. The CdS NCs were synthesized from 1:2 cadmium and sulphide precursor ratio or by keeping the reaction parameters constant (conditions maintained as that in the synthesis of 1:1 CdS quantum dots). The absorption spectrum of the CdS 1 sample prepared with 10 mL/min sulphide precursor addition rate and CdS 2 with 1 mL/min sulphide addition rate obtained from 1:2 precursor ratios are shown in Figure IV.1.8. As the precursor addition rate is reduced from 10 mL/min to 1 mL/min, the exciton peak and the absorption onset in the absorption spectrum gradually shifts towards the longer wavelength. This result is very much akin to that observed in the case 1:1 CdS QDs. A red shift in the emission peak maximum was observed in the emission
spectrum (Figure IV.1.9) when the addition rate of the sulphide precursor is decreased. This observation is again in line with the earlier trend observed for the 1:1 CdS QDs.

**IV.1.11 X-ray diffraction studies of 1:2 CdS 1 and CdS 2**

X-ray diffraction studies were also carried out to determine the crystal structure of the CdS 1 and CdS 2 formed from 1:2 precursor ratio (Figure IV.1.10 & Figure IV.1.11) respectively. The X-ray diffractogram showed 2θ values of 24.89 {100}, 26.15 {002} and 27.25 {101} and their corresponding d-spacing values are close to 3.57, 3.40 and 3.05 Å respectively. These 2θ values, their corresponding lattice planes and d-spacing values confirm the hexagonal pattern (JCPDS Card No. 06-0314) of the 1:2 CdS 1 and CdS 2 QDs. These results clearly indicate that the nanocrystal formed from 1:2 precursor ratio is very similar to that of the nanocrystals formed from 1:1 precursor ratio.

**IV.1.12 HRTEM studies of 1:2 CdS 1 and CdS 2**

HRTEM images (Figure IV.1.12 & Figure IV.1.13) of 1:2 CdS 1 and CdS 2 QDs showed nanorods and nanospheres respectively which is very much in agreement with that of the CdS QDs obtained from 1:1 precursor ratio. These results further add strength to our inference that only the rate of addition of the precursor i.e., the concentration of the precursor at the single instant of nucleation as proposed in the mechanism plays the key role in
shape tuning of the QDs and not the bulk concentration of the precursors.

The other parameters which can influence the shape tuning of the nanoparticles were also studied i.e., the CdS nanoparticles were synthesized with twice the earlier concentration of the stabilizing agent TOAB.

**IV.1.13 Absorption and emission studies of 1:1 CdS 1 and CdS 2 @2TOAB**

To further explore the mechanism of formation of CdS nanorods and nanospheres, another parameter i.e., the stabilizer concentration was doubled from 10 to 20 mM. The QDs synthesized by doubling the stabilizer concentration were characterized by absorption and emission studies and are shown in Figure IV.1.14 & Figure IV.1.15 respectively. The absorption spectrum showed an exciton peak at 390 and 403 nm for CdS 1 (10 mL/min) and CdS 2 (1 mL/min) respectively. The absorption onset for both CdS 1 and CdS 2 were observed at 450 nm. The emission spectrum was recorded for CdS 1 and CdS 2 by exciting the sample at 370 nm. The emission peak maximum was observed at 551 and 571 nm respectively. A red shift in the emission peak is observed as the rate of addition is decreased from 10 mL/min to 1 mL/min.

**IV.1.14 HRTEM imaging of 1:1 CdS 1 and CdS 2 @2TOAB**

HRTEM images were recorded for 1:1 CdS 1 and CdS 2 synthesized with twice the concentration of TOAB to explore the size and shape of the
QDs obtained. HRTEM images (Figure IV.1.16 & Figure IV.1.17) clearly show that at higher stabilizer concentration, both CdS 1 and CdS 2 show a spherical morphology. The SAED picture in Figure IV.1.16b & Figure IV.1.17b shows the crystallinity of the NCs formed. The observed result may be explained as follows in a convincing manner to support the shape tuning of CdS QDs. When the concentration of the stabilizing agent is low, it forms a flexible coating over the Cadmium ions and a faster addition rate of the sulphide precursor facilitates the nucleation and growth of CdS QDs unidirectionally to form nanorods. When the stabilizer concentration is higher, larger number of stabilizer molecules form a comparatively rigid coating over the Cadmium ions. This does not facilitate the growth of CdS seeds unidirectionally and hence grows steadily in all directions leading to the formation of nanospheres. The above observation evidences that the concentration of the stabilizer plays a vital role, where the optimum value can be fixed around 10 mM for the shape tuning to take place. A scheme (Scheme IV.1.2) is put forth to explain the reason for the formation of CdS nanospheres for both higher and lower addition rate of the sulphide precursor. The above mentioned experiment also emphasize the importance of fixing the optimum concentration of the stabilizing agent for shape tuning.
IV.1.15 Absorption studies of 1:1 CdS 3 and CdS 4

1:1 CdS (QDs) were also synthesized with two other addition rates of the sulphide precursor, CdS 3 of 7 mL/min and CdS 4 of 3 mL/min respectively to strongly emphasize on the mechanism put forth for the formation of nanorods and nanospheres. This experiment was carried out to get a better idea on the specific addition rate of the sulphide precursor at which the shape transition takes place. The absorption spectrum of CdS 3 and CdS 4 is shown in Figure IV.1.18. The exciton peak of CdS 3 was observed at 380 nm and that of CdS 4 was observed at 387 nm. From the absorption spectrum it is clear that the exciton peak and the absorption onset shift to the red region with the decrease in the addition rate.

IV.1.16 Emission studies of 1:1 CdS 3 and CdS 4

The emission spectra of CdS 3 and CdS 4 are shown in Figure IV.1.19. The emission peak maximum lies at 534 nm and 539 nm for CdS 3 and CdS 4 respectively. This observation reveals that the emission maximum lies between 1:1 CdS 1 and CdS 2 and the spectral shape is also very similar to that of CdS 1 and CdS 2.

IV.1.17 HRTEM studies of 1:1 CdS 3 and CdS 4

CdS 3 and CdS 4 nanocrystals were also characterized by TEM studies (Figure IV.1.20 & Figure IV.1.21 respectively). CdS 3 revealed a nanorod morphology (Figure IV.1.20a,b,c,d & e). The interesting observation in the
TEM image of CdS 3 is that it shows a mixture of nanorods and nanospheres, where the nanorods are shown by circles in Figure IV.1.21e, whereas only nanospheres are obtained for the sample CdS 4. From the above studies, it is evident that there is a clear transition in shape from rod to sphere occurring around the addition rate of 7 mL/min. A scheme (Scheme IV.1.3) is put forth to clearly show the transition in the shape of NCs from nanorod to nanosphere on decreasing the addition rate of the precursor.

**IV.1.18 Luminescence Lifetime studies of 1:1 CdS 1 and CdS 2**

Emission lifetime studies were carried out for 1:1 CdS 1 (nanorods) and CdS 2 (nanospheres) by exciting the sample at 370 nm and monitoring the lifetime decay at its emission maximum. The lifetime decays are shown in Figure IV.1.22. Lifetime decay of both nanorods and nanospheres are fitted tri-exponentially. The longer lifetime component of 1:1 CdS 1 is around 16.2 ns (60%) and the shorter lifetimes are around 0.33 ns (8%) and 2.03 ns (32%) whereas in the case of nanospheres CdS 2 the longer lifetime component is around 18.7 (67%) ns and the shorter lifetimes are around 2.5 ns (25%) and 0.39 ns (8%). The longer lifetime component (16.2 ns) and the shorter component (0.33 ns) is attributed to the deep trap state and shallow trap state emissions respectively and another shorter lifetime component (2.03 ns) is attributed to emission arising from the band edge state.\(^{23}\) In CdS 2, the shorter lifetime component (2.5 ns) that is assigned to the band edge emission
decreases in amplitude when compared to CdS 1 whereas the longer lifetime component increases in amplitude.

**IV.1.19 Time-Resolved Emission Studies (TRES) of 1:1 CdS 1**

The spectrally resolved dynamics of the different states involved in the emission of CdS nanorods and nanospheres is further investigated using time-resolved emission spectrum (TRES). Detailed studies on the luminescence lifetime of these nanoparticles have been carried out by various groups earlier.\textsuperscript{24,26-30} In this study, the photoluminescence decays of 1:1 CdS 1 were measured at different wavelengths between 430 and 630 nm by exciting at 373 nm (Figure IV.1.23). As the monitoring wavelength is changed from the blue region to red region, an increase in the average lifetime was observed. The lifetime of visible emission (530 nm) is fitted tri-exponentially with lifetimes of 1.96 ns (22.8%), 0.25 ns (10.8%) and 15.55 ns (66.4%), where the shorter lifetime of 1.96 ns with a relative amplitude of 22.8% is characteristic of band edge emission. The longer lifetime of 15.55 ns is characteristic of deep trap state of the nanoparticles.\textsuperscript{28} It is evident from the lifetime analysis data (Table IV.1.2) that the amplitude of the band edge emission decreases and the amplitude of deep trap state emission increases as we shift the monitoring wavelength to red region, which implies that at longer wavelength i.e., at the visible region, the deep trap state emission predominates while at shorter wavelength, band edge emission predominates with a maximum amplitude of 50%. It is well documented in
the literature that the photogenerated electrons and holes are captured by the shallow trap states on time scales faster (0.2 ns) than the exciton lifetime. The faster component of the tri-exponential decay is attributed to the presence of shallow trapped carriers. A constructed decay was plotted using the lifetime decay and is presented in Figure IV.1.24. The time-resolved emission spectrum, $I(\lambda, t)$, was constructed from the steady state fluorescence spectra, $I_{ss}(\lambda)$:

$$I(\lambda, t) = I_{ss}(\lambda) \sum a_i(\lambda) \exp\left[-t \tau_i(\lambda)\right]/ <\tau(\lambda)> \quad (1)$$

where $<\tau(\lambda)>$, the average decay time is given by

$$<\tau(\lambda)> = \sum a_i(\lambda) \tau_i(\lambda) \quad (2)$$

TRES is constructed from the wavelength-dependent decays together with the steady state fluorescence spectrum$^{29,30}$ and given in Figure IV.1.25. At shorter delay times, the dominant feature is the peak at 435 nm and also a peak at 530 nm is observed. As we increase the delay time from 0.1 ns to 15 ns, the peak at 435 nm decreases and a red shift is observed in the peak at 530 nm and beyond the time delay of 15 ns it remains constant. Time-resolved area normalised spectrum (TRANES) (Figure IV.1.26) was constructed from the TRES spectrum between the delay times of 0.1 ns and 15 ns. An isoemissive point at 485 nm was observed, which clearly indicates the presence of two different states; band edge and trap states. The intensity of the band edge emission (435 nm) decreases and the trap state emission
(520 nm) intensity increases with a red shift as the delay time is increased from 0.1 ns to 15 ns. The time-resolved emission studies carried out in this investigation clearly resolves contribution of the different states present in the emission process.

**IV.1.20 Femtosecond up-conversion studies 1:1 CdS 1 and CdS 2**

The faster component observed in the TCSPC technique is resolved using femto upconversion technique. Femtosecond emission decay of 1:1 CdS 1 and CdS 2 were recorded at their emission maximum of 530 and 550 nm respectively and is shown in Figure IV.1.27. The femtosecond lifetime decay was recorded for CdS QDs to study the dynamics of the faster component which was attributed to the trap state emission earlier. The emission lifetime decay is fitted using a tri-exponential function (Table IV.1.3). The emission decay consists of an ultrafast component of 0.7 ps and another faster component of 8 ps and a slower component of 3 ns which was detected using the TCSPC technique. The ultrafast component of 0.7 ps is attributed to the solvent profile, and 8 ps component is attributed to the trap state emission of the CdS quantum dots.

**IV.1.21 Conclusion**

In conclusion, the experimental findings clearly illustrate the methodology of controlling the rod and sphere shaped morphology of the CdS nanocrystals by simple manipulation of anion (sulphide) precursor
addition rate in a non-aqueous medium. The method also clearly resolves the specific addition rate of the sulphide precursor where the shape transition takes place. The study also reveals that, the variation in the precursor ratio do not alter the shape tuning mechanism. The synthesis of CdS QDs with higher concentration of the stabilising agent reveals the need for an optimum concentration of the stabilizer in shape tuning of the CdS nanoparticles. Further variation in the addition rates also evidence the shape transition taking place from nanorods to nanospheres. Time-resolved emission studies clearly shows the presence of two different types of emissive states i.e., the band edge state and trap state where the trap states may be sub classified as deep trap state and shallow trap state. Femtosecond up-conversion studies resolves the short lived components which is attributed to the shallow trap state components in the CdS nanorods and nanospheres.
IV.1.22 References


27. (a) J.W. Mullin. *Crystallization*, 4th Ed., Butterworth Heinemann, Boston, **2001**.


IV.2.1 Introduction

Nanocomposites provide the possibility for enhancement of functionality and multifunctional properties in contrast with their more limited single component counterpart.\(^1\) A wide variety of nanocomposite materials have been investigated in the literature, among which core-shell composites form an important group.\(^2\)-\(^5\) These core-shell structures have enhanced luminescence,\(^5\) improved stability,\(^6\) which is exploited in designing light harvesting devices\(^6\) and engineered band structures.\(^7\) Among these nanocomposites, the hybrid self assembled heterostructures have also acquired importance as that of the core-shell structures owing to their enhanced multi-functionality and novel properties.\(^10,11\) Semiconductor/metal nanocomposite is a typical example of these heterostructures. Self assembled building blocks leading to various structures like metal tipped semiconductor nanorods\(^12\) and metal shelled semiconductor nanowires\(^13\) were discussed earlier in the literature. Positioning of single metal nanoparticle on the semiconductor quantum dots was manipulated by AFM imaging.\(^14\) Understanding the surface and interface properties between the atoms in a nanocomposite material is a key area for developing new materials with novel applications.\(^15\) Basic excitations in an exciton and a plasmon have very different properties and therefore the interaction between them is an interesting subject of research. The physical properties of the excitons in hybrid nanocomposites containing semiconductor and metal nanoparticles have been studied elaborately in the literature\(^16\)-\(^21,22\) and the observations are mainly explained as energy transfer
and electron transfer between the semiconductor and metal nanoparticles in the heterostructures. The interaction of an individual semiconductor quantum dot and metal nanoparticle is the focus of this chapter. The optical properties of these heterostructures vary strongly when compared to their single component system. Hence, the understanding on the variation in luminescence properties, especially on the luminescence enhancement of the semiconductor quantum dots by the other component in the nanocomposite system becomes a very important factor in the construction of new materials. In this chapter, the synthesized CdS/Au nanocomposite revealed a highly enhanced and blue shifted emission with a decrease in their luminescence lifetime. The nanocomposite synthesised is a metal doped semiconductor nanorods and nanospheres without forming a complete core-shell type of heterostructures.

**IV.2.2 Abstract**

Nanoheterostructure consisting of CdS nanorods (NRs) and nanospheres (NSs) with gold nanoparticles (NPs) were synthesized by a phase transfer method. A considerable enhancement in the emission intensity around 9 fold and 5 fold was observed for the CdS (NR)/Au and CdS (NS)/Au nanocomposite respectively. When compared with the single component bare CdS counterpart a substantial blue shift in the emission peak maximum along with a decrease in the excited state lifetime was observed. The plasmons of the Au NPs collectively interact with the excitons of the CdS NRs and NSs which induces the enhancement of the luminescence. Time-resolved emission studies
clearly indicate the variation in the emission states of the nanoheterosructure when compared to its single component counterpart.

IV.2.3 Synthesis of CdS/Au nanocomposite

a. Materials

Chloroauric acid (99%) CDH chemicals, CdBr$_2$.4H$_2$O and Na$_2$S.9H$_2$O Sigma-Aldrich, Tetraoctyl ammonium bromide (TOAB) Lancaster chemicals were used as received. Doubly distilled water was used for the synthesis. Toluene, HPLC grade and sodium borohydride of analytical grade were purchased from SRL chemicals. All the chemicals purchased were used without any further purification unless otherwise stated.

b. Synthesis procedure

CdS nanoparticles that are used to prepare CdS/Au heterostructure was synthesized using phase transfer method. Typical synthesis procedure of CdS nanoparticles is given below. An aqueous solution of CdBr$_2$.4H$_2$O was mixed with a toluene solution of TOAB and stirred for 1 hour in an inert atmosphere. The toluene layer containing Cd$^{2+}$ ions stabilized by TOAB was separated and treated as cadmium precursor solution. Aqueous Na$_2$S was added uniformly to Cd$^{2+}$/TOAB solution to get CdS nanoparticles in the toluene layer, which was extracted from the solvent to get yellow solid of CdS nanoparticles. Na$_2$S was added with a different addition rate to prepare CdS nanorods and nanospheres. Detailed synthesis procedure is published elsewhere.$^{30}$
CdS nanoparticles synthesized by the above method forms the precursor for synthesizing CdS/Au hybrid nanocomposite.

**Synthesis of CdS/Au nanocomposite in solution:**

*Step 1: Preparation of CdS/Au$^{3+}$ composite.*

A known volume of CdS nanoparticles (nanorods) synthesized by the above method was diluted to 5 ml in toluene. To this a known volume of Au$^{3+}$/TOAB (0.2 ml) was added and stirred for 1 hour. Au$^{3+}$/TOAB were prepared by the method reported in the literature. The volume ratio of CdS and Au was maintained at around 50:1.

*Step 2: Reduction of Au$^{3+}$ in the composite*

The CdS/Au$^{3+}$ composite was taken and purged with Argon to create an inert atmosphere. A known amount of NaBH$_4$ (0.002 g approx. in 1 ml of water) was added and stirred for 1 minute. The toluene layer turned pale pink in colour indicating the reduction of Au$^{3+}$ to Au$^0$. The toluene layer containing the CdS/Au nanocomposite was separated and stored for further studies. Same procedure was carried out for the synthesis of CdS/Au nanocomposite from CdS nanospheres.

**IV.2.4 Absorption studies of CdS nanorod/Au nanoheterostructure**

The absorption spectrum of the nanoheterostructure is shown in Figure IV.2.1. A distinct peak at 356 nm characteristic of the CdS exciton peak and a prominent shoulder at 500 nm characteristic of the surface plasmons of the Au nanoparticles is seen in the absorption spectrum of CdS NR/Au nanocomposite.
Absorption spectrum of its single component counterpart CdS nanorods is also given in Figure IV.2.1 for comparison. A blue shift of 17 nm was observed in the exciton peak (356 nm) for the CdS NR/Au nanocomposite when compared with the single component counterpart (373 nm). The peak observed at 500 nm is typical of the surface plasmons of Au nanoparticles. An increase in the absorbance near the surface plasmon region is a clear indication of the formation of a nanocomposite between CdS QDs and Au nanoparticles. Interestingly, these CdS/Au nanocomposite in the present report, shows an increase in the absorption at the surface plasmon region (510 nm), clearly indicating the formation of a composite between Au nanoparticles and CdS QDs. The blue shift in the exciton peak of CdS QDs in the nanocomposite when compared to the absorption spectrum of bare CdS QDs suggests that the trap states are minimised by the Au nanoparticles in the nanocomposite.

**IV.2.5 Emission studies of CdS nanorod/Au nanocomposite**

Emission spectrum was recorded for CdS nanorod/Au nanocomposite and bare CdS nanorods. The normalized emission spectrum of CdS/Au nanoheterostructure and CdS nanorods are shown in Figure IV.2.2. The CdS/Au nanocomposite showed a peak maximum at 490 nm with an enormous enhancement in the luminescence intensity when excited at 360 nm. The enhancement is about 9 fold when compared to that of the bare CdS nanorods which is evidenced clearly from Figure IV.2.3. It is reported in the literature that the band edge emission of CdS nanoparticles is observed around 450 nm,
whereas the trap state emission shows peak around 600 nm. The significant observation here is that the emission intensity of the nanocomposite is highly enhanced and the FWHM is considerably reduced to \(~100\) nm when compared to the emission spectrum of bare CdS NRs. This observation is attributed to the fact that the formation of the nanocomposite reduces the presence of trap states which in turn reduces the trap state emission. The emission spectrum has a major contribution from the band edge states and hence the observed decrease in the FWHM.

**IV.2.6 HRTEM studies of CdS nanorod/Au nanocomposite**

The HRTEM images of the nanocomposite gives a clear insight on the morphology and structure of the hybrid nanocomposites of CdS/Au obtained from the present synthesis method. Figure IV.2.4 shows the CdS NR/Au NP hybrid nanoheterostructure where the presence of Au nanoparticles of diameter around 5 nm is seen and they are deposited along the length of the CdS nanorods with a length of approximately 200-300 nm. It is also evident from the figure that the Au NPs do not form a complete shell over the CdS nanorod which is well in accordance with the photophysical results.

**IV.2.7 EDAX studies of CdS nanorod/Au nanocomposite**

The EDAX spectrum of the CdS NR/Au nanocomposite is given in Figure IV.2.5. The EDAX spectrum is very much in accordance with the TEM image. The spectrum showed peaks of Au, Cd & S between 1.5 and 4 keV. The
peaks at this energy region indicate the coexistence of Au, Cd & S in the nanocomposite which is in accordance to the earlier literature reports.\textsuperscript{11} Au peak is also observed at 8 keV which is attributed to the free Au nanoparticles present in the sample. These free Au nanoparticles were also observed in the HRTEM image of CdS NR/Au nanocomposite. The above observations reaffirm our mechanism and hypothesis on the formation of the heterostructure and also this observation rules out the formation of core-shell type structures.

**IV.2.8 Absorption spectral studies of CdS nanosphere/Au nanocomposite**

Absorption spectrum of the CdS NS/Au nanocomposite obtained from CdS nanospheres is given in Figure IV.2.6. The absorption spectrum showed an exciton peak at 350 nm and the surface plasmon peak was observed at around 500 nm. There is a shift in the exciton peak which is observed as a shoulder when compared to its bare component. The absorption spectrum shows the surface plasmon peak of Au nanoparticles around 500 nm which is an indication for the formation of CdS and Au nanocomposite. This result is similar to that observed for the CdS NR/Au nanocomposite confirming that both CdS nanorods and nanospheres form nanocomposite with Au nanoparticles.

**IV.2.9 Emission studies of CdS nanosphere/Au nanocomposite**

The emission spectrum of CdS NS/Au nanocomposite is given in Figure IV.2.7. A peak at 460 nm was observed which is shifted to the blue region
when compared to its single component counterpart. It is also observed that the emission intensity is enhanced ~5 times than the bare CdS nanoparticles. It is also observed that the FWHM of the emission spectrum is drastically reduced when compared to the broad emission spectrum which was observed for the bare CdS nanoparticles. This observation clearly indicates that the band edge emission is dominant in the CdS NS/Au nanocomposite than in the CdS nanoparticles which shows both band edge and trap state emission. These observations were also similar to that observed earlier for the CdS NR/Au nanocomposites.

IV.2.10 HRTEM imaging of CdS nanosphere/Au nanocomposite

Figure IV.2.8 shows the HRTEM image of the hybrid nanoheterostructure obtained from CdS NSs and Au NP. Here again, the NPs of Au are deposited on the surface of the CdS NSs excluding the probability of formation of a complete shell on the NSs. There are approximately 4 to 5 Au NPs of size ~3-5 nm deposited on the CdS nanospheres of size 15 nm in diameter. A scheme was put forth to explain the probable mechanism of formation of the nanoheterostructure through the current method of synthesis (Scheme IV.2.1).

IV.2.11 EDAX studies of CdS nanosphere/Au nanocomposite

The EDAX spectrum of the CdS NS/Au nanocomposite is given in Figure IV.2.9. The EDAX spectrum of the nanocomposite is very much similar
to that of the CdS NR/Au nanocomposite observed earlier. Here again, the spectrum showed peaks between 1.5 and 4 keV indicating the coexistence of Au, Cd & S in the nanocomposite. Au peak is also observed at 8 keV which is attributed to the free Au nanoparticles present in the sample. The above observations confirm the formation of heterostructure in the CdS NS/Au nanocomposite similar to that of CdS NR/Au nanocomposite.

**IV.2.12 CdS/Au nanocomposite with excess loading of Au nanoparticles**

To completely eliminate the possibility of the formation of the core-shell structure, the CdS/Au nanocomposite was prepared with excess loading of Au precursor. The emission spectrum is shown in Figure IV.2.10. It is observed that the emission maximum is further blue shifted as the concentration of Au$^{3+}$ is increased, evidencing the fact that the higher concentration of Au$^{3+}$ further facilitates the exciton-plasmon interaction on the CdS surface by increasing the density of the Au nanoparticles deposited.

The TEM image of the nanocomposite of CdS/Au with excess loading of Au shown in Figure IV.2.11 still reveals a nanoheterostructure where Au nanoparticles are deposited on the CdS nanoparticles and it is also clearly observed that there is more number of free Au nanoparticles. This clearly confirms that the excess loading of Au precursor does not facilitate the formation of the core-shell structure between CdS and Au nanoparticles.
IV.2.13 Luminescence lifetime studies of CdS nanorod/Au and CdS nanosphere/Au nanocomposite

Luminescence lifetime decay of CdS NR/Au nanocomposite was recorded using Time correlated single-photon counting (TCSPC) technique by exciting at 370 nm and monitoring the decay at its emission maximum (Figure IV.2.12). The decay was fitted bi-exponentially. A component with a lifetime of 1 ns with a relative amplitude of 58% and another component with lifetime of 4 ns with a relative amplitude of 42% was observed. The single component counterpart (inset of Figure IV.2.12) showed tri-exponential decay (Table IV.2.1). It was observed that the longer lifetime of CdS quantum dot (88 ns) completely disappears in the CdS/Au nanocomposite. This observation reaffirms our hypothesis that the trap state emission in the bare CdS nanoparticles disappears when Au nanoparticles are deposited on it to form the nanocomposite.

The lifetime decay of CdS NS/Au nanocomposite was also recorded by exciting at 370 nm and monitoring the decay at its emission maximum and is shown in Figure IV.2.13. The inset of the figure shows the lifetime decay of the bare CdS nanospheres. The decay was fitted bi-exponentially and the longer lifetime component with a lifetime of 87 ns which is attributed to the trap state emission of CdS nanospheres completely disappears. This clearly evidences that the trap states are eliminated upon the formation of the nanocomposite.
IV.2.14 Discussion

The dependence of the luminescence intensity on the amount of attached Au NPs as well as the spectral shift of NRs and NSs emission indicated that the observed optical effects are likely to be related to the interaction of plasmons in Au NPs and the excitons in CdS NRs and NSs. Interestingly, as the luminescence intensity increases, the photoluminescence lifetime gradually decreases. This is in contrast to the classical observation in organic fluorophores where in an emission enhancement is accompanied by longer lifetimes. Several factors contributing to the luminescence enhancement has been discussed in the literature both theoretically and experimentally:16 (1) the decrease of non-radiative lifetime of an exciton in the presence of Au NPs, (2) the discreteness of NPs and (3) the randomness of NP positions. The first factor reduces the enhancement coefficient. The second factor can increase the electromagnetic enhancement since almost any type of deviation from the simplest geometries results in a local enhancement of the electromagnetic fields. Regarding the third factor, it is known from surface enhanced Raman scattering (SERS) and experiments on photoluminescence that the random fields induced by a rough metallic surface results in a strong electric field enhancement. One can conclude that the plasmon induced enhancement of electric fields can originate from collective excitations in a system of interacting Au NPs. Single; non-interacting Au NPs cannot provide any enhancement. In contrast, single Au-NPs will likely lead to a suppression of fluorescence due to an increase of non-radiative losses. It is well explained in
the literature\textsuperscript{16} that there are two terms, the radiative and non-radiative rates composing the reciprocal of the lifetime of an exciton. The radiative lifetime increases with the field enhancement factor and this is attributed to the local density of states. The blue shift in the emission of the composite can also be explained on the basis of plasmon–exciton interaction. In the presence of the Au nanoparticles the lifetime of the excitons decreases which consequently decreases the diffusion length of the excitons. These excitons cannot diffuse into the regions of smaller band gaps and hence the excitons emit photons in the regions of comparatively larger band gaps and hence blue shift in the emission spectrum of the superstructures is observed. Similar observation is reported in the present investigation, which is well correlated with the plasmon-exciton interaction along the CdS nanorods and nanospheres which depends on the homogeneity of the quantum dot surface.

IV.2.15 Time-resolved emission studies of CdS NR/Au nanocomposite

Time-resolved emission studies were carried out to further add strength to the above discussion. The time resolved emission studies of bare CdS quantum dots are explained and reported elsewhere in detail.\textsuperscript{30} The lifetime decay of CdS/Au nanocomposites was monitored from 380 to 580 nm at a regular interval of 10 nm. The lifetime decay is given in Figure IV.2.14a and the decay is fitted bi-exponentially (Table IV.2.2). Decay was constructed using the steady state emission and lifetime decay and is presented in Figure IV.2.14b. Time-resolved emission spectrum (TRES) was constructed using the
constructed decay using the literature methods,\textsuperscript{32} the peak maximum was found to shift to the red region as the time delay was increased from 0 ps to 300 ps (Figure IV.2.15). The time-resolved area normalised emission spectrum (TRANES) (Figure IV.2.16) was constructed from the TRES. It is observed that the emission intensity at 435 nm decreases and shifts to longer wavelength thus creating a clear isoemissive point at 450 nm. Though the band edge emission observed at 435 nm decreases as we increase the delay time, there is no increase observed in the intensity in the longer wavelength region, whereas in the case of bare CdS quantum dots, the longer wavelength emission maximum attributed to the trap state increases as we increase the delay time. This observation clearly reaffirms our hypothesis that the trap state emission density is considerably decreased when the Au nanoparticles are deposited on the CdS nanoparticles due to the collective interaction of the surface plasmons of Au nanoparticles with the excitons of CdS nanoparticles and hence a blue shifted enhanced emission is observed in the CdS/Au nanocomposites.

\textbf{IV.2.16 Conclusion}

CdS/Au nanoheterostructure synthesized by a solution process resulted in a highly enhanced and blue shifted emission and a quenching in the emission lifetime. The enhanced blue shifted emission and the lifetime quenching is nicely correlated and attributed to the collective interaction of the plasmons and the excitons in the hybrid nanoheterostructure. The HRTEM images confirmed the decoration of Au nanoparticles on the surface along the length of the
nanorod and similarly on the surface of the nanospheres. The TRANES resolved the emission states in the CdS/Au nanocomposite and confirmed the decrease in the density of the trap states.
IV.2.17 References


IV.3.1 Introduction

Nanoheterostructure assemblies are getting widespread attentions due to their multifunctionalities and wide range of applications. Charge separation in semiconductors is an important factor in constructing new efficient light-energy conversion materials.\(^1\) Charge separation in semiconductors can be enhanced through electron acceptors, such as metals,\(^2\) carbon derivatives,\(^3\) and other semiconductors with appropriate band structures.\(^4\) The metal-semiconductor interface induced charge separation favours photo catalysis. The most commonly used semiconductor photo catalysts are metal oxides like TiO\(_2\), which exhibits ultraviolet absorption ability only due to its large bandgap energy.

In a metal-semiconductor nanohybrid, where a semiconductor nanorod and a metal are in contact, image potential and lateral confinement may compete, possibly affecting carrier localization.\(^5\) Due to the size quantization, the electron–hole interaction of photo excited pairs is also expected to give a large contribution to the spectral properties of SNRs. Metal-semiconductor core-shell nanoparticles are generally synthesized using wet chemical methods. A common synthetic strategy involves harvesting seed crystals of the core material and treating them to induce growth of the shell material.\(^6-10\) The thickness of the semiconductor shell is usually predetermined by the amount of precursor added into the system, which makes it somewhat difficult to control the morphology.\(^11,12\) In the present chapter a nanoheterostructure assemblies of
Au and CdS have been synthesised in a non-aqueous medium and its optical properties were studied in detail.

**IV.3.2 Abstract**

Nanoheterostructure assembly was synthesised using a room temperature phase transfer method. The CdS was formed as nanosheets on the Au nanoparticles and the resulting nanoheterostructure showed emission in the blue region and this observation is attributed to the collective interaction of the surface plasmons with the excitons. Increase in the loading of Cd precursor to form the CdS nanosheets on the Au nanoparticles resulted in a gradual red shift in the emission maximum. The observations indicated that the thickness of the CdS surrounding the Au nanoparticles increases as we increase the concentration of the loaded Cd precursor. A decrease in the interaction of surface plasmon with the excitons of the CdS nanosheets resulting in a red shifted emission characteristic of free CdS nanoparticles was observed. TEM and XPS studies also confirm the increase in the thickness of the nanosheets of CdS on the Au nanoparticles. TRES studies of Au/CdS showed no considerable shift in the emission maximum which confirms that there is only one emitting state in the blue emitting assembly.
IV.3.3 Synthesis of Au/CdS nanoheterostructure assembly

a. Materials

Chloroauric acid (99%), CDH chemicals, CdBr$_2$$\cdot$4H$_2$O and Na$_2$S.$\cdot$9H$_2$O Sigma-Aldrich chemicals, Tetraoctyl ammonium bromide (TOAB) Lancaster chemicals were used as received. Doubly distilled water was used for the synthesis. Toluene, HPLC grade and sodium borohydride of analytical grade were purchased from SRL chemicals. All the chemicals purchased were used without any further purification.

b. Synthesis procedure

85 mg (2.5 mM) of CdBr$_2$$\cdot$4H$_2$O was dissolved in 100 mL of Argon saturated distilled water. 548 mg (10 mM) of TOAB was dissolved in Argon saturated toluene. The solutions were deaerated for 10 minutes, then mixed together and stirred for 1 hour in a three necked round bottom flask with simultaneous Argon purging. The organic layer was later separated and treated as the precursor for Cadmium ions.

Synthesis of Au nanoparticles

Au nanoparticles were synthesised using literature methods.$^{13}$ The typical synthesis procedure is as follows. Approximately 0.0105 g in 5 ml of water and 0.1 g of TOAB is dissolved in toluene. Both the solutions are mixed together and allowed to stir in an inert atmosphere. TOAB acts as phase transfer catalyst and it helps in transferring the Au$^{3+}$ to the toluene layer. It also plays a dual role as a stabilising agent. The toluene layer containing
Au$^{3+}$@TOAB is separated from the aqueous layer and then sodium borohydride solution is added dropwise and stirred for half an hour in an inert atmosphere. The Au$^{3+}$ ions are reduced to Au nanoparticles by NaBH$_4$ and stabilised by TOAB.

**Synthesis of Au/CdS nanoheterostructure assemblies**

0.5 ml (0.05 mM) of Cd$^{2+}$@TOAB solution is taken in a round bottom flask and diluted to 10 mL using toluene. To this 0.4 mL of Au nanoparticles (stabilised solution) is added and stirred for 2 hours and this is followed by the addition of dodecanethiol and the resulting solution was again stirred for further 2 hours to obtain higher stability of the nanocomposite. Na$_2$S solution is added drop wise to this mixture and stirred for half an hour so that the resulting CdS has 1:1 ratio of Cd and S. The toluene layer containing the nanocomposite was separated and used for further studies. The Au/CdS nanoassembly was synthesized for various concentrations of Cd precursor viz. 1 mL (0.1 mM), 2 mL (0.2 mM) and 5 mL (0.5 mM) so that the deposited CdS concentration is increased in the nanoassembly. The Au concentration was maintained as 0.4 mL for all the samples. The samples were labelled as Au/CdS 1, Au/CdS 2, Au/CdS 3 and Au/CdS 4 for 0.05, 0.1, 0.2, 0.5 mM concentration of Cd precursor respectively.

IV.3.4 Absorption studies of Au/CdS nanoheterostructure assembly

The absorption spectrum of Au/CdS nanoassembly synthesised from various concentration of CdS were recorded and shown in Figure IV.3.1 and
labelled as Au/CdS 1, Au/CdS 2, Au/CdS 3 & Au/CdS 4 for increasing concentrations of Cd precursor respectively. For lower concentration of CdS (Au/CdS 1), the surface plasmon peak was observed as a hump at around 520 nm and the CdS exciton peak was observed at 330 nm and a shoulder around 380 nm. The surface plasmon peak of Au nanoparticles in Au/CdS 2 was observed at 525 nm and the exciton peak showed a red shift (peak was observed around 365 nm) when compared to Au/CdS 1. Exciton peak at 380 nm was observed for CdS in the Au/CdS 3 sample and the surface plasmon peak of Au nanoparticles do not show any significant change. The exciton peak of CdS in Au/CdS 4 was further red shifted to 400 nm without any significant change in the plasmon absorption of Au nanoparticles. From the absorption spectrum it is clear that the exciton peak shifts to the red region as we increase the loading of CdS and this observation suggests that higher number of CdS nanoparticles is surrounding the Au nanoparticles.

**IV.3.5 Emission studies of Au/CdS nanoheterostructure assembly**

The emission spectra of Au/CdS nanoheterostructure assembly for various concentrations of CdS is shown in the figure IV.3.2. The emission maximum of Au/CdS 1 is observed at 417 nm. The emission maximum of Au/CdS 2 was observed at 460 nm, the emission maximum was further shifted to the red region (505 nm) for Au/CdS 3. The emission maximum was observed at 550 nm for the highest loading of Cd precursor (Au/CdS 4). This observation is very much in accordance with the absorption spectrum of the
Au/CdS nanoheterostructures. The blue emission of Au/CdS 1 and Au/CdS 2 is attributed to the collective interaction of the surface plasmons with the excitons of CdS which allows only the band edge emission of CdS nanoparticles whereas the red shifted emission observed for the Au/CdS 3 and Au/CdS 4 is attributed to both band edge and trap state emission typical of CdS nanoparticles. As the CdS concentration is increased, the interaction of the surface plasmons and the excitons becomes weaker and hence the combined emission from band edge and trap state arise. The weaker interaction of the surface plasmons and the excitons observed for higher concentration of CdS samples is attributed to the increase in the thickness of the CdS formed around the Au nanoparticles which suppresses the surface plasmon-exciton interaction.

**IV.3.6 TEM and EDAX studies of Au/CdS nanoheterostructure assembly**

To further understand the type of nano assembly formed by the CdS and Au nanoparticles, and explore their type of interactions, TEM images were recorded for all the four samples of Au/CdS heterostructures, Au/CdS 1, Au/CdS 2, Au/CdS 3 and Au/CdS 4 and they are shown in Figure IV.3.3, Figure IV.3.5, Figure IV.3.6 and Figure IV.3.8 respectively. The TEM image of Au/CdS 1 in the Figure IV.3.3 shows a thin layer of CdS formed on a cluster of Au nanoaparticles. It is also observed that the nanoheterostructure is assembled as a ring like structure where the Au nanoparticles are surrounded by a nanosheet like structure of CdS. To confirm the formation of CdS nanosheets on the Au nanoparticles, EDAX spectrum was recorded for Au/CdS
at the selected region of interest in the TEM image (white circles) in Figure IV.3.3 a. The EDAX spectrum is shown in figure IV.3.4 which shows peaks of Cd, S and Au between 2.0 and 4.0 eV. This confirms the coexistence of the three elements in the nanoheterostructure assembly.

The TEM image of Au/CdS 2 shows CdS nanosheets surrounding the Au nanoparticles. When compared with the TEM image of Au/CdS 1 it is observed that a thicker layer of CdS is formed which surrounds the Au nanoparticles. It is also observed here that the regular ring assembly like structure is slightly disturbed when compared to Au/CdS 1 sample. These observations indicate that with an increase in the concentration of CdS, thicker nanosheet of CdS is formed which surrounds the Au nanoparticles. The maximum distance between the Au nanoparticle and the CdS nanosheet is approximately 20 nm (shown in the TEM image with pink lines).

TEM image of Au/CdS 3 also shows CdS nanosheets surrounding the Au nanoparticles. When compared to the other two heterostructures, the observed nanosheet layer is thicker in Au/CdS 3. The maximum distance between the Au nanoparticle and CdS nanosheet is approximately around 40 nm as shown by the pink lines in Figure IV.3.6b. It is also observed that the assembled structure is completely disturbed. EDAX spectrum (Figure IV.3.7) of Au/CdS 3 was recorded which showed the coexistence of Cd, S and Au atoms. The intensity of Au peak observed at around 2.5 eV is comparatively weaker than the observed Au intensity in the EDAX spectrum of Au/CdS 1 confirming the formation of thicker layer of CdS nanosheets in Au/CdS 3.
The TEM image of Au/CdS 4 shows even thicker CdS nanosheet that are formed on the Au nanoaprticles. It is also observed that the Au nanoparticles is almost buried (shown by circles in Figure IV.3.8b) inside the nanosheets of CdS clearly evidencing the formation of thicker layer of CdS on the Au nanoparticles.

The TEM images of the hetrostructures formed by varying the concentration of CdS clearly indicates that the thickness of CdS nanosheet increases monotonously as the concentration of CdS is increased. The ordered assembly is also disturbed when higher concentration of CdS is used for the formation of the nanosheets. Lower concentration of CdS orients a group of Au nanoparticles in to an ordered assembly and surrounds the Au nanoparticle.

**IV.3.7 X-ray photoelectron spectroscopy studies of Au/CdS nanoheterostructure assembly**

X-ray photoelectron spectrum of Au-CdS core shell structures were well studied in literature.\(^{14}\) X-ray photoelectron spectrum was recorded for Au/CdS 1 and Au/CdS 3 and shown in Figure IV.3.9 and Figure IV.3.10 respectively. The survey scan of Au/CdS 1 showed peaks of Cd, S and Au. The spectrum was corrected for 2 eV with respect to the carbon peak as standard. A binding energy of 405 eV of Cd 3d5/2 was observed for Au/CdS 1 which is typical of bulk CdS. Sulphur showed peak at 164 eV for 2p3/2. Two types of sulphur peaks were observed characteristic of CdS sulphur and thiol sulphur. The typical binding energy peaks of Cd and S for simple CdS is seen at 405 and 164
eV. When compared to the bulk metal binding energy, the binding energy of Cd and S shifted to positive binding energy. This is due to the interaction of CdS with Au nanoparticles respectively. A binding energy of 84.1 eV of Au 4f7/2 peak was found for pure Au colloid sample,\textsuperscript{15} but in Au/CdS 1 there is a slight positive shift in the binding energy of Au which is again due to its interaction with CdS. Au/CdS 3 also showed typical peaks of Cd and S but interestingly the Au peak was very insignificant even after scanning 4-5 regions in the sample during the experiment. This clearly confirms that the thickness of the CdS layer is increased and Au is buried inside the shell and unavailable for probing.

IV.3.8 Luminescence lifetime studies of Au/CdS nanoheterostructure assembly

Luminescence lifetime decay was recorded for all the four samples of Au/CdS heterostructure assemblies and is shown in Figure IV.3.11. The decay analysis data is given in Table IV.3.1 The samples were excited at 375 nm and monitored at their corresponding emission maxima. All the samples were fitted triexponentially. Au/CdS 1 showed lifetimes of 20 ps (2%), 1 ns (81%) and 3 ns (17%). The contribution of the shortest and longest lifetime component is very less and is attributed to the trap state emission of CdS nanoparticles and the component with 1 ns lifetime typical of band edge emission was the major component. This clearly evidences that the band edge emission predominates the trap state emission in the nanoassembly with a thin layer of CdS. The
samples Au/CdS 2, Au/CdS 3 and Au/CdS 4 showed a gradual increase in the trap state lifetimes with an increase in their corresponding relative amplitudes. It was also observed that there is a simultaneous decrease in the band edge component. This clearly reveals that the trap state emission enhances with a suppression of the band edge emission as we increase the loading of CdS. Time resolve emission studies were carried out to further explore the contributions of the trap state and band edge emission in the Au/CdS heterostructure assemblies.

**IV.3.9 Time-resolved emission studies of Au/CdS nanoassembly**

Time-resolved emission studies were carried out to probe the blue edge emission of Au/CdS 1. The sample was excited at 375 nm and the decay monitoring wavelength was varied from 400 to 650 nm. The lifetime decays as a function of monitoring wavelength is shown in Figure IV.3.12 and decay analysis data is give in Table IV.3.2. The lifetime decay are fitted triexponentially. Time-resolved emission spectrum was constructed with the method discussed in detail in Chapter IV.1. The time-resolved emission spectrum is shown in Figure IV.3.13. As the delay time was increased from 0.1 ns to 15 ns, there was no considerable shift in the peak maximum. Generally a red shift in the TRES emission maximum is the attribute of CdS nanoparticles with both the band edge and trap state emission. In the present study there was no shift in the TRES emission maximum and this observation clearly reveals that the emission of Au/CdS 1 is completely due
to a single component. This single component is attributed to the band edge emission of CdS nanosheets.

IV.3.10 Femto up-conversion studies of Au/CdS nanoheterostructure assembly

Femto up-conversion studies were carried out to account for the shorter lifetime components of the Au/CdS heterostructure assemblies observed in the picosecond lifetime studies. The sample was excited at 375 nm and monitored at its emission maximum. The decay is given in Figure IV.14. The longer lifetime was fixed as 3 ns for fitting the data which was obtained from the picosecond lifetime studies. A lifetime of 3 ps and 40 ps (Table IV.3.3) was obtained which is attributed to the shallow trap states but the contribution of the shorter component is insignificant.

IV.3.11 Discussion

Au/CdS nanoheterostructure assemblies were synthesised by phase transfer method in non-aqueous medium in which the Au nanoparticles are shelled by the CdS nanosheets. The subject of interest in the present chapter is the observed photophysical changes of Au/CdS nanoheterostructure assembly as a function of CdS concentration. Blue emitting Au/CdS assembly was obtained when lower concentration of Cd precursor was used for the synthesis of CdS. As the concentration of the Cd precursor was increased the emission maximum was shifted to the red region. This observation was elaborately
explored using TEM and time resolved studies. As the concentration of Cd precursor was increased, a thicker layer of CdS nanosheet surrounds the Au nanoparticle cluster which was confirmed by the TEM images. The XPS spectrum also confirms that the Au nanoparticles were buried inside the CdS nanosheets (observed lower intensity peaks of Au nanoparticles).

In Au/CdS \textbf{1}, a thin layer of CdS is formed over the Au nanoparticles which show a blue emission. The observed blue emission is due to the interaction of the surface plasmons of Au nanoparticles and the excitons of CdS nanosheet. The complete interaction of the surface plasmon and excitons in the nanoassembly prevents the formation of surface traps, leading to an enhanced band edge luminescence in this system. Since a thin layer of CdS is formed, the Au nanoparticles are more than for the complete interaction of surface plasmon and excitons in the CdS nanosheets, whereas this is not the case with Au/CdS \textbf{2}, where a comparatively thicker layer of CdS is formed on the Au nanoparticles. This does not allow the surface plasmon interaction of Au nanoparticles completely with the excitons which suppresses the trap state emission and hence resulting in the band edge emission alone. When further thicker layer of CdS is surrounding the Au nanoparticles, the surface plasmons interact only with the excitons of CdS in contact with the Au nanoaparticles and hence interaction of surface plasmons with the excitons on the outer surface of the CdS is very weak. This results in both band edge and trap state emission of CdS nanosheets but still the band edge emission dominates. When the thickness of the nanosheet is further increased the interaction between the
surface plasmons of Au nanoparticles buried deep inside the nanosheets becomes weaker than Au/CdS 2 and the emission arises more from the CdS which are far away from the Au nanoparticles and lesser emission is observed from those nearer. Hence, the contribution of trap state emission is further enhanced which is also revealed from the lifetime studies of Au/CdS 3.

Au/CdS 4 showed a larger red shift in emission maximum when compared to Au/CdS 3. The emission arose from both the CdS interacting with Au and the CdS away from the Au nanoparticles. Since the Au nanoparticles are buried deep inside the nanosheets of CdS, major portion of the emission is from the CdS away from the Au nanoparticles and hence much red shifted emission is observed where the trap state emission dominates the band edge emission. The emission of Au/CdS nanoheterostructure assembly as a function of thickness of CdS is given in the Scheme IV.3.1. The photophysical and TEM studies show that an optimum distance between Au and CdS is required for efficient interaction between surface plasmons and excitons. Blue emission is observed for Au/CdS where the maximum distance between Au and CdS is approximately 20 nm and above which the interaction between Au and CdS becomes weaker and hence a red shifted emission is observed which is a combination of both trap state and band edge emission.

IV.3.12 Conclusion

Au/CdS was synthesised by phase transfer method. Highly blue emitting nanoheterostructure assembly was obtained due to the strong surface plasmon -
exciton interaction between the Au nanoparticles and CdS shells. The emission was further tuned by varying the concentration of CdS. The varied emission is due to the variation in the thickness of the CdS layer over the Au nanoparticles. More the thickness of the CdS nanosheet, larger is the red shift in the emission maximum which is due to the weaker surface plasmon-exciton interaction. The variation in the thickness of the CdS shell is confirmed by the TEM images and also the XPS studies. The TRES spectrum also shows that the emission arises completely from the band edge emission in the blue emitting Au/CdS assembly. Femtosecond up conversion studies also resolve the short lived components detected in TCSPC technique.
IV.3.13 References


