

Plasmon - Exciton Interaction in Gold - CdTe Nanostructures



A thesis submitted towards partial fulfillment of the BS-MS Dual
Degree Program

by

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under the guidance of

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Certificate

This is to certify that this thesis “*Plasmon-Exciton Interaction in Gold-CdTe Nanostructures*” submitted towards partial fulfillment of the BS-MS dual degree programme at Indian Institute of Science Education and Research, Pune represents original research carried out by **Prashant Bhaskar** at Indian Institute of Science Education and Research, Pune under the supervision of **Prof. Dr. Sulabha K. Kulkarni** during the academic year 2013-2014.

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Dr. Sulabha K. Kulkarni

Professor

Dedicated to my family.

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Abstract

In this work, conjugation of metal and semiconductor nanoparticles was chemically done and the properties of Au-CdTe hybrid nanostructures were studied using various characterization methods. Intriguing properties were observed due to coupling of excitons in semiconductor nanoparticles and plasmons in metal nanoparticles. When combined into heterostructures, the nanometer-scale vicinity of the two systems leads to interaction between quantum-confined electronic states in semiconductor nanostructures and dielectric-confined electronic states in the metal counterparts. The interaction between individual nanoparticles has been revealed as an enhancement or suppression of emission in case of conjugated gold nanorods and CdTe quantum rods as well as suppression of emission in gold nanostars and CdTe quantum rods heterostructures where enhancement of excitonic absorption was also observed. Enhanced emission comes from electric field amplified by the plasmon resonance, whereas emission suppression is a result of energy transfer from semiconductor to metal nanoparticles. Such exciton-plasmon interactions allow designing of absorption and emission properties, control of nanoscale energy-transfer processes which can have potential applications in the fields of optical sensing, fluorescence based sensors, photovoltaic systems and various other fields.

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Chapter 1

Introduction

1.1 Importance of Nanostructures

Nanoscience and Nanotechnology is a broad and interdisciplinary area of research that has been growing explosively with potential for revolutionizing the ways in which materials can be used in our day-to-day lives. Nanomaterials are defined as a set of materials with at least one dimension in less than ~ 100 nm. Figure 1.1 shows some possible types of nanostructures.

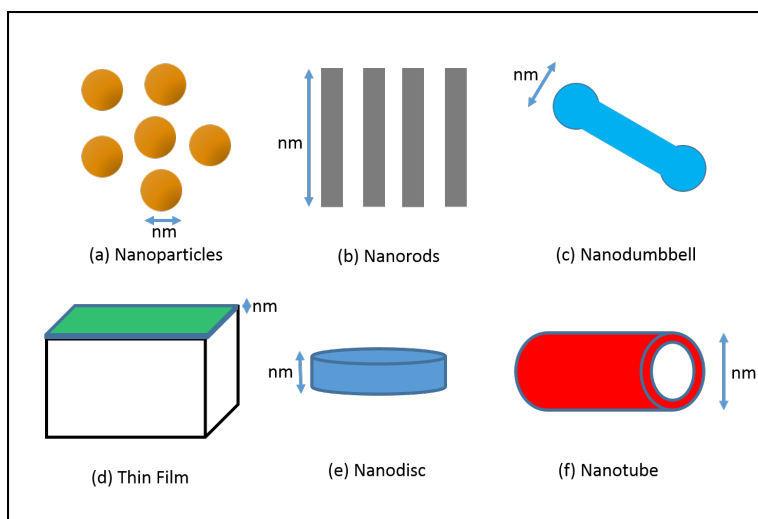


Figure 1.1: *Schematic diagram of some possible shapes of nanoparticles*

Nanomaterials are important because at this scale unique optical, magnetic, electrical and other properties change due to quantum confinement in semiconductor nanoparticles and dielectric confinement in metal nanoparticles. Thus, these unique properties have potential for great impacts in various fields and applications.

1.2 Types of Nanomaterials

Nanomaterials can be categorized into two types namely ‘Semiconductor nanoparticles’ and ‘Metal nanoparticles’. Both of these materials show intriguing properties at nanoscale sizes.

1.3 Quantum Confinement in Semiconductor Nanoparticles

Below a characteristic size, every material shows size-dependent properties. Semiconductors and insulators are known to have energy band-gap between valence band and conduction band. The band-gap energies of semiconductor nanostructures change as the size and shape of semiconductor nanostructures change. Upon photon illumination with minimum energy equal to the band gap, an electron from valence band can get excited to conduction band in a semiconductor leaving a hole in valence band. A hole is just absence of an electron from a filled valence band. It is a positively charged particle. Due to opposite charges, the electron in conduction band is electrostatically attracted to hole in the valence band. An electron hole pair is known as exciton. The Coulomb force between two oppositely charged particle with charges $+e$ and $-e$ and at a separation of r can be given as follows.

$$F = -\frac{ke^2}{\epsilon r^2} \quad (1.3.1)$$

Where k is universal constant and ϵ is the dielectric constant of semiconductor material. Excitons can be classified into two types.

a) *Frenkel Excitons*: In materials which have small dielectric constants, the Coulomb interaction between an electron and a hole becomes stronger and the excitons thus tend to be tightly bound. The diameter of excitons become comparable to lattice constant. These are called Frenkel excitons and have a typical binding energy of the order of 0.1 to 1 eV.

b) *Mott-Wannier Excitons*: Mott-Wannier excitons are typically found in semiconductor crystals with small energy gaps and high dielectric constants which results into reduced Coulomb interaction because of electric field screening. Thus the size of these excitons are larger than lattice spacing. These excitons have a typical binding energy on the order of few meV.

An electron and positron combines together to form an atom called positronium which has bound state energies given by Rydberg's formula first introduced by Neils Bohr to explain hydrogen atom. The bound state energy can be written as follows.

$$E = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2} = -\frac{6.8}{n^2} \text{ eV} \quad (1.3.2)$$

Here a_0 is Bohr's radius given by

$$a_0 = \frac{4\pi\epsilon_0 \hbar^2}{m_0 e^2} = 0.0529 \text{ nm} \quad (1.3.3)$$

and m_0 denotes the mass of electron (or positron), ϵ_0 denotes the dielectric constant of free space and quantum number n takes on the values $n = 0, 1, 2, 3, 4, \dots, \infty$.

An analog of positronium system can be an excitonic system. Let the effective masses of electron and hole be m_e and m_h which may not be same as the mass (m_0) of a free electron. So the effective mass m^* of this excitonic system can be given as

$$m^* = \frac{m_e m_h}{m_e + m_h} \quad (1.3.4)$$

When effective mass of electron is appreciably less than effective mass of hole ($m_e \ll m_h$), then the above term can be rewritten as

$$m^* = \frac{m_e}{1 + \frac{m_e}{m_h}} \quad (1.3.5)$$

which shows that in such a case, m^* becomes comparable with the mass of electron. If we consider equation (1.3.2) and (1.3.3) then we can see that the energy of n^{th} level and radius depend upon effective mass of system and dielectric constant of medium. Both m^* and ϵ factors have the effect of decreasing the exciton energy E_{ex} from that of positronium and the equation is given by

$$E_{ex} = \frac{\frac{m^*}{m_0} e^2}{\left(\frac{\epsilon}{\epsilon_0}\right) 4\pi\epsilon_0 a_0 n^2} = \frac{13.6 \frac{m^*}{m_0}}{\left(\frac{\epsilon}{\epsilon_0}\right)^2 n^2} eV \quad (1.3.6)$$

These two factors consequently increase the exciton radius which can be given by

$$a_{eff} = \frac{\frac{\epsilon}{\epsilon_0}}{\frac{m^*}{m_0}} a_0 = \frac{0.0529 \frac{\epsilon}{\epsilon_0}}{\frac{m^*}{m_0}} nm \quad (1.3.7)$$

Using electron effective mass values and dielectric constant for semiconductors like GaAs or CdTe, we can see that the value of energy comes to be around few meV and correspondingly effective radius of excitons fall in range of tens of nanometers which can be the size of quantum dot itself, and in such a case quantum confinement occurs. So, the exciton radius can be considered as an index of the extent of quantum confinement in semiconductor nanoparticles. The limiting regions of confinement can be identified on the basis of ratio of dimension d of a nanoparticle and to the effective excitonic radius a_{eff} . The two limiting regions are called “weak-confinement regime” ($d > a_{eff}$) and “strong-confinement regime” ($d < a_{eff}$). Under weak-confinement regime, the excitons can undergo unrestricted translational motion, just as in bulk material but in case of strong confinement, this translation gets restricted. So, Frenkel excitons come under strong-confinement regime while Mott-Wannier excitons come under weak-confinement regime which are weakly bound electron-hole pairs. The energy of such an exciton is slightly less than the energy gap (E_g) between valence and conduction band because that is how an exciton is formed (excitonic energy is lesser than band gap).^[1] Figure 1.2 shows a schematic diagram of energy level in a semiconductor and a Mott-Wannier exciton.

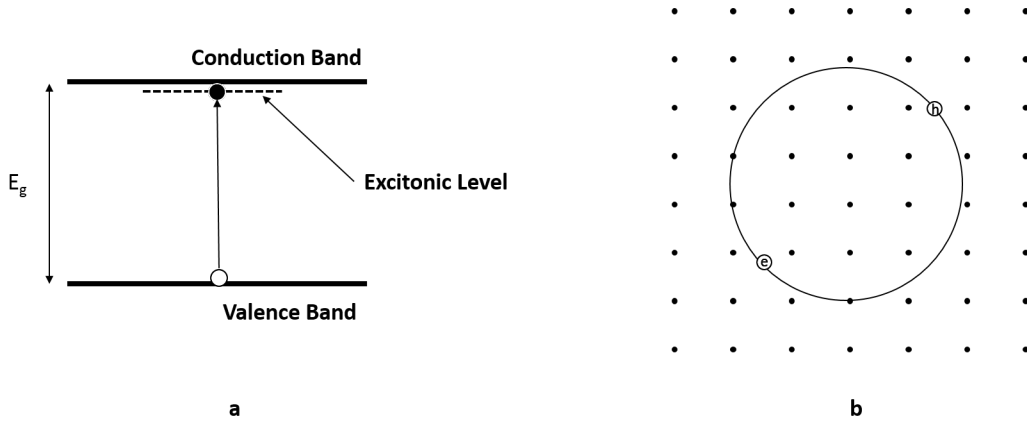


Figure 1.2: (a) Energy level diagram for a typical semiconductor along with the excitation energy level.^[1] (b) Mott-Wannier exciton in a typical lattice.^[1]

For a Mott-Wannier exciton, the Hamiltonian can be written as

$$H = \frac{P_e^2}{2m_e} + \frac{P_h^2}{2m_h} + \frac{e^2}{\epsilon|r_e - r_h|} \quad (1.3.8)$$

Here m_e and m_h are effective masses of electron and hole respectively and ϵ is dielectric constant of semiconductor material. The first two terms in equation 1.3.8 correspond to kinetic energies of electron and hole and the third term corresponds to Coulomb energy of electron-hole pair. The Bohr radius of such an exciton can be written as

$$r_B = \frac{\hbar^2 \epsilon}{e^2} \left[\frac{1}{m_e} + \frac{1}{m_h} \right] \quad (1.3.9)$$

Using effective mass approximation and time independent Schrödinger equation, the term for excitation energy can be derived from equation (1.3.8) and can be written as

$$\Delta E = \frac{\hbar^2 \pi^2}{2R^2} \left[\frac{1}{m_e} + \frac{1}{m_h} \right] - \frac{1.8e^2}{\epsilon R} + \text{polarization term} \quad (1.3.10)$$

Here R is the radius of cluster or a nanoparticle trapping the exciton. With decreasing particle size, the spatial overlap of electron and hole wave function increases and this results in enhancement of electron-hole interaction. So as a result of quantum confinement, the energy levels in one or more dimensions get shifted due to change in size and shape.^[2,3] It also has been well observed that the absorption profile gets blue-shifted with decreasing nanoparticle size. Another result of the confinement is the appearance of excitonic features in absorption spectra at the room temperature that are observed only at low temperatures in case of bulk materials.

1.4 Localized Surface Plasmon Resonance in Metal Nanoparticles

Since ancient times window glasses of churches and palaces had been beautifully designed with different colored glasses. Such glasses were used to be prepared by inclusion of metallic powders like Au, Ag, and Cu etc. resulting into beautiful shades. Besides showing yellow color in bulk, it was shown by M. Faraday in 1857 that Au nanoparticles solution shows intense red color.

In an attempt to understand the red intense color shown by gold nanoparticles, Gustav Mie came up with a solution to Maxwell's equations by considering light interaction with spherical particles dispersed in a dielectric medium. In this solution, the spherical particles are considered to be much smaller than the optical wavelength ($D \leq \frac{\lambda}{10}$) suspended in medium with dielectric constant ϵ_m which is nothing but quasi-static approximation.^[4] In this context, the quasi-static approximation means that the applied electromagnetic field remains uniform within each spherical particle and these spherical particles are well apart from each other in order to accommodate the negligence of any kind of inter particle interactions. If the intensity of incident light is assumed to be I_0 then the intensity of transmitted light can be written as in equation (1.4.1) (from Lambert-Beer Law). Here we have also assumed that particles are dispersed in a dielectric system of length ' x '. Figure 1.3 shows a simplified schematic diagram of the system.

$$I = I_0 e^{-\mu x} \quad (1.4.1)$$

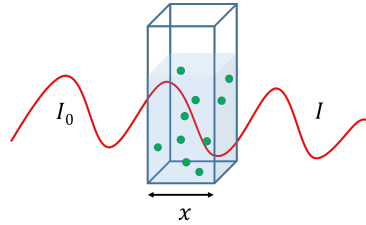


Figure 1.3: Incident electromagnetic radiation with intensity I_0 passing through medium of thickness x with transmitted intensity I .

Here μ is extinction coefficient which can be written as

$$\mu = \frac{N\sigma_{ext}}{V} \quad (1.4.2)$$

where N is number of particles embedded in the medium, V is volume of particles and σ_{ext} is the extinction cross section of the particles. The term σ_{ext} can be defined as

$$\sigma_{ext} = \sigma_{abs} + \sigma_{scat} \quad (1.4.3)$$

The extinction, scattering and absorption cross sections are calculated from Mie theory and can be written as follows.^[5]

$$\sigma_{ext} = \frac{2\pi}{|k^2|} \sum_{L=1}^{\infty} (2L+1) \operatorname{Re} \{a_L + b_L\} \quad (1.4.4)$$

$$\sigma_{scat} = \frac{2\pi}{|k^2|} \sum_{L=1}^{\infty} (2L+1) (|a_L|^2 + |b_L|^2) \quad (1.4.5)$$

$$\sigma_{abs} = \sigma_{ext} - \sigma_{scat} \quad (1.4.6)$$

Here, a_L and b_L are scattering coefficients and they are functions of a and λ in terms of Ricatti-Bessel functions and k is defined as

$$k = \frac{2\pi\sqrt{\epsilon_m}}{\lambda} \quad (1.4.7)$$

In case of very small particles with radius R ($kR \ll 1$), the extinction cross section is dominated by mainly absorption part which can be given as

$$\sigma_{ext} = \frac{24\pi^2 R^3 \epsilon_m^{3/2}}{\lambda} \frac{\epsilon_2}{(\epsilon_1 + 2\epsilon_m)^2 + \epsilon_2^2} \quad (1.4.8)$$

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega) \quad (1.4.9)$$

Here $\epsilon(\omega)$ is the dielectric constant of the particles and $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are real and imaginary parts of the dielectric constant. In equation 1.4.8, we can see that the extinction cross section has a dependence on R^3 and extinction coefficient (1.4.2) has a dependence on $\frac{1}{V}$ which makes absorption a size independent entity. It can be seen from equation (1.4.8) that the extinction cross section has maxima when

$$\epsilon_1 + 2\epsilon_m = 0 \quad (1.4.10)$$

or

$$\epsilon_1 = -2\epsilon_m \text{ and if } \epsilon_2 \text{ is small}$$

This results into strong resonance band. The band width and peak height is mainly determined by $\epsilon_2(\omega)$ (interestingly σ_{ext} vanishes if $\epsilon_2(\omega)$ is infinitely large as well as zero).^[1,5] An extension to this theory was developed by Richard Gans in 1912 which focused on extrapolating the theory from spherical particles case to ellipsoidal particles case. In this theory, the absorption depends only upon the aspect ratio of particles but not on their absolute dimensions. Here, the polarization or shape factors related to three dimensions of a particle is considered to calculate and estimate absorption profile for ellipsoidal nanoparticles, as in our case we will be mostly dealing with gold nanorods (Au NRs).

Ultimately whole calculation boils down to a conclusion that if we have very small metallic nanoparticles (size ~ 20 nm in case of gold) then absorption profile can be understood by Mie's theory but it does not explain the red shift in absorption spectra for metal nanoparticles with increasing size since the dipole approximation no longer remains valid. Therefore, one should consider dielectric constant which depends on frequency as well as particle size. For metals the dielectric response is appropriately described by Drude Model.

According to Drude model, free electrons in the conduction band can be considered as plasma. Upon light illumination on a metallic surface, these free electrons (loosely bound plasma) oscillate coherently about their fixed ions with the frequency of light. These collective oscillations are quantized and are known as plasmons and their frequency of oscillation is known as plasma frequency (ω_p) which can be written as

$$\omega_p = \sqrt{\frac{ne^2}{m\epsilon_0}} \quad (1.4.11)$$

Here, n is conduction electron density, e is electronic charge, m is mass of electron and ϵ_0 is permittivity of free space. If the frequency of light incident on a metal is lower than its plasma frequency, the light gets reflected back and if it's greater, it passes through the metal as in that case electrons are not fast enough to screen such a high frequency. In most metals, the plasma frequency is in the ultraviolet region, making them shiny (reflective) in the visible range. In some metals, electronic interband transitions occur in the visible region resulting into absorption of specific light energies thus yielding distinct color. These plasmons can be excited by high energy electrons as well. A limitation for incident electromagnetic waves is their penetration depth into the metal which is generally low. So, contribution of surface electrons is significantly greater than bulk electrons. Hence, the observed plasmon bands are termed as 'surface plasmons'. Surface plasmons (SPs) are coherent oscillation of electrons present at the interface of a metal and a dielectric medium where the real part of the dielectric function changes sign. SPs are energetically weaker than those of bulk plasmons. When an electromagnetic radiation with frequency equal to the natural frequency of surface electrons is incident on a metal surface, a phenomenon called "surface plasmon resonance (SPR)" occurs which is nothing but collective oscillation of the surface electrons. SPR in case of nanomaterials where size of nanoparticles are low (usually less than 200 nm), the surface electrons oscillate coherently with incident photons and such plasmons are called as "localized surface plasmons. When the frequency of incident photons is equal to the plasma frequency of metal then due to constructive interference, surface plasmon resonance occurs.

Following the model of the reduction of the effective electron mean free path and enhanced electron-surface scattering,^[6] the size dependence of the surface plasmon resonance can be very well understood. It starts with considering a free conduction electrons model and considering dielectric function as a combination of an interband term $\epsilon_{IB}(\omega)$ and a Drude term $\epsilon_D(\omega)$ that can be written as

$$\epsilon(\omega) = \epsilon_{IB}(\omega) + \epsilon_D(\omega) \quad (1.4.12)$$

And $\epsilon_D(\omega)$ is given by the following expression.^[7]

$$\epsilon_D(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma\omega} \quad (1.4.13)$$

Here, ω_p is bulk plasmon frequency of a metal defined as in equation (1.4.11), γ is an introduced damping constant and is equal to plasmon absorption bandwidth for the case of a perfectly free-electron gas in the limit $\gamma \ll \omega$.^[5] The damping constant γ is related to lifetimes of all electron scattering processes (electron-electron, electron-photon, electron-defect) in a bulk material^[5] which can be written as follows.

$$\gamma_0 = \sum_i \tau_i^{-1} = \tau_{e-e}^{-1} + \tau_{e-ph}^{-1} + \tau_{e-d}^{-1} \quad (1.4.14)$$

Where τ denotes lifetime of electron scattering processes. For nanoparticles smaller than mean free path of the conduction electrons, electron-surface scattering has been considered as an important entity needed to be included in the above formalism which includes a new term that is dependent on the radius r of the particle and can be written as follows.

$$\gamma(r) = \gamma_0 + \frac{Av_F}{r} \quad (1.4.15)$$

Where A is a theoretical parameter dependent upon details of scattering processes^[5] and v_F is the velocity of electrons at Fermi energy level. This gives the correct $\frac{1}{r}$ dependence^[6] of the plasmon bandwidth as a function of size of nanoparticles.

1.5 Importance of Coupling of Metal and Semiconductor Nanoparticles

Metal nanoparticles are known to have controllable absorption and scattering resonances due to surface plasmon excitations while semiconductor nanoparticles are known to have tunable highly efficient emission and absorption properties. The advantage of these nanomaterials is not limited to their controllability of optical properties but a set of whole new

unique possibilities gets unlocked when these two kinds of nanomaterials get conjugated into composite structures. Such hybrid nanocomposites feature properties corresponding to individual components and potentially synergistic properties arise due to interaction between these components. Here most of the focus has been given to the part of interactions of optical excitations in metal-semiconductor hybrid nanostructures. Both the systems have tunable optical excitations which can be designed to be resonant with each other. This can give rise to coupled excitations which may produce results not generally seen in individual optical excitations upon bringing them in close proximity. The coupling between metal and semiconductor nanoparticles are perceived in two cases namely, weak coupling regime and strong coupling regime.

In case of weak coupling regime, the wave functions and electromagnetic modes of excitons and plasmons remain unperturbed. By metal-semiconductor interaction, we mean the coupling of the exciton dipole and electromagnetic field of surface plasmons. This model was explained by experiments done by Drexhage where change in excitation decay rate of an emissive dipole in the proximity of metal surface has been studied.^[8] In general, enhanced absorption cross-sections, increased radiative rates and exciton-plasmon energy transfer are described in weak coupling regime. In case of strong coupling regime, resonant exciton-plasmon interactions modify the exciton wave function and surface plasmon modes and hence changes exciton and surface plasmon's resonance energies to larger values if compared with their natural line widths. In this regime, the excitation energy is shared and oscillates between excitonic and plasmonics systems.

The theoretical analysis for these phenomena are quite complicated and are not very well understood to scientific community. However a lot of work has been done in this field since last decade. The statistics of the same can be seen in Figure 1.4 which shows the number of papers on excitons and plasmons published per year and its increasing trend.

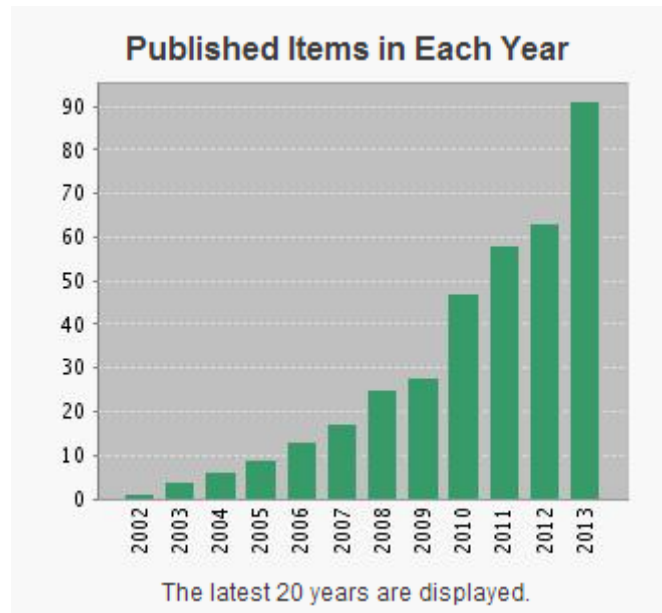


Figure 1.4: *Plot of number of publications per year since 2002, searched for string "exciton and plasmon" in web of science.*

A variety of semiconductors has been considered for exploring exciton-plasmon interactions. Even silicon (being an indirect band-gap semiconductor) has been considered for

exploring exciton-plasmon coupling and has been known to show luminescence.^[9] However direct-band gap semiconductors have been given more attention to study such interactions.

Mostly, metal and semiconductor nanoparticles are synthesized separately and then conjugated either by simply drop casting one over other or using some specific linker molecule. The conjugation process has to be well defined in terms of location, mutual orientation, number of metal nanoparticles attaching with semiconductor nanoparticle. These factors play crucial role in modification of absorption or luminescence properties of hybrid nanoparticles. Recently, numerous types of conjugations have been done using colloidal chemistry resulting into different morphologies namely core/shell^[10,11], dumb-bells, dot-on-rod^[12] and so forth. Approaches where spacer layers are avoided and linker molecules are made use of for conjugation, results in enhanced interaction of excitons and plasmons thus more efficient and stable nanocomposites.^[13] One should keep in mind that in applications of luminescence enhancement, if dielectric spacer layers are being used, the non-radiative energy transfer should be omitted.^[14]

The motivation of combining metals and semiconductor nanoparticles comes from the fact that they exhibit complimentary optical properties which are long-lived excitations that give rise to high emission yield and light-harvesting capabilities in semiconductors and localized electromagnetic modes in metal nanostructures that enables the concentration of electromagnetic energy and enhance optical fields and nonlinearities. This unlocks opportunities to modify and design specific optical properties and observe new phenomena as a result of such coupling. A schematic image of exciton-plasmon interaction in metal-semiconductor nanocomposites is shown in Figure 1.5.

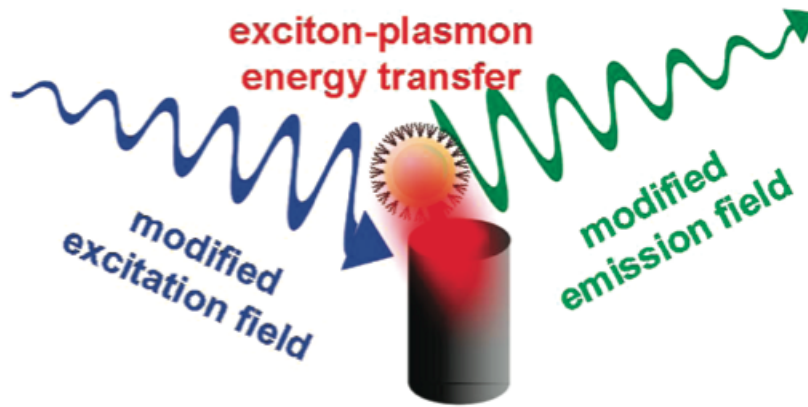


Figure 1.5: *Schematic diagram of resonant exciton - plasmon interaction in metal-semiconductor nanocomposites.*

Lot of work is being done across the globe in order to modify and design these nanocomposites and churn out new overwhelmingly interesting properties out of new materials. Recently scientists have succeeded in modifying absorption and emission properties,^[14] energy transfer between excitonic and plasmonics systems,^[15] and strong coupling with coherent exciton-plasmon interactions.^[16] Such interactions can attract potential applications in optical sensing, light emitters, photovoltaic systems, quantum information and communication applications.

1.6 Bulk Properties of CdTe

CdTe is a II-VI direct band semiconductor with a band-gap energy of ~ 1.44 eV at 300 K. It is generally used in photovoltaic solar cells in combination with CdS to form a p-n junction. CdTe crystallizes into a zinc blende (cubic) structure while its thin films crystallize into a wurtzite (hexagonal) structure. Some basic properties have been summarized in Table 1.1 (below).

Property	Value
Molar Mass	240.01 g/mol
Density	5.85 g/cm ³
Melting Point	1314 K
Boiling Point	1323 K
Lattice Constant	0.648 nm at 300 K

Table 1.1: *Some basic properties of CdTe.*

1.7 Effects of Quantum Confinement in CdTe

CdTe upon size reduction into nano regime shows interesting optical properties. CdTe nanocrystals show tunable emission properties from green to red due to quantum confinement and has been used in various applications related to LEDs, photonic crystal and biological labels. The quantum dots of the same material, but with different sizes, can emit light corresponding to different wavelengths. The reason behind this is quantum confinement. CdTe quantum dots and rods are synthesized via colloidal bottom-up syntheses techniques. Two of the most successful techniques are organic phase synthesis^[17] and aqueous synthesis of thiol-capped CdTe nanocrystals.^[18] The plots of absorption and emission spectra of CdTe quantum rods synthesized in an aqueous medium^[19] have been shown in Figure 1.6 (a) and (b) respectively.

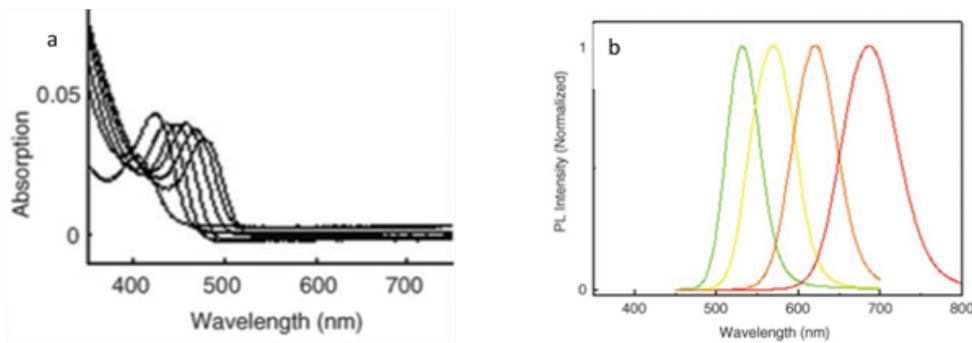


Figure 1.6: (a) *Absorption spectra for CdTe quantum rods.*^[19] (b) *Photoluminescence spectra of CdTe quantum rods.*^[19]

1.8 Bulk Properties of Gold

Gold is known to be the noblest metal known to mankind. Chemically, it is a transition metal and a group 11 element of periodic table. It is the second densest metal of periodic table after osmium. Gold crystallizes into a face centered cubic (fcc) lattice.

Property	Value
Atomic Number	79
Atomic Mass	196.96 g/mol
Electronic Configuration	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ¹
Density	19.30 g/cm ³
Melting Point	1337.18 K
Boiling Point	3243 K
Lattice Constant	0.408 nm at 300 K

Table 1.2: *Some basic properties of gold.*

1.9 LSPR in Gold

Spherical gold nanoparticles are known to show an intense red color (size less than 100nm) while gold nanorods/nano-dumbbells show magenta color. The optical and electronic properties of gold nanoparticles are tunable by changing the size, shape, surface chemistry, or aggregation state. For gold nanoparticles of size around 30 nm, the SPR phenomena causes an absorption of light in the blue-green portion of the spectrum (~530 nm) and red light (~700 nm) is reflected hence yielding a rich red color. With increase in particle size, the wavelength of SPR related absorption shifts to longer wavelengths (red-shift). Red light is then absorbed, and blue light is reflected, yielding solutions with a pale blue or purple color. As particle size continues to increase toward the bulk limit, surface plasmon resonance wavelengths move into the IR portion of the spectrum and most visible wavelengths are reflected, giving the nanoparticles clear or translucent color. The surface plasmon resonance can be tuned by varying the size or shape of the nanoparticles, leading to particles with tailored optical properties for different applications.

Gold nanorods are known to have anisotropic morphology which is reflected in their LSPR behavior as well, showing LSPR peaks corresponding to transverse and longitudinal modes of electron oscillation. The absorption spectrum for a gold nanorods solution and scanning electron microscopic images for the same have been shown in Figure 1.8 (a) and (b) respectively. These nanorods were synthesized by a method reported earlier.^[20,21]

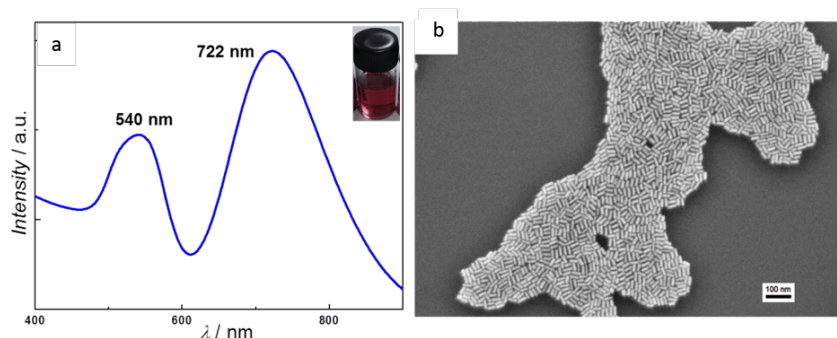


Figure 1.7: (a) Absorption spectrum of a gold nanorods solution (synthesized at Nano LAB, IISER). (b) FESEM image of a gold nanorods solution (synthesized at Nano LAB, IISER).

1.10 Summary

In this chapter, the importance of the two types of nanostructured materials viz. metal and semiconductor nanoparticles has been discussed briefly. Then a brief introduction followed by theoretical background has been discussed to understand “Quantum Confinement” in semiconductor nanoparticles. Mie theory has been discussed in order to understand the colors shown by spherical metallic nanoparticles. Mie-Gans theory, an extension of Mie’s theory to understand two peaks in case of gold nanorods (in general ellipsoidal particles) have been mentioned. Terms like, plasmons, surface plasmons and surface plasmon resonance have been introduced and Drude model has been discussed to understand the absorption and scattering behavior of metallic nanoparticles with size variation. At the end, the importance of exciton-plasmon coupling in metal-semiconductor nanoparticles and its applications have been discussed followed by list of few bulk properties of CdTe and gold relevant to this work.

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Chapter 2

Experimental Techniques

In this chapter, methods used to synthesize gold nanorods, gold nanostars and CdTe quantum rods via colloidal methods in aqueous media have been discussed along with self-developed technique to conjugate these metal and semiconductor nanoparticles and their characterization method.

2.1 Synthesis of CdTe Quantum Rods (CdTe QRs)

There are two possible routes of synthesizing quantum dots or rods via wet-chemical synthesis technique. The syntheses can be done in either aqueous medium or non-aqueous medium. The non-aqueous method generally requires high temperature precursor injection method which results into well defined, mono-dispersed nanoparticles. But the aqueous method has limitation of operating temperature below 100°C. Here, the aqueous method has been chosen in order to carry out experiments with gold nanorods which would be prepared in aqueous medium.

Water-soluble CdTe quantum rods (QRs) were synthesized according to a method reported by earlier by Haifeng Bao and group.^[1] Cadmium Chloride ($CdCl_2$), Sodium Tellurite (Na_2TeO_3) and L-cysteine were purchased from Sigma Aldrich Inc. Trisodium Citrate was purchased from Alfa Aesar. Sodium Borohydride ($NaBH_4$) was purchased from SRL Chem Pvt. Ltd. All chemicals were used as received. For all the experiments, deionized water was used.

In a typical reaction, $CdCl_2$ (0.04 M, 4 ml) was diluted with water up to 50 ml in a 100 ml round-bottom flask fitted with a water-cooled condenser. To this, Trisodium Citrate dihydrate (100 mg), Na_2TeO_3 (0.01 M, 4 ml), L-cysteine (50 mg), and $NaBH_4$ (50 mg) were added in the given sequence with continuous stirring. Once the color of the solution turned green, the resulting solution was refluxed at 100°C. An aliquot of 5 ml volume was taken after a time period of 240 min which resulted in an orange fluorescence, checked quickly using a UV-lamp enclosure. The whole procedure has been described with the help of a flow chart in Figure 2.1.

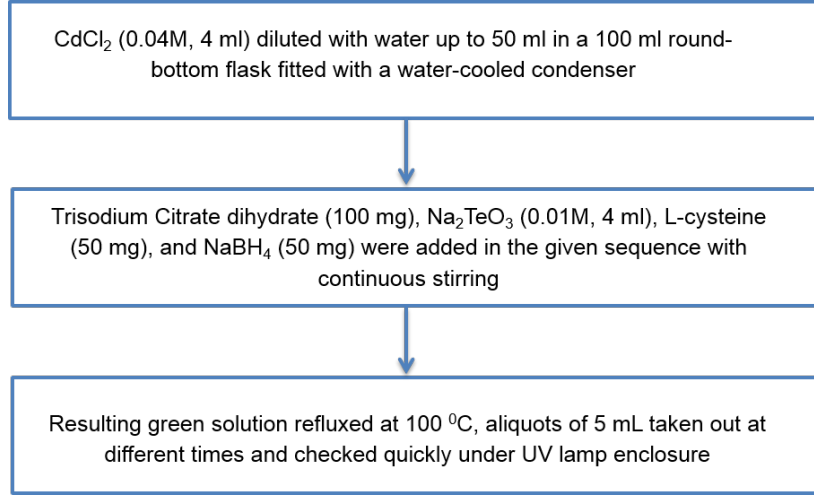
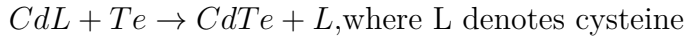


Figure 2.1: Flow chart summarizing the procedure followed for synthesis of CdTe Quantum Rods.

Underlying Reaction:

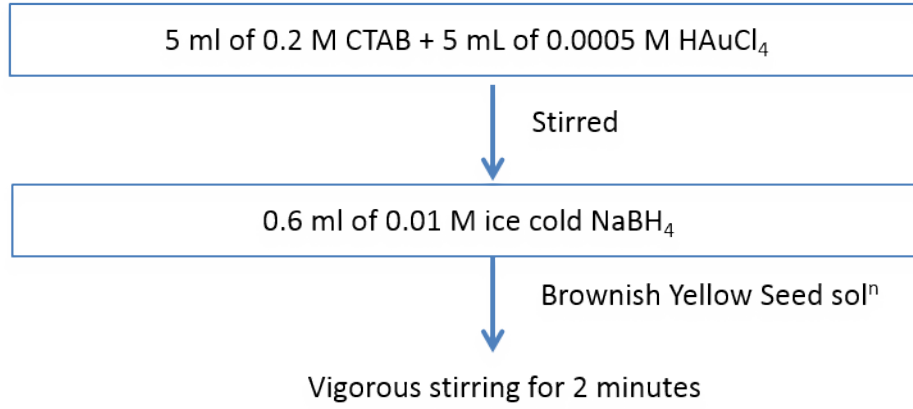


2.2 Synthesis of Gold Nanorods (Au NRs)

There are two general approaches for synthesis of Gold nanorods, which are bottom-up and top-down methods. Bottom-up methods include wet-chemical, electrochemical, sonochemical, solvothermal, microwave-assisted and photochemical reduction techniques, while top-down methods include various combination of physical lithographic processes and gold deposition. In our case, wet-chemical route was followed. Gold nanorods (Au NRs) were synthesized via a two-step seed mediated growth method at room temperature.^[2] Gold Chloride Hydrate ($HAuCl_4 \cdot 3H_2O$), Cetyl Trimethyl Ammonium Bromide (CTAB), Benzyl Dimethyl Hexadecyl ammonium chloride (BDAC), and Ascorbic Acid were purchased from Sigma Aldrich Inc. Silver Nitrate ($AgNO_3$) was purchased from Merck. Sodium Borohydride ($NaBH_4$) was purchased from SRL Chem. Pvt. Ltd. All chemicals were used as received. For all the experiments, deionized water was used.

In a typical reaction, the ‘seed solution’ was prepared by mixing CTAB (0.2 M, 5 ml) and $HAuCl_4$ (5×10^{-4} M, 5 ml). After gentle stirring, freshly prepared ice-cold $NaBH_4$ (0.01 M, 0.6 ml) was added, followed by vigorous stirring for two minutes. This caused the color of the solution to turn brownish-yellow. The ‘growth solution’ consisted of a binary surfactant solution of CTAB (0.2M, 2.5 ml) and BDAC (0.15M, 2.5 ml). To this, $AgNO_3$ (0.004M, 0.2 ml) was added, followed by addition of a solution of $HAuCl_4$ (0.001M, 5 ml) with gentle mixing. This caused the solution to turn golden yellow. Ascorbic Acid (0.0788M, 0.07 ml) was then added with shaking, which caused the resulting solution to turn colorless. Finally, 20 μ l of the seed solution was added into the growth solution, and the latter was kept at room temperature overnight. A dark magenta color of the growth solution indicated successful formation of gold nanorods. The whole procedure has been described with the help of a flow chart in Figure 2.2.

Step 1: Preparation of Seed Solution



Step 2: Preparation of Growth Solution

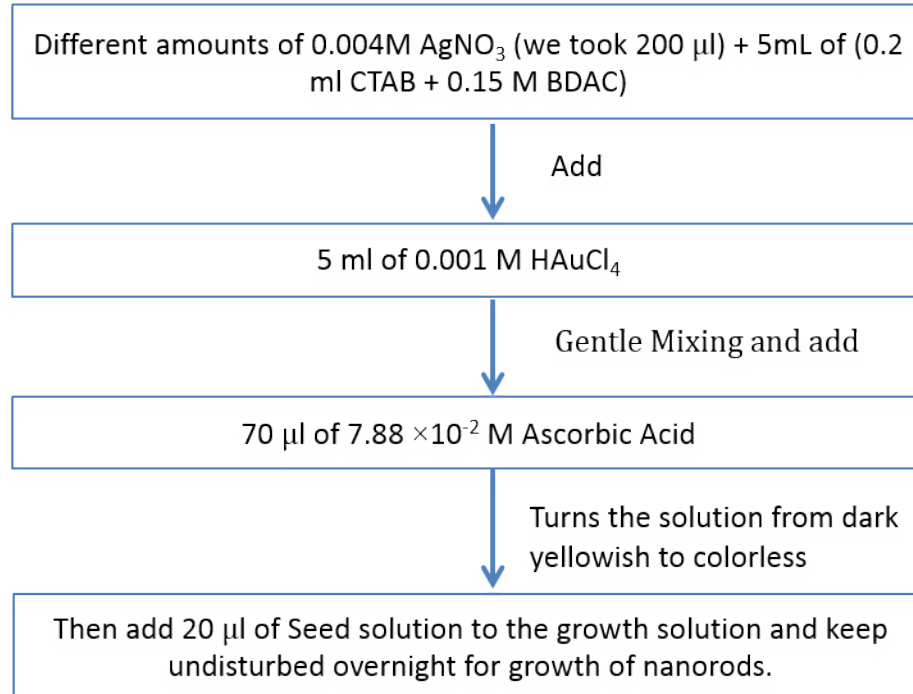


Figure 2.2: Flow chart summarizing the procedure of synthesis of Au nanorods.

2.3 Synthesis of Gold Nanostars

Another interesting morphology of gold is nanostars. Gold Nanostars (Au NS) were synthesized by wet-chemical route reported earlier by Colleen and group.^[3] This method is a slightly modified version of the method used for synthesis of Au NRs. Gold Nanostars were synthesized via a two-step seed mediated growth method at room temperature. Gold Chloride Hydrate ($HAuCl_4 \cdot 3H_2O$), Cetyl Trimethyl Ammonium Bromide (CTAB), Benzyl Dimethyl Hexadecyl ammonium chloride (BDAC), and Ascorbic Acid were purchased from Sigma Aldrich Inc. Silver Nitrate ($AgNO_3$) was purchased from Merck.

Sodium Borohydride ($NaBH_4$) was purchased from SRL Chem. Pvt. Ltd. All chemicals were used as received. For all the experiments, deionized water was used.

In a typical synthetic method, ‘surfactant-stabilized seed solution’ was prepared by mixing 0.025 ml of 10 mM $HAuCl_4$ and 7.5 ml of 0.1 M CTAB and further adding 0.600 ml of 0.01 M ice cold $NaBH_4$ which resulted into a seed solution of pale brown color after vigorous stirring. The ‘growth solution’ was prepared by subsequently mixing 4.75 ml of 0.1 M CTAB, 0.2 ml of 10 mM $HAuCl_4$ and 0.03 ml of 10 mM $AgNO_3$. Addition of these three resulted into a yellow brown colored solution. After this, 10 μ l of seed solution was added into it followed by addition of 0.032 ml of 100 mM ascorbic acid which turned the solution colorless. Finally, 0.025 ml of 0.1 M NaOH was added followed by gentle mixing and the color of the solution turned to bluish purple within 15 minutes and it deepened in next 3 hours. The whole procedure has been described with the help of a flow chart in Figure 2.3.

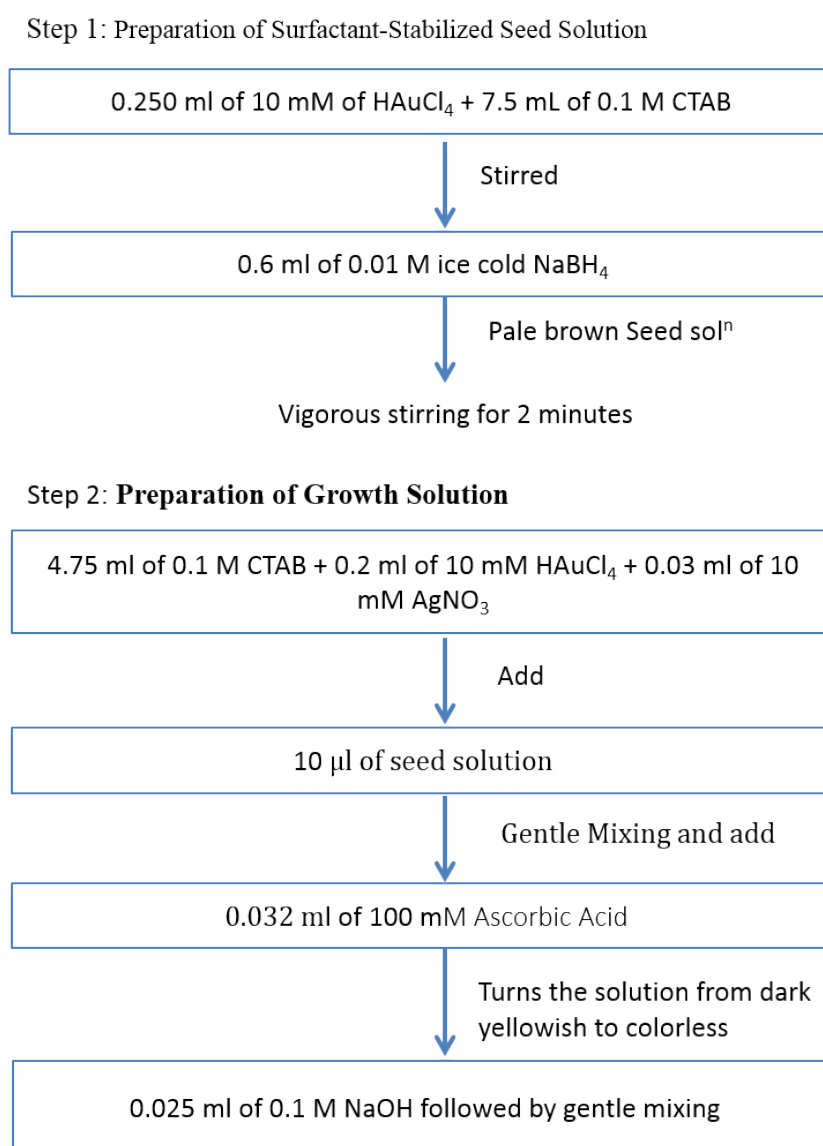


Figure 2.3: Flow chart summarizing the procedure of synthesis of Au nanostars.

2.4 Chemical conjugation of gold nanorods and CdTe quantum rods

The chemical conjugation of gold nanorods and CdTe quantum rods was done using a one step, self-developed procedure. In a particular procedure, 1 ml of the above-prepared Au NR solution was thoroughly centrifuged and washed in order to remove excess *CTAB* and spherical Au nanoparticles which occur as a by-product. The precipitate was re-dispersed in 1 ml water for further use. In a typical procedure, 0.5 ml CdTe solutions from one of the aliquots were initially taken in different glass vials, followed by equal amounts of sequential addition of Ascorbic Acid (0.0788M) and Au NR solutions, in an increasing manner for each vial, ranging from 40 μL up to 580 μL . After preparing each mixture, a quick check of the resulting photoluminescence was done using the UV lamp enclosure.

2.5 Analysis Techniques

2.5.1 UV-Vis Absorption Spectroscopy

In the ultraviolet (190 nm -380 nm), visible region (380 nm – 750 nm) or near IR (750 nm – 1200 nm), light interacts with matter which causes excitation of electrons from ground state to higher energy states. Molecules containing π -electrons or non-bonding electrons can absorb the energy in the form of ultraviolet or visible light to excite these electrons to higher anti-bonding molecular orbitals. The more easily excited the electrons (i.e. lower energy gap between the HOMO and the LUMO), the longer the wavelength of light it can absorb.

In Nano Science and Material Science, this technique is used to quantify the absorption and scattering of light by a sample (a quantity known as extinction coefficient, which is defined as sum of absorption coefficient and scattering coefficient derived from Mie’s theory). In a typical procedure, a sample in a quartz cuvette is placed between a light source and a photodetector. A D_2 lamp ($\lambda < 319$ nm) is used as a UV radiation source and a tungsten lamp is used as a source for light in visible range. A collimated beam of light is passed through the sample and the intensity of light is measured before and after passing through the sample. A monochromator is used to tune the incident wavelength. These measurements are compared at each wavelength to quantify the sample’s wavelength dependent extinction spectrum. The data is typically plotted as extinction as a function of wavelength. Each spectrum is background corrected using a “reference” – a cuvette filled with only the dispersing medium to remove unwanted spectral features due to solvent used for synthesis of the sample. A photomultiplier tube is used as a photodetector in UV and infrared region, while a PbS detector is used to detect absorption in near infrared region. In our case a Perkin Elmer UV-Vis spectrophotometer was used for recording all absorption spectra.

Nanoparticles have optical properties that are sensitive to size, shape, concentration, agglomeration state, and refractive index near the nanoparticle surface, which makes UV/Vis/IR spectroscopy a valuable tool for identifying, characterizing, and studying these materials. Nanoparticles made from certain metals, such as gold and silver, strongly interact with specific wavelengths of light and the unique optical properties of these materials is the foundation for the field of plasmonics. Similarly, nanoparticles made from semiconductor materials such as CdTe and ZnO strongly interact with light resulting into creation

of excitons thus showing excitonic peak which again depends on sizes of semiconductor nanoparticles. The schematic illustration of a typical UV-Vis-NIR spectrophotometer is shown in Figure 2.4.

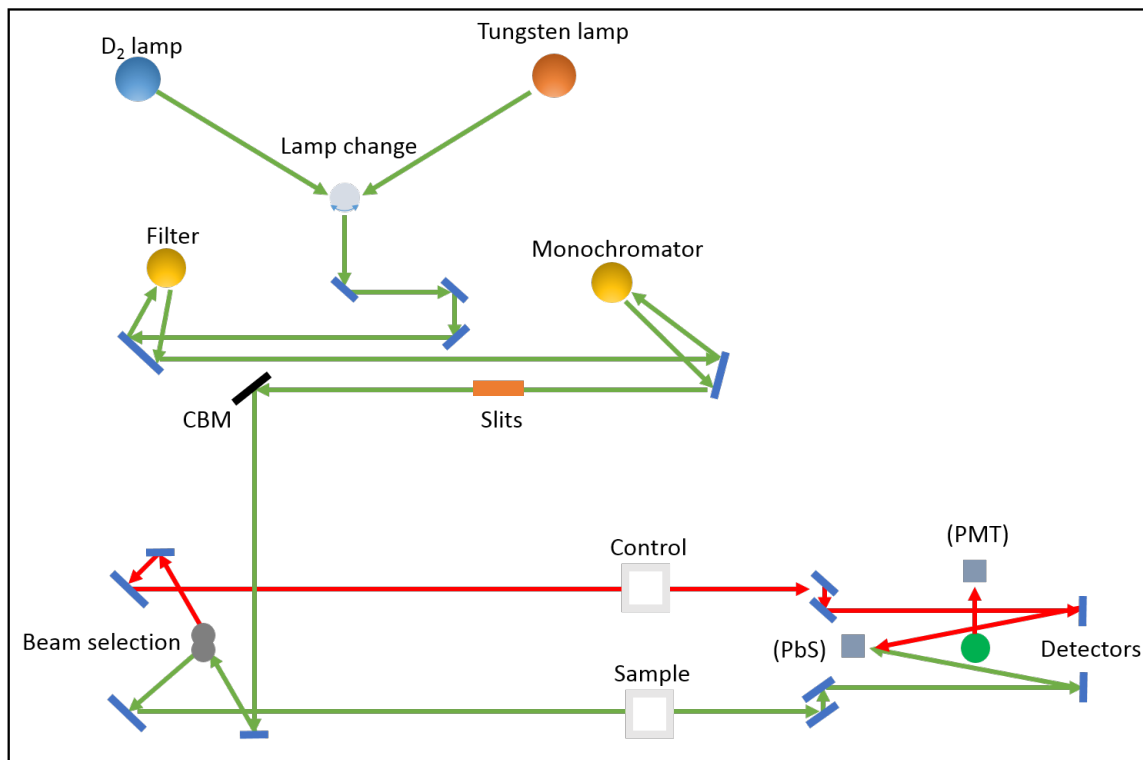


Figure 2.4: *Schematic diagram of a UV-Vis-NIR Spectrophotometer.*

2.5.2 Photoluminescence

The photoluminescence studies of nanoparticles are done to investigate their emission profile when illuminated with a light beam of particular wavelength optimum enough to excite ground state electrons to higher states (usually excited by a UV radiation). As mentioned in chapter one, quantum dots/rods show fluorescence properties due to quantum confinement. When the size of these nanoparticles changes, the electronic states also consequently change resulting into change in absorption profile as well as fluorescence properties. When the size of a nanoparticle increases, the energy states decrease (as it's inversely proportional to size), thus resulting into redshift in absorption spectra as well as in fluorescence color. In a typical fluorescence measurement procedure, a liquid sample is kept in quartz cuvette between a UV light source and photodetector (sometimes placed at right angles). This incident light then excites electrons from ground state to higher energy levels. Then these electrons relax to lower vibrational states of the excited energy level and finally comes back to ground state emitting photon corresponding to the energy difference of the two states. These photons are then recorded by photodetector. The photodetector records the emitted photons from the sample either at a single wavelength, or preforms a scan to record the intensity versus wavelength profile, also called an emission spectrum. Generally, a photomultiplier tube (PMT) is used as detector. The term fluorescence is used when emission of light takes place within 10^{-4} s of stimulus. If the emission persists

for even longer time, say few tens of milliseconds or even seconds, then this phenomena is called phosphorescence.

In our case a Fluoromax-4 spectrofluorometer from Horiba Scientific was used for all PL measurements that has 150 watt Ozone-free xenon lamp which can excite the samples from 200 nm to 900 nm and can detect emissions in the same range. Figure 2.5 shows a schematic diagram of a spectrofluorometer.

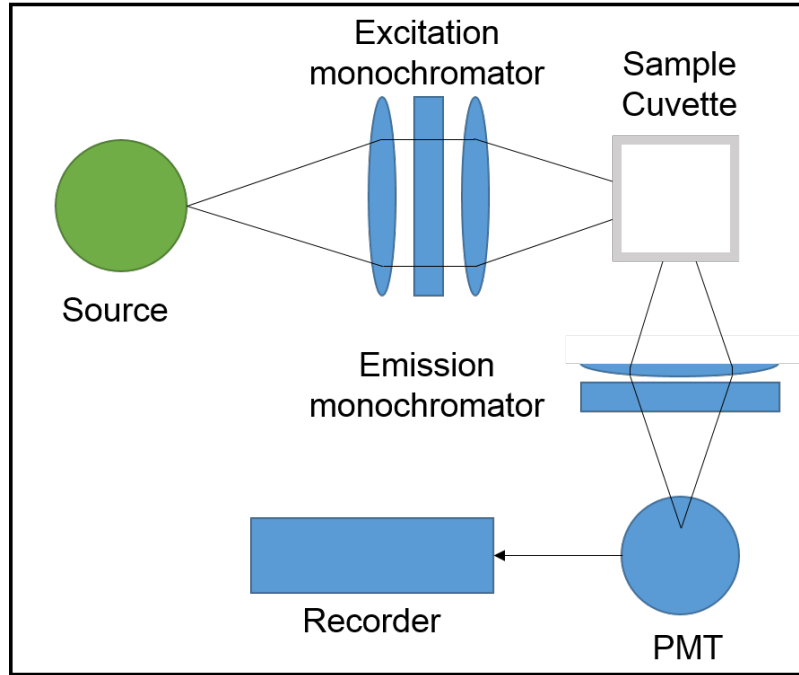


Figure 2.5: *Schematic diagram of a spectrofluorometer.*

2.5.3 Field-Emission Scanning Electron Microscopy (FESEM)

The resolution of traditional microscopy is limited by the wavelength of electromagnetic wave used to see an object which can resolve up to few micrometers. In order to improve microscopy techniques and further image objects in sub-micron or nano-scale level, electrons are being used instead of electromagnetic radiation as their wavelengths can be tuned to lower values thus increasing beam energy and improving resolving power. A Scanning electron microscope (SEM) is used to visualize morphology, shapes and sizes of very small particles ranging from micrometers to few nanometers. In a SEM, electrons emitted from a hot tungsten/zirconium oxide cathode or cold filament (using electric field for electron emission, FESEM) are accelerated in a high electrical field gradient generated by dual anodes, beamed in a collimated fashion passing through In-lens annular secondary electron detector with no crossover using field lenses and magnetic lenses within a high vacuum column (10^{-6} torr), in a raster fashion as a fine probe over a solid sample. These primary electrons are focused and deflected by condenser lenses to produce a narrow beam that bombards the sample. The interaction between electrons and solids can result into production of Auger electrons, secondary electrons, back-scattered electrons, visible light, X-rays, etc. The secondary electrons emitted from each spot of sample are then

collected by in-lens annular SE detector which relates their angle and velocity to the surface structure of the sample and produces an electric signal. This signal is amplified and transformed to a video scan-image that can be shown on a monitor. Typically, electrons can be accelerated up to 3 -30 keV and resolution up to 3-5 nm can be achieved. But in case of Field emission electron microscope where electrons are emitted from filament using strong electric field instead of heating, the electrons are less scattered and more focused which can improve the resolution to reach up to 1 – 2 nm.^[4] In our case all SEM imaging were done by a Zeiss Ultra Plus Field Emission Scanning Electron Microscope. The schematic image of a SEM /FESEM is shown in Figure 2.6.

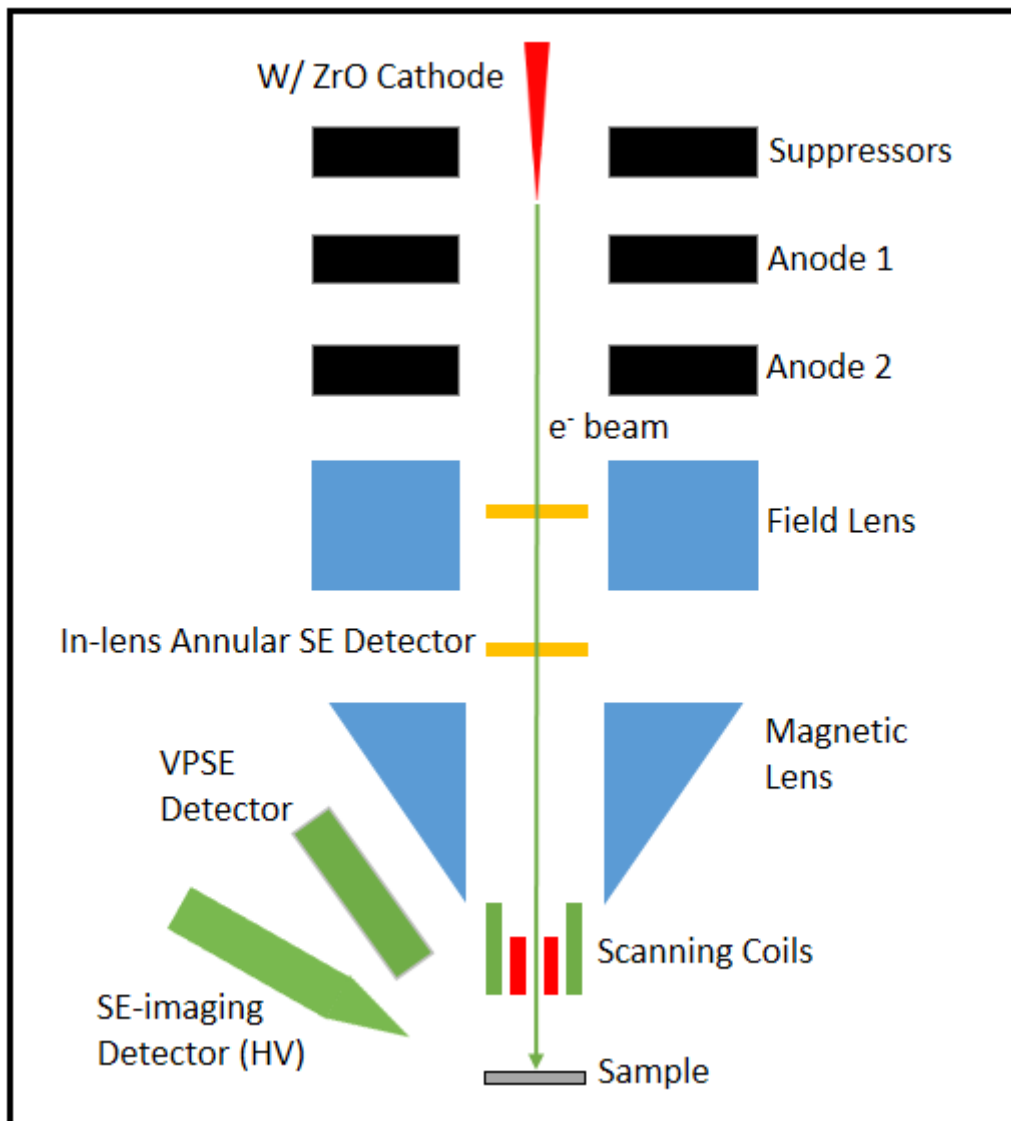


Figure 2.6: *Schematic diagram of a Scanning Electron Microscope*

2.5.4 Time Correlated Single Photon Counting (TCSPC)

Time correlated single photon counting (TCSPC) technique is used to study the life-time of a fluorescent sample at its excited state. It allows us to measure the time that a molecule stays in its excited state. Steady-state measurement of fluorescence produces an averaged

picture of a substance: its absorption and resultant emission of light in the UV, visible, and IR region of the spectrum but by using time-discrimination we can resolve individual emission characteristics of components of a sample. There are two main, complementary techniques for obtaining lifetime, or dynamic, data from fluorescent sample.

- a) Frequency domain
- b) Time domain

In the frequency domain, the excitation source has its intensity modulated at a high frequency, as a result the sample's emission is also modulated, but out of phase with the excitation. The phase difference and the modulation of the emission are directly linked to lifetime.

In the frequency domain, the excitation source has its intensity modulated at a high frequency, as a result the sample's emission is also modulated, but out of phase with the excitation. The phase difference and the modulation of the emission are directly linked to lifetime.

In the time domain, the sample is excited by a pulse source with a pulse-width ideally less than the sample's lifetime. By collecting many emission photons, and timing the arrival of those photons relative to the excitation pulses, a decay trace is accumulated. From the decay trace, the lifetimes of the components can be calculated. In our case we have used a HORIBA Jobin Yvon's TCSPC with picosecond-lifetimes resolving power.

2.6 Bibliography

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Chapter 3

Results and Discussions

3.1 Colloidal Gold Nanorods

Colloidal gold nanorods were synthesized in aqueous medium by using a two-step seed mediated procedure described earlier in chapter 2. In this procedure, a seed solution and a growth solution are prepared separately and then a small amount ($20\ \mu\text{l}$) of seed solution is added to the growth solution which results into formation of gold nanorods with spherical gold nanoparticles as byproducts. The byproducts can usually be filtered out by centrifuging and washing the growth solution at 9500 rpm. In the seed solution, Au^{3+} ions are produced by reducing chloroauric acid with sodium borohydrate in a *CTAB* solution. This results into formation of seed of gold nanoparticles with size $\sim 1.5\ \text{nm}$. A growth solution is obtained by reducing Au^{3+} into Au^+ complex ions with ascorbic acid in a mixture of *CTAB* and *BDAC* solution. In order to obtain gold nanorods with high aspect ratio, *CTAB* is usually accompanied with *BDAC*.^[1] In the growth solution, a little amount of AgNO_3 is also used and it plays a crucial role in formation of anisotropic gold nanorods. When a small amount of seed solution is added to growth solution, the Au^+ ions are believed to bond to the higher-energy $\{110\}$ facets of Au nanocrystals and slowdown the growth on these facets. Then, the Au atoms predominantly get deposited onto the $\{100\}$ facets leading to a longitudinal growth.^[2] Figure 3.1 shows a picture of seed solution and gold nanorods solutions and a schematic illustration of the nanorods formation has been shown in Figure 3.2.

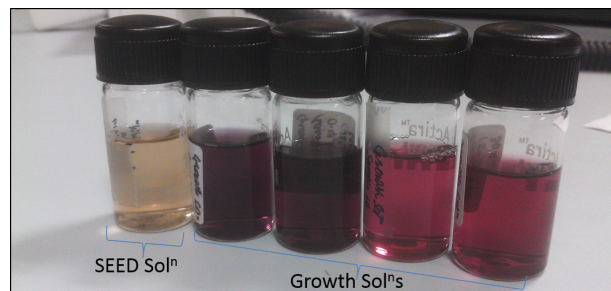


Figure 3.1: Picture of seed solution and growth solutions after addition of seed into the growth solution with different amounts of additions resulting into different sizes of gold nanorods.

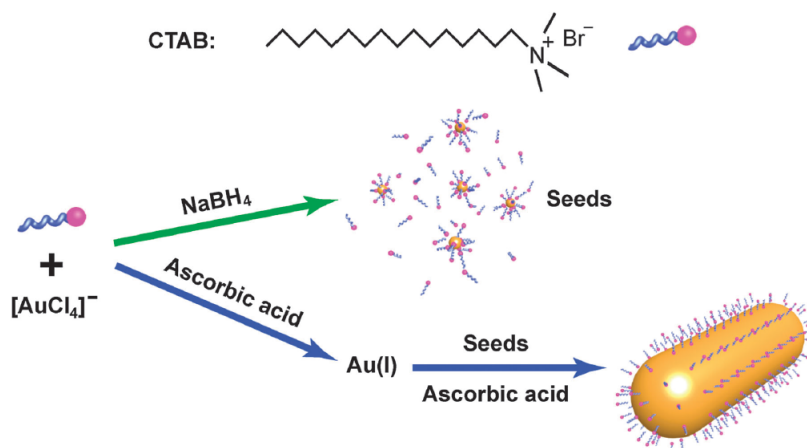


Figure 3.2: A schematic illustration for the seed-mediated growth of gold nanorods.^[2]

As discussed in chapter 1, gold nanorods being anisotropic nanoparticles show two localized surface plasmon resonance bands corresponding to longitudinal mode as well as transverse mode. Figure 3.3 shows the absorption spectra of gold nanorods seed solution and growth solution prepared using same method as described in chapter 2.

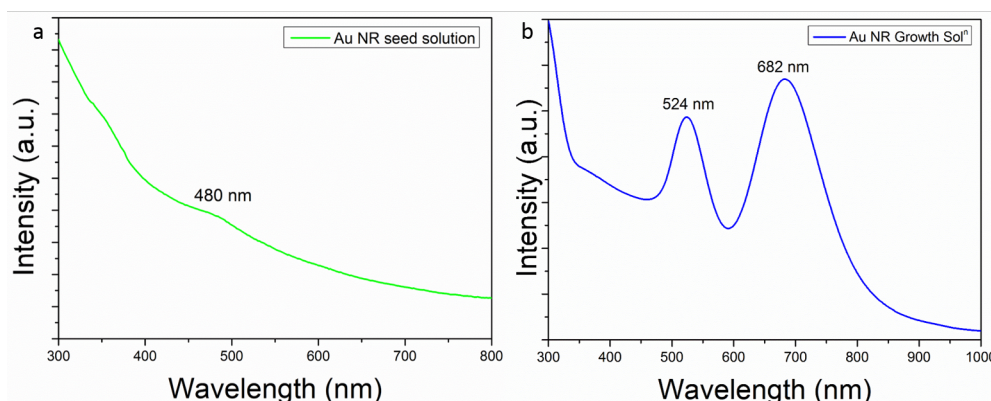


Figure 3.3: (a) Absorption spectrum of gold seed solution. (b) Absorption spectrum of a gold nanorods (growth) solution.

The seed solution shows an absorption peak at 480 nm corresponding to the LSPR in spherical gold nanoparticles (seeds are spherical in shape).^[3] In this case, Au NRs show two distinct absorption peaks, a smaller one at 524 nm and a bigger one at 682 nm, corresponding with the transverse and longitudinal surface plasmon resonances, respectively. With increase in aspect ratio of Au NRs, the longitudinal mode of LSPR shifts towards longer wavelengths.^[3] With an aim to study the effect of variation of amount of seed on growth of Au NRs, a joint experiment was conducted where a seed solution and four growth solutions were prepared. All the precursors were kept same and procedure was followed as described in chapter 2. Then, 20 μl , 30 μl , 40 μl and 50 μl of seed solution were added in to the four growth solutions. The UV-Vis spectrograph in Figure 3.4 shows gradual shifts in the LSPR peaks which has earlier been reported.^[4]

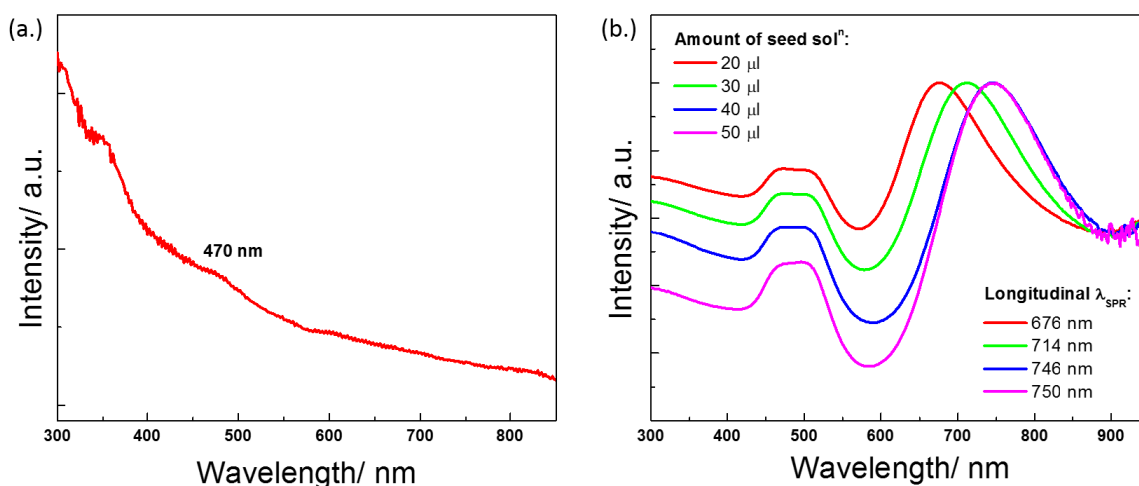


Figure 3.4: (a) UV-Vis absorption spectrum of a seed solution. (b) Shifts in UV-Vis absorption spectra for all four growth solutions.

Scanning electron micrographs were recorded for all the samples prepared in order to see morphology of prepared nanoparticles. Figure 3.5 shows a FESEM image of one of the as prepared samples of Au NRs drop-casted on a silicon wafer. The average length and diameter of nanorods were measured to be 31 ± 0.1 nm and 9 ± 0.1 nm by an open source imaging software called ImageJ.

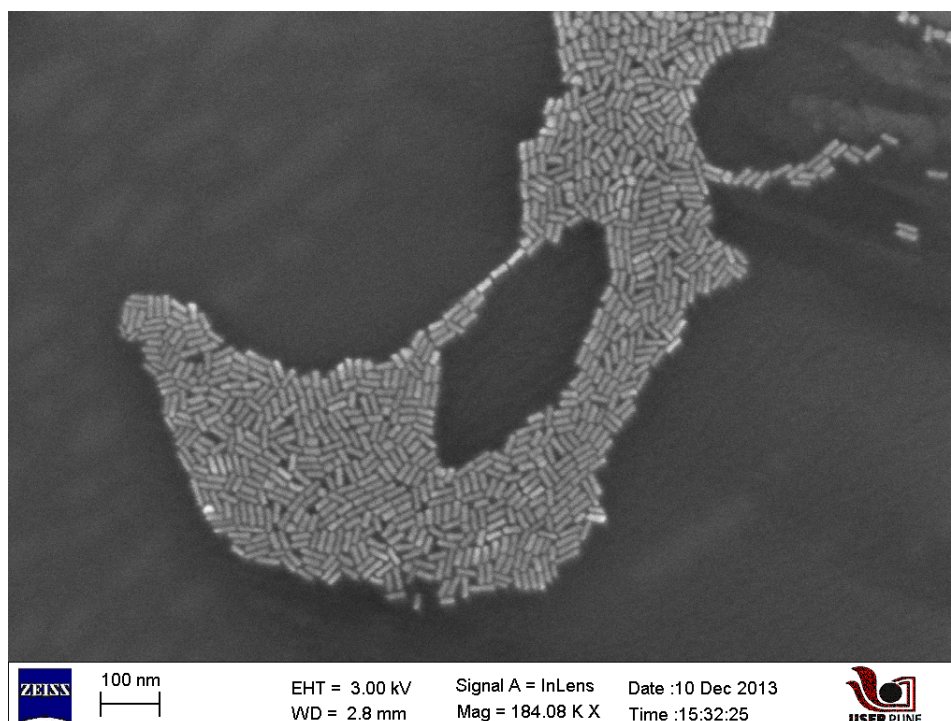


Figure 3.5: FESEM image of Au NRs

3.2 End Modification of Au NRs

As discussed in chapter 2, this process of synthesizing Au NRs is a two steps seed-mediated process. There can be a number of variations possible in the synthesis procedure like changing concentration of surfactants or changing the amount of seed solution. In this work, apart from changing the amount of seed solution, modifications in morphology due to change in pH of the growth solution has also been studied. In order to obtain the changes in the morphology of Au NRs with changing pH, ascorbic acid and NaOH has been used.

In a particular procedure, 0.5 ml of Au NRs solution was re-dispersed in MilliQ water to make it up to 2 ml solution. Ascorbic acid (0.0788 M, 100 μ l) was added gradually to the Au NRs solution. The absorption spectra were recorded consecutively after each addition of ascorbic acid. The additions were done until the position of LSPR peak did not change. It was observed that with increasing amount of ascorbic acid, the longitudinal LSPR mode first shifted towards longer wavelength and then blue-shifted and finally stopped shifting. As a result, the ends of nanorods were modified into arrow-head dumbbells as reported earlier.^[5] Figure 3.6 shows an overlaid UV-Vis absorption spectra of gold arrow-headed nano-dumbbells with shifts in transverse mode of LSPR position and a FESEM image of the same sample.

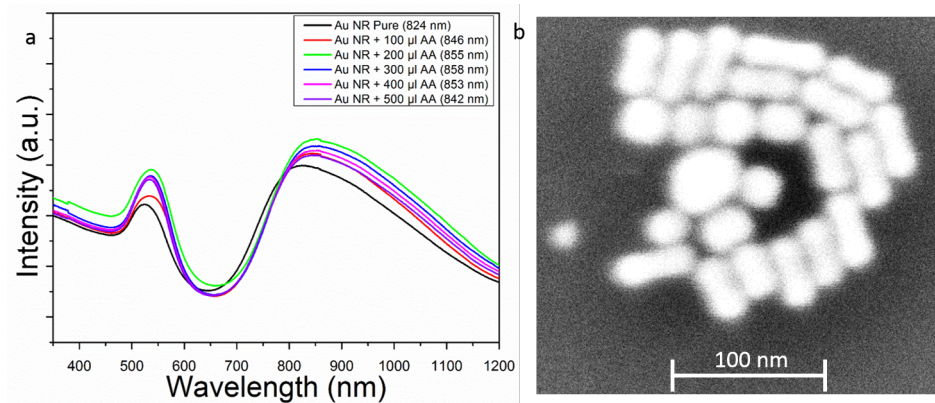


Figure 3.6: (a) Overlaid absorption spectra of arrow-head gold nano-dumbbells shifts in LSPR. (b) FESEM image of arrow-headed gold nano-dumbbells.

Similarly, 0.1 M NaOH was also sequentially added to an Au NR solution in similar fashion. In this case also, shifts in position of longitudinal LSPR peak of Au NR solution were observed. Figure 3.7 (b) shows that the ends of gold nanorods were modified into fine spherical ended nano-dumbbells. Figure 3.7 (a) shows the shifts in position of longitudinal mode of LSPR peaks of nano-dumbbells as well as change in absorption intensity of transverse mode of LSPR. The whole procedure of altering pH boils down to a conclusion that in basic medium, nanorods tend to modify into spherical ended nano-dumbbells and in acidic medium they modify into arrow-headed nano-dumbbells.

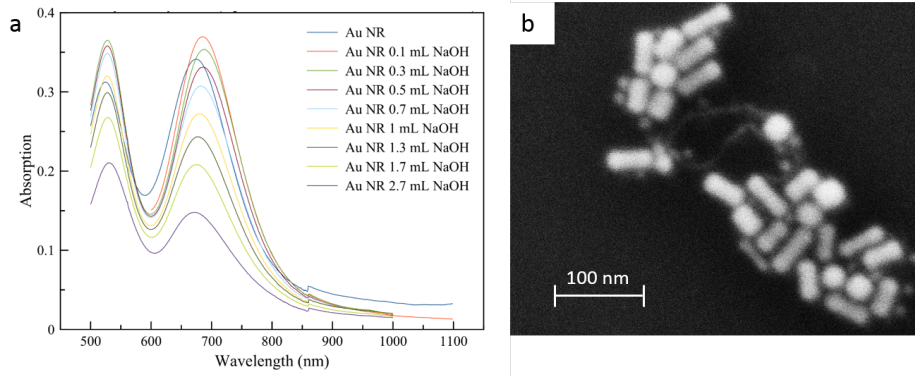


Figure 3.7: Overlaid absorption spectra of spherical gold nano-dumbbells and (b) FESEM image of spherical gold nano-dumbbells.

Figure 3.8 shows a schematic illustration of possible route of end modifications and the explanation of these modifications had been reported earlier.^[5] The surfactants used in synthesis of gold nanorods are *CTAB* and *BDAC* which act as soft micelle templates to control size and shape of gold nanorods. It has been reported earlier that with increasing and decreasing the pH of a gold nanorods solution, *CTAB* layers from ends of the nanorods are removed as the surface energy at the ends ($\{110\}$ facets) of these nanorods are higher than cylindrical (side) surface^[5] and then excess of Au^+ ions in the solution get deposited and modifies the ends of nanorods.

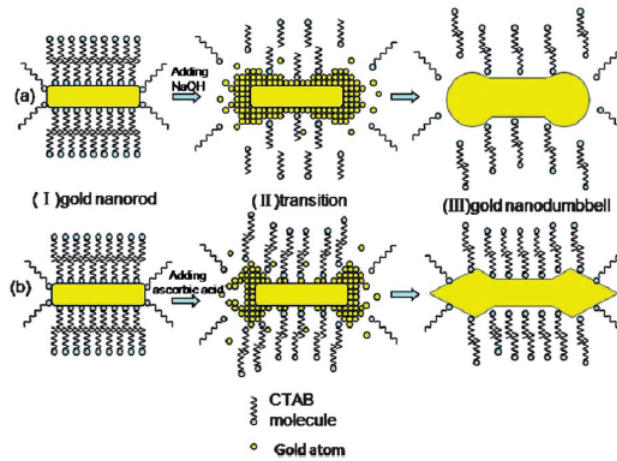


Figure 3.8: Schematic illustration of the formation of the two types of gold nano-dumbbells by continuously adding (a) NaOH and (b) ascorbic acid solution.^[5]

3.3 Colloidal Gold Nanostars

Colloidal gold nanorods were synthesized in aqueous medium by using a two-step seed mediated procedure described earlier in chapter 2. The nanostars solution looked brownish visually but upon light illumination, it showed ink-blue colored solution. Figure 3.9 shows pictures of the same solution in two conditions.

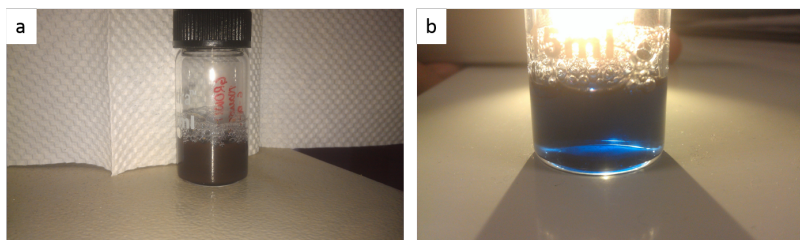


Figure 3.9: (a) Brownish color of gold nanostars solution (b) Ink-blue color shown by the same solution upon light illumination.

Figure 3.10 shows the UV-Vis absorption spectrum of a gold nanostars solution. As discussed in chapter one, spherical gold nanoparticles show one surface plasmon resonance peak and gold nanorods show two peaks corresponding to transverse mode and longitudinal mode of LSPR. This was explained by Mie-Gans theory and this results because of anisotropy in nanorods. A star shaped nanoparticle may have multiple anisotropic axes and it may show two or more than two peaks or superimposed peaks merging together to form a shoulder. In this case, two peaks at 588 nm and 710 nm with a shoulder at 530 nm have been observed.

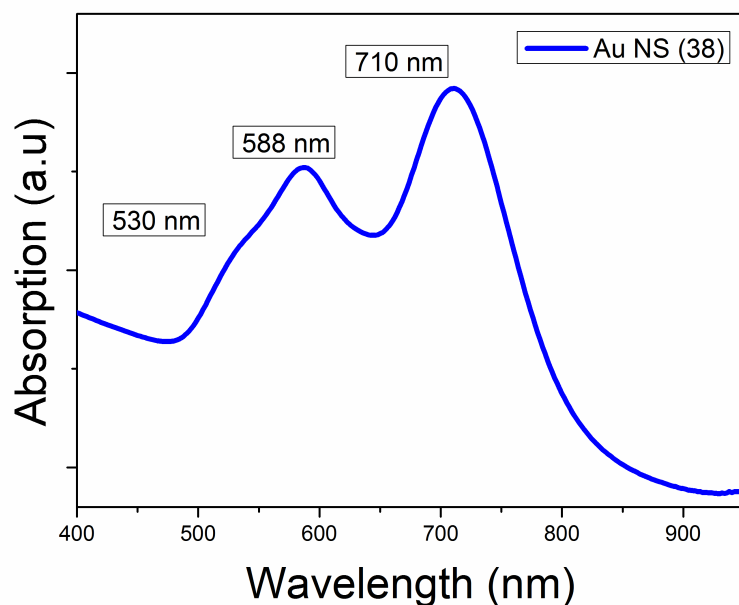


Figure 3.10: UV-Vis absorption spectrum of a gold nanostars solution.

Figure 3.11 shows FESEM images of a gold nanostars solution. It is thought that during nucleation, if few facets energetically higher than other facets of a seed just like {110} in case of nanorods formation, get blocked by Ag^+ ions and capping reagent *CTAB*, then growth and deposition of Au^+ ions will occur only at other facets with comparatively lower energy and seed will elongate along those directions which may result into formation of star shape nanoparticles.

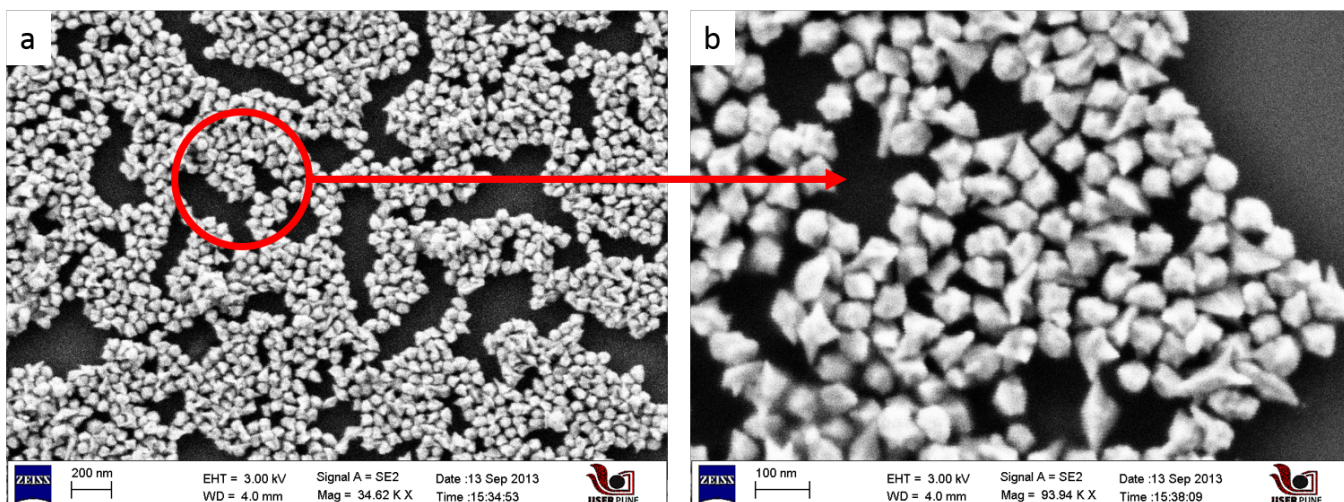


Figure 3.11: *FESEM images of Gold nanostars.*

3.4 CdTe Quantum Rods

CdTe quantum rods were prepared in an aqueous medium using a method discussed earlier in chapter 2. For CdTe, synthesis through non-aqueous methods result into well-defined and mono-dispersed quantum dots and quantum rods. Since this work focused on chemically conjugating metal and semiconductor nanoparticle in order to study exciton-plasmon coupling and wet-chemical methods have been chosen for all the syntheses, it was important to keep the media of both the nanoparticles compatible to each other in terms of miscibility. Gold nanorods were synthesized in aqueous medium so aqueous method was preferred for synthesis of CdTe quantum rods over non-aqueous method. A number of aliquots were taken out to obtain different sizes of CdTe quantum rods with emission at different wavelengths. A quick check up of successful synthesis of quantum rods was done by looking into their fluorescence under UV lamp enclosure with UV illumination (~ 250 nm). The quantum rods are believed to be formed by oriented attachment of small CdTe seeds in one direction and further capping by cysteine (a thiol functionalized amino acid with $-NH_2$ and $-COOH$ groups at one end and $-SH$ group on other end). During capping process, L-cysteine gets attached to CdTe rods through thiol bonding leaving amino group free at other end. Various other thiol based stabilizers have been used earlier for synthesis of CdTe quantum dots indicating the fact that stabilization of CdTe quantum rods are done by thiol bonds of cysteine.^[6] A picture of fluorescent CdTe aliquots illuminated under UV enclosure with total time of synthesis has been shown in Figure 3.12.

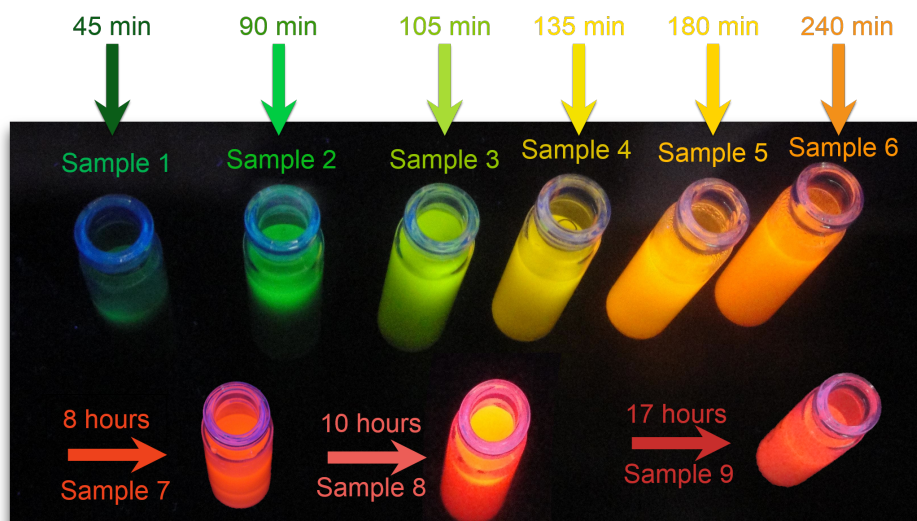


Figure 3.12: Colors shown by aliquots of CdTe taken at different times under UV lamp enclosure.

CdTe being a direct band-gap semiconductor shows very well defined excitonic peaks in their absorption spectra. An overlaid plot of absorption spectra for some of the synthesized CdTe quantum rods are shown in Figure 3.13. It has been observed that the excitonic peaks kept on red-shifting with increased reflux time (which results into longer rods). In Figure 3.13 CdTe 3 (green), CdTe 4 (yellow), CdTe 6 (orange), CdTe 8 (magenta) and CdTe 9 (red) correspond to aliquots taken out after 105 minutes, 135 minutes, 240 minutes, 10 hours and 17 hours of refluxing.

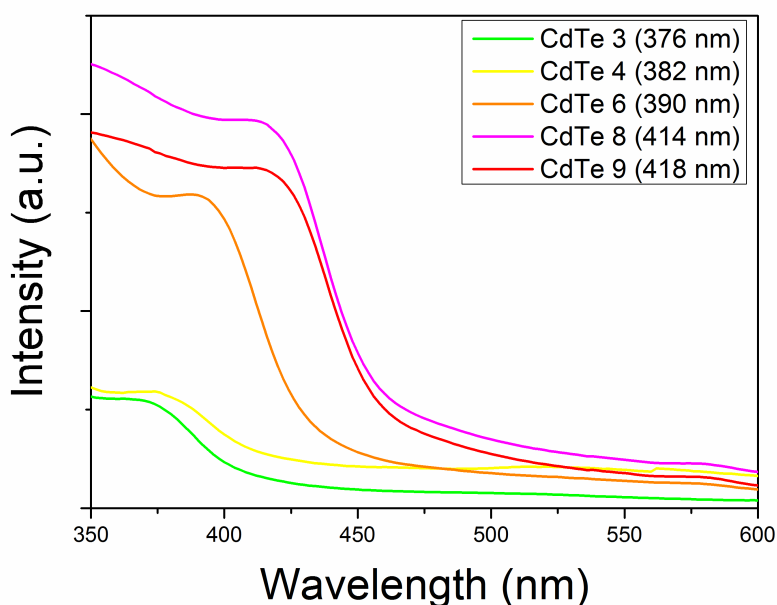


Figure 3.13: UV absorption of CdTe quantum rods.

In semiconductor nanoparticles, as it has been discussed earlier in chapter 1, light

illumination causes an electron excitation from valence band to conduction band and this process leaves behind a hole which forms an exciton pair with the excited electron. The condition for such an excitation to occur is restricted by the band gap energy between valence band and conduction band and energy of exciting photons. So if the illuminated light have photons of energy value equal to or greater than the band gap energy of the semiconductor nanoparticle then only transition will occur. Since the band gap energy changes due to quantum confinement with decreasing size of semiconductor nanoparticles, the energy of the photons required for excitation also changes. The excited electron can lose energy by emitting a phonon (collective oscillation of crystal lattice) in a relatively shorter time ($\sim 10^{-12}$ to 10^{-13} sec) before it can relax and make a radiative transition. Another possibility of non-radiative decay of excitons can be due to presence of defects in lattice where electron or hole may get trapped. The lifetime of radiative process is of the orders of 10^{-7} seconds and it may go up to few milliseconds (fluorescence) or even few seconds (phosphorescence) which are much longer than non-radiative process.^[7] Figure 3.14 shows fluorescence spectra recorded for different aliquots taken at different times of refluxing. Here in case of CdTe quantum rods, emission wavelength has been observed to be shifting towards longer wavelengths for samples with increased reflux time. Another observation was increment of FWHM of PL spectra with increased reflux time. This indicates that with increase in size emission wavelength has increased and it indicates decrement in band gap energy which agrees with the literature. It is thought that during synthesis of CdTe, nucleation starts with very small seeds with uniform size and as the refluxing progresses the seeds grow into bigger sizes resulting into longer quantum rods with varying sizes. Since the method of synthesis adopted here is a chemical route, not every rod can be of same length so due to non-uniformity, different sizes of quantum rods have different band gap energies thus different emission profiles and hence the convolution of all such emission profiles might have resulted into broadened emission spectra. So for samples with less reflux time, narrower emission profile has been observed while for those with longer reflux time show broader emission profile.

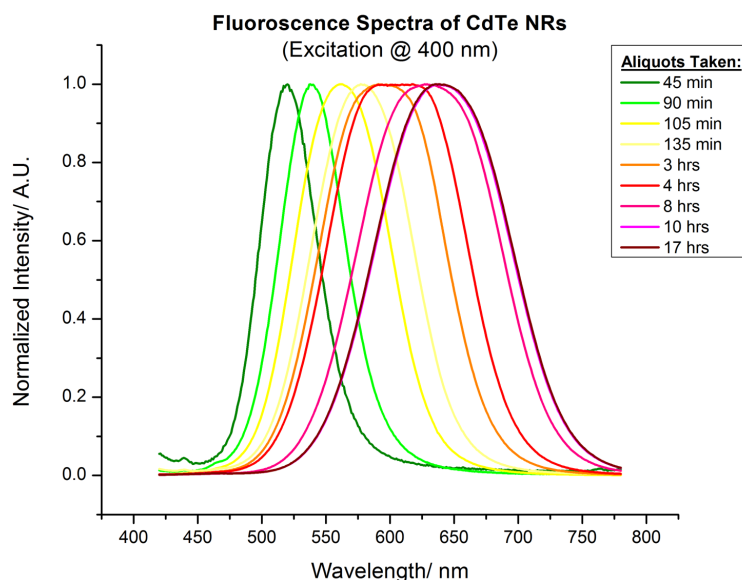


Figure 3.14: Photoluminescence spectra of CdTe quantum rods of different sizes.

Figure 3.15 shows FESEM images of one of the synthesized CdTe quantum rods sample (CdTe Sample 3). FESEM imaging could not be done for all the samples due to operational limitations. The diameter of the quantum rods were found to be ~ 20 nm and length ranged between 120 nm to 160 nm. This method does not yield highly mono-dispersed rods. A detailed analysis of quantum rods' measurements could not be performed because of over agglomeration of CdTe quantum rods in presence of excess of cysteine. The CdTe samples were drop-casted and imaged on silicon wafers.

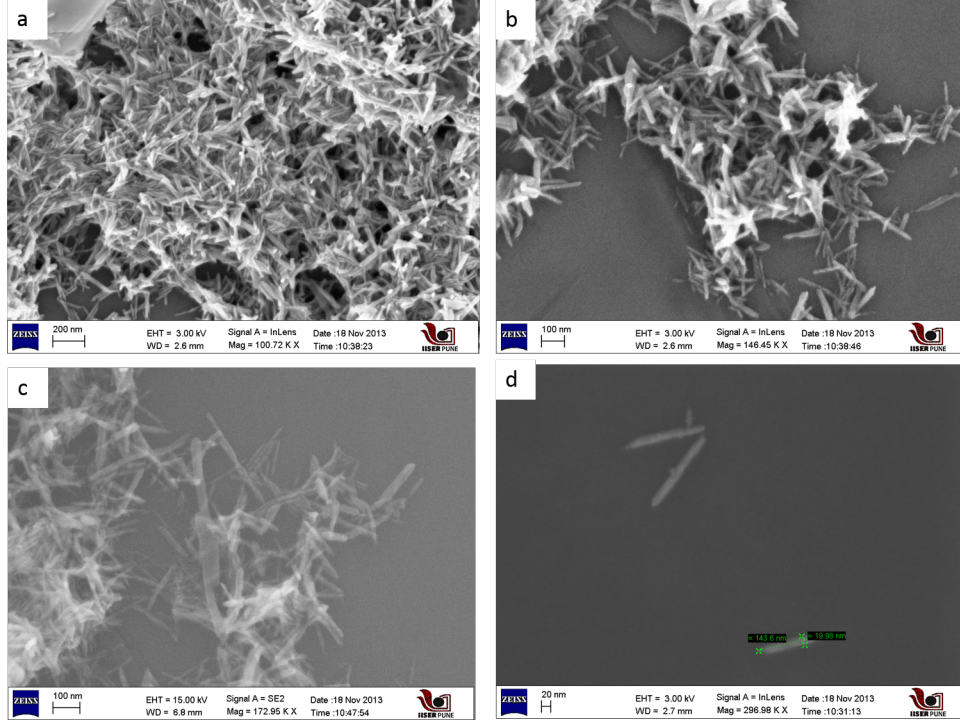


Figure 3.15: *FESEM images of CdTe Quantum Rods.*

Figure 3.16 shows a FESEM image of a CdTe QRs sample and an EDAX (energy-dispersive X-ray spectroscopy) analysis of the same sample focused at a point with tag “Spectrum 1” in Figure 3.16 (a) in order to check the composition of quantum rods. EDAX is an analytical technique used for elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique sets of peaks in its X-ray spectrum. In this case, elemental analysis by EDAX shows cadmium and tellurium as components of quantum rods. Although the ratio is not 1:1, it was also observed that at one end of the quantum rods, atomic percentage of Te was greater in few cases and for some cases it was greater for Cd. In Figure 3.16 (b), a table shows the composition by weight % and atomic %. In the same figure it can be seen that there’s a big peak (yellow) which has not been included in compositional calculation, this corresponds to Si and peak comes because Si wafers have been used for all imaging.

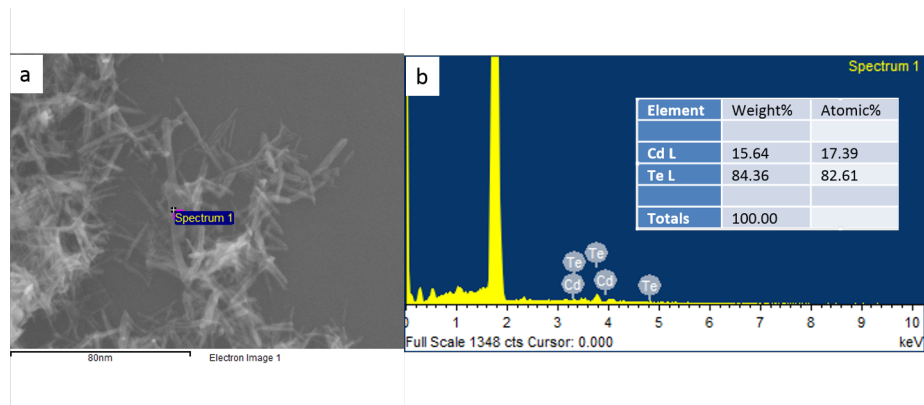


Figure 3.16: (a) FESEM image of CdTe QRs. (b) EDAX analysis of same sample in a region shown in image (a).

3.5 Au-CdTe Conjugation

3.5.1 Conjugation of Au NRs with CdTe QRs

For conjugation of Au NRs and CdTe QRs, a new and self-devised method has been used which has not been reported earlier. Au NRs solution contains excess of *CTAB*, *BDAC* and Au^+ ions. Au NRs in growth solution continue to grow longer with time and it's believed that the growth stops only after consumption of excess of Au^+ ions. One way to stop the growth is by centrifuging the Au NR solution and remove excess of ions and surfactant as supernatant and filter out nanorods settled as precipitate and re-disperse in MilliQ water.

As we have seen in section 3.2, the ends of Au NRs can be modified by altering pH of the growth solution using either ascorbic acid or *NaOH*. Ascorbic acid and *NaOH* on addition to an Au NR growth solution removes *CTAB* layers from the ends of nanorods which are known to have higher surface energy.^[5] Depending upon the mechanism reported earlier,^[5] spherical ended nano-dumbbells or arrow-headed nano-dumbbells are formed due to further deposition of free Au^+ ions available in growth solution. As a model case, ascorbic acid was chosen as a role-player in conjugation in this work. The conjugation was done as described in chapter 2. In this procedure, after centrifuging the Au NRs sample at 9600 rpm for 20 minutes followed by washing with MilliQ water thrice, the excess of Au^+ ions and *CTAB* are believe to be removed and it stops further growth of nanorods as well. When CdTe, ascorbic acid and Au NRs are mixed then ascorbic acid quickly removes *CTAB* layers from the ends of nanorods and since CdTe is capped with cysteine through thiol bond, $-NH_2$ group is left free. Amine group forms bond easily with gold (weak covalent bond), so the free $-NH_2$ group binds to the ends of the gold nanorods. Another possible thing that can happen is end-to-end attachment of Au NRs. Both has been observed separately. Figure 3.17 shows a schematic illustration of the conjugation of Au NRs and CdTe QRs. A quick check up of conjugation was done by seeing the fluorescence quenching under UV lamp enclosure. Figure 3.18 shows the fluorescence quenching of two such samples together.

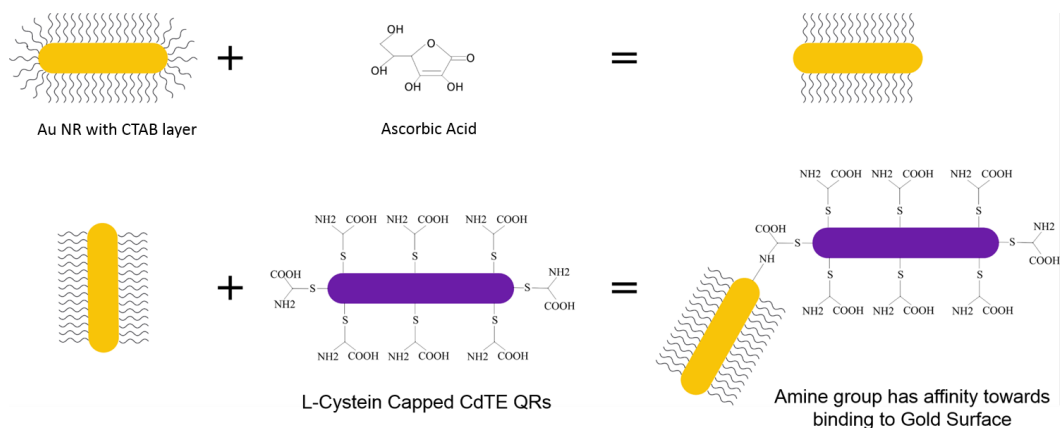


Figure 3.17: *Schematic illustration of conjugation of Au NRs and CdTe QRs.*

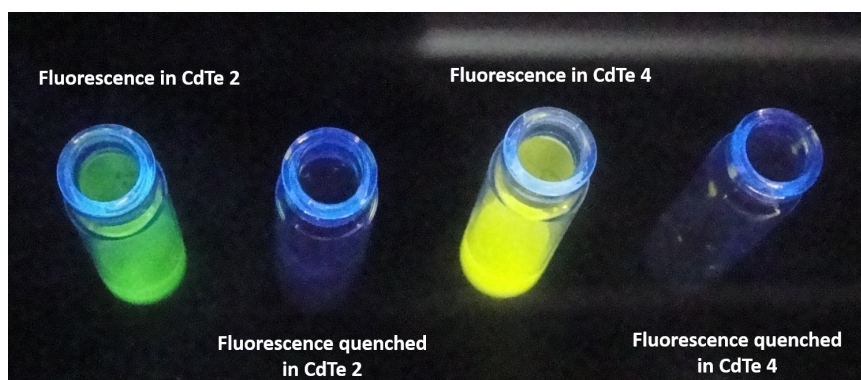


Figure 3.18: *Fluorescence quenching in CdTe 2 and CdTe 4.*

Figure 3.19 (a) shows the UV-Vis absorption spectra of the synthesized Au NRs (black) and CdTe QRs (red). The CdTe QRs show a characteristic excitonic absorption shoulder at 390 nm, whereas the Au NRs show two distinct absorption peaks, one at 522 nm and a bigger one at 848 nm, corresponding with the transverse and longitudinal surface plasmon resonances, respectively.

Figure 3.19 (b) shows the overlaid absorption spectra of the various Au-CdTe hybrid nanostructures. The spectra show three peaks, one corresponding with the excitonic absorption due to CdTe and the other two with the SPR modes of Au NRs. The excitonic absorption and transverse SPR occur at an almost constant position of 390 nm and 524 nm, whereas the longitudinal SPR peak is shifted from 848 nm (for the case of pure Au NRs) to 882 nm. Such a considerable redshift could be a possible indication of successful attachment of Au NRs to CdTe QRs. For the last two samples, the peaks corresponding with excitonic absorption and transverse SPR have merged into a single wide envelope, which has a considerable quenching effect on their photoluminescence properties.

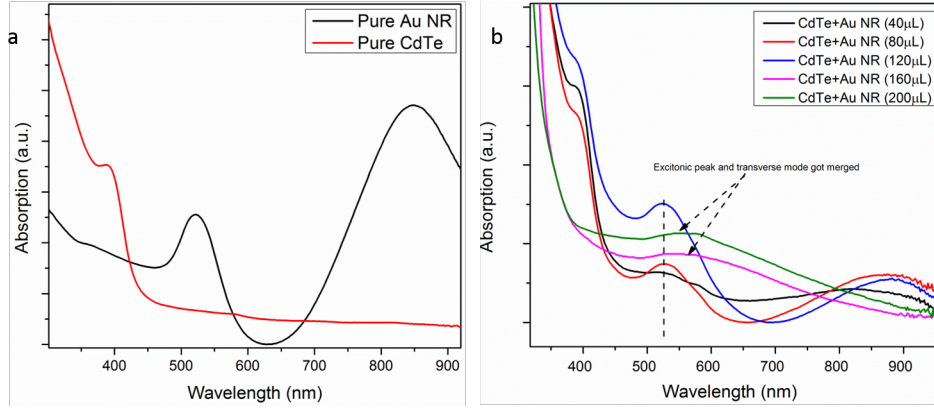


Figure 3.19: (a) UV-Vis absorption spectra of Au NRs and CdTe QRs. (b) UV-Vis absorption spectra of Au-CdTe hybrid nanostructures.

Similar results were found in experiments performed with other aliquots of CdTe QRs for which absorption spectra of pure Au NRs and CdTe are shown in 3.20 (a), 3.21 (a) and 3.22 (a) and overlaid absorption spectra of all conjugated Au NRs and CdTe QRs are shown in Figures 3.20 (b), 3.21 (b) and 3.22 (b). One remarkable difference is that for others the excitonic peaks of CdTe QRs and transverse mode of LSPR of Au NRs have not merged to form a big envelope.

UV data of Au₂₃-CdTe₅:

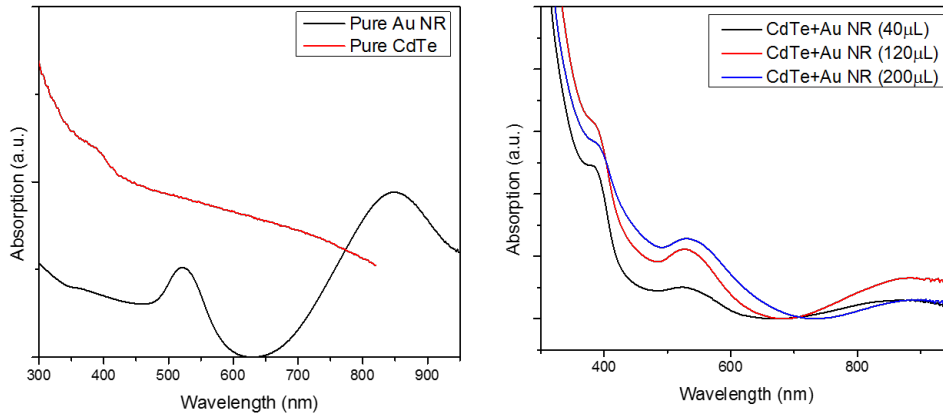


Figure 3.20: (a) UV-Vis absorption spectra of Au NRs and CdTe QRs. (b) UV-Vis absorption spectra of Au-CdTe hybrid nanostructures.

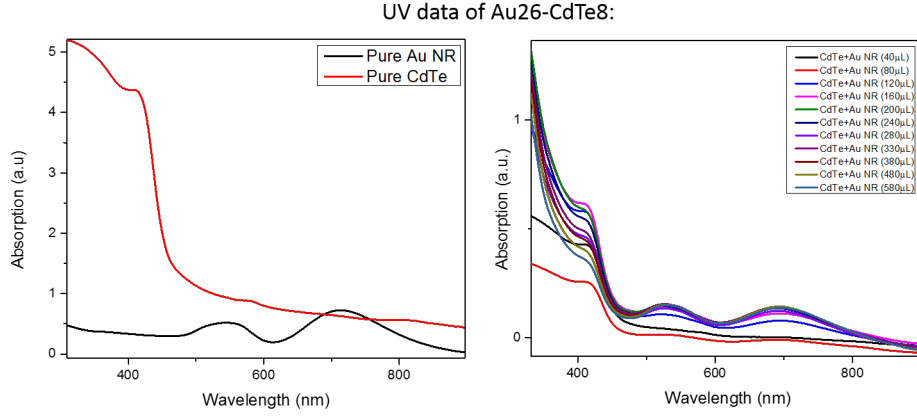


Figure 3.21: (a) UV-Vis absorption spectra of Au NRs and CdTe QRs. (b) UV-Vis absorption spectra of Au-CdTe hybrid nanostructures.

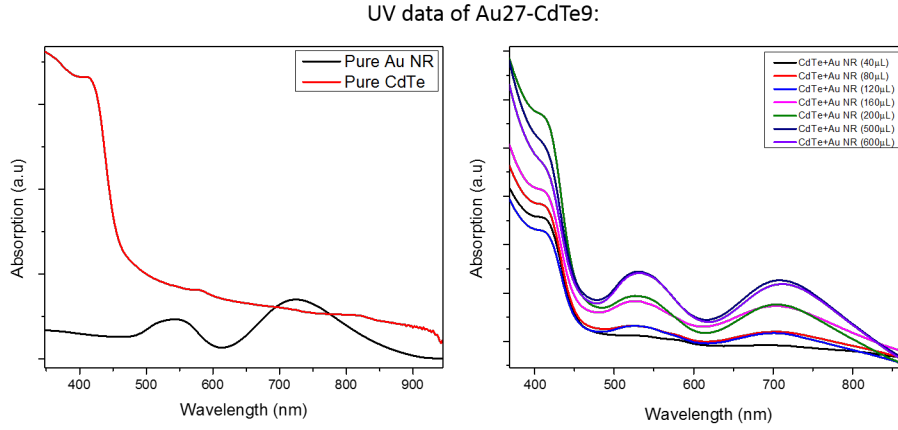


Figure 3.22: (a) UV-Vis absorption spectra of Au NRs and CdTe QRs. (b) UV-Vis absorption spectra of Au-CdTe hybrid nanostructures.

Fig. 3.23 (a) shows the overlaid photoluminescence spectra of pure CdTe QRs and the Au-CdTe hybrid nanostructures, with increasing amounts of Au NRs. These emission spectra were recorded at a fixed excitation wavelength of 400 nm, and the entrance/ exit slit-widths equal to 1nm/4nm respectively. Care was taken to maintain same levels of sample dilution and amounts for the ease of comparing the emission intensities.

It was expected that due to exciton-plasmon coupling, the emission intensity of pure CdTe QRs solution would reduce with increasing amount of Au NRs, indicative of conjugation. However, as the amount of Au NRs was increased from zero, we observed initial enhancement of the original emission levels which then led to reduction, followed by complete quenching. This kind of enhancement has been earlier reported and this occurs when a metal and semiconductor nanoparticle come very close to each other (distance $\sim 3\text{nm}$).^[8] This can be seen from Figure 3.23 (b), which depicts the intensity maxima of emission versus increasing amount of Au NRs in the solution.

Another interesting observation was the gradual redshift in the position of the emission peaks as compared with the original CdTe solution, due to increasing amount of Au NRs.

The emission of pure CdTe QRs was centered at 597 nm, which later shifted to 602 nm, 607 nm, and 613 nm with increased amount of Au NRs. The last two solutions showed complete quenching.

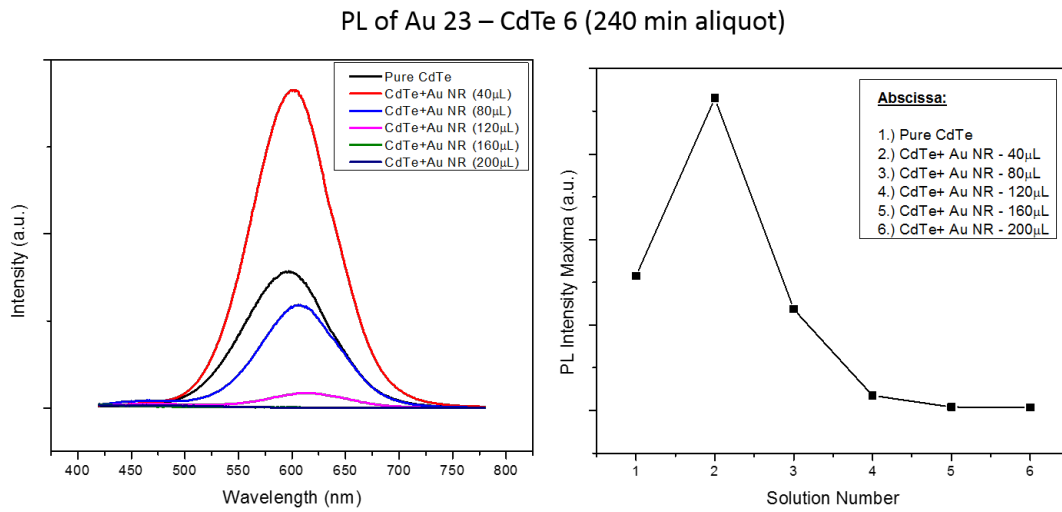


Figure 3.23: (a) PL spectra of Au-CdTe (CdTe 6) hybrid nanostructures. (b) PL Intensity maxima of Au-CdTe hybrid nanostructures.

Similar results were found in experiments performed with other CdTe aliquots (CdTe 5, CdTe 8 and CdTe 9) for which overlaid photoluminescence spectra of pure CdTe QRs and the Au-CdTe hybrid nanostructures are shown in Figures 3.24 (a), 3.25 (a) and 3.26 (a) and intensity maxima of emission versus increasing amount of Au NRs in the solution are shown in Figures 3.24 (b), 3.25(b) and 3.26(b).

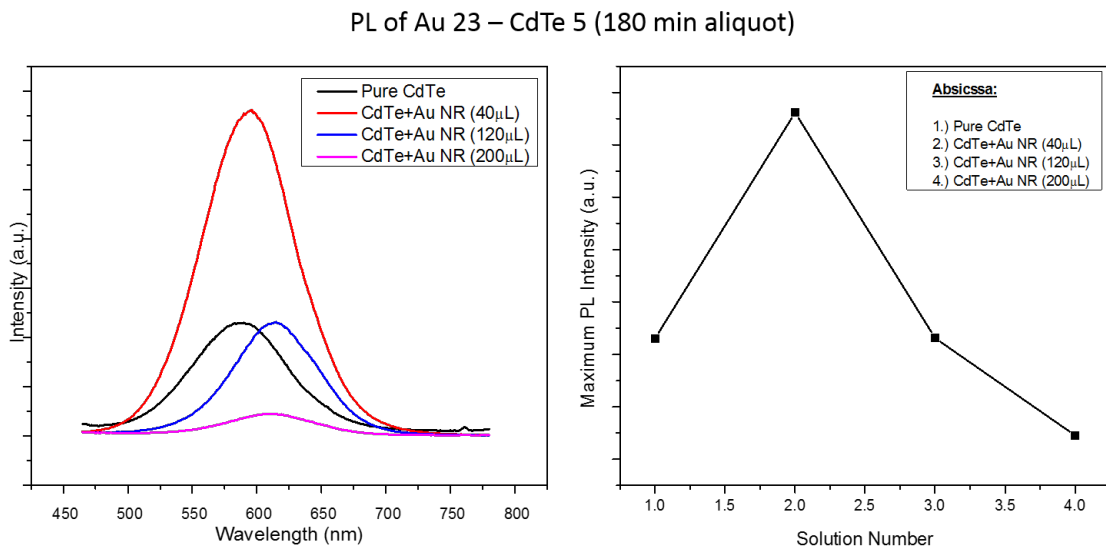


Figure 3.24: (a) PL spectra of Au-CdTe (CdTe 5) hybrid nanostructures. (b) PL Intensity maxima of Au-CdTe hybrid nanostructures.

PL of Au 23 – CdTe 8 (10 hours aliquot)

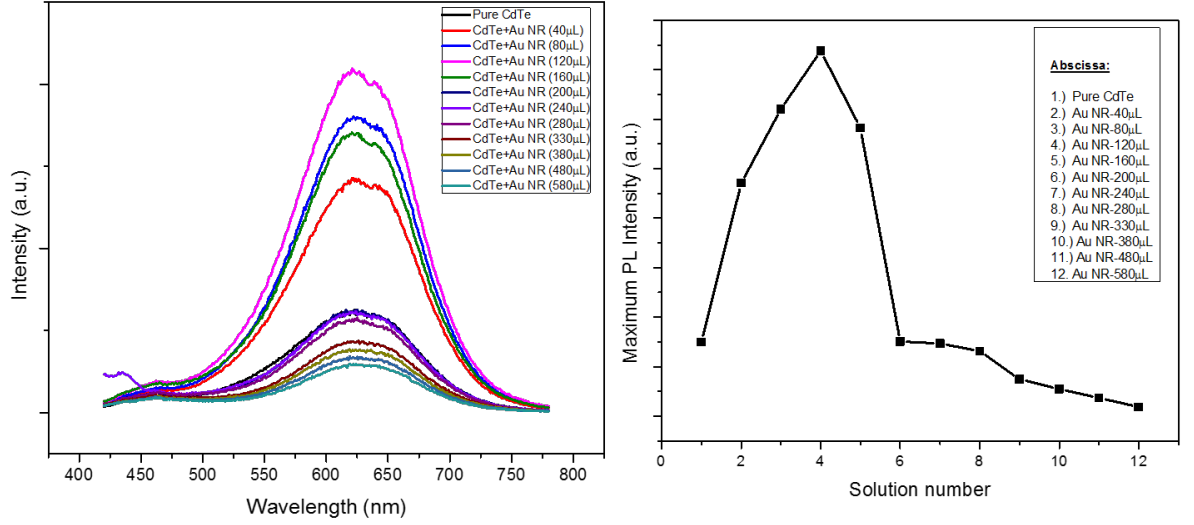


Figure 3.25: (a) PL spectra of Au-CdTe (CdTe 8) hybrid nanostructures. (b) PL Intensity maxima of Au-CdTe hybrid nanostructures.

PL of Au 23 – CdTe 9 (17 hours aliquot)

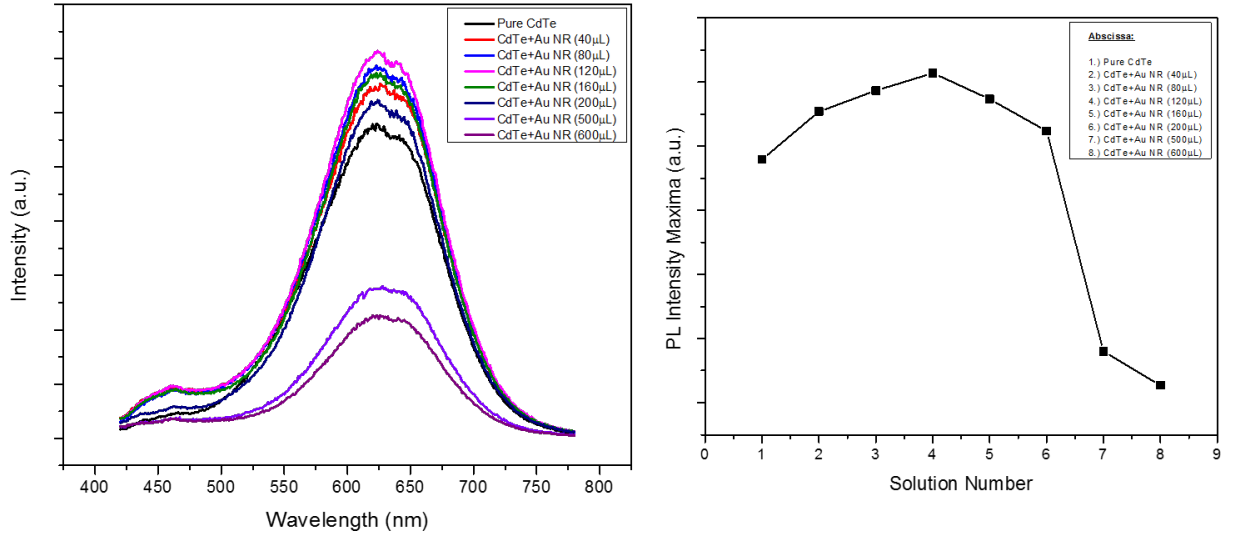


Figure 3.26: (a) PL spectra of Au-CdTe (CdTe 9) hybrid nanostructures. (b) PL Intensity maxima of Au-CdTe hybrid nanostructures.

FESEM images of the conjugated Au NRs and CdTe QRs are shown in Figure 3.27 (a) and (b) which clearly shows successful conjugation.

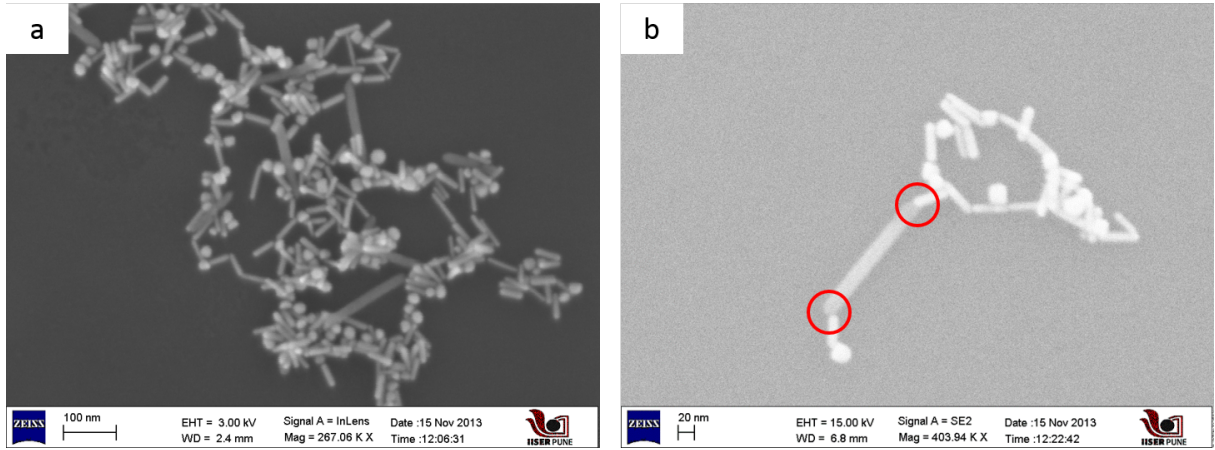


Figure 3.27: (a) FESEM images of Au NR and CdTe conjugated heterostructures with a (b) zoomed view showing conjugation at the end of the Au NRs.

Time correlated single photon counting (TCSPC) study was done to obtain lifetime variations of the different concentration of Au NRs in CdTe QRs solution. Figure 3.28 shows the time-resolved fluorescence spectra of pure CdTe QRs and Au-CdTe hybrid nanostructures. At a glance, the decay rate of pure CdTe (red) seems less than that of the first Au-CdTe hybrid solution, echoing the observations of the PL study. For more elucidation about the individual lifetimes, all the spectra were fitted with a double-exponential decay function, and the weighted averages of the two decay constants per spectra, were calculated. The results have been summarized in the table below:

Fitted model : $y = y_0 + A_1e^{-x/t_1} + A_2e^{-x/t_2}$ (A_1 and A_2 are pre-factors (a.u.), t_1 and t_2 are decay constants and WAT is weighted average lifetime in nano-seconds).

Sr. No.	Sample	A_1	A_2	t_1	t_2	WAT(ns)	Adj. R^2
1	Pure CdTe	247.09	1780.02	22.97	1.36	3.99	0.96
2	CdTe+Au NR (40 μ l)	473.37	285.46	2.52	27.11	11.77	0.97
3	CdTe+Au NR (80 μ l)	236.87	2644.26	14.92	1.35	2.47	0.98
4	CdTe+Au NR (120 μ l)	224.50	1.10E+09	4.05	0.23	0.23	0.95
5	CdTe+Au NR (160 μ l)	7.91 E+26	1.24E+23	6.00	0.07	0.06	0.85
6	CdTe+Au NR (200 μ l)	4.84 E+25	4.84E+25	0.06	0.06	0.06	0.79

Table 3.1: Weighted average life time of Au-CdTe heterostructures.

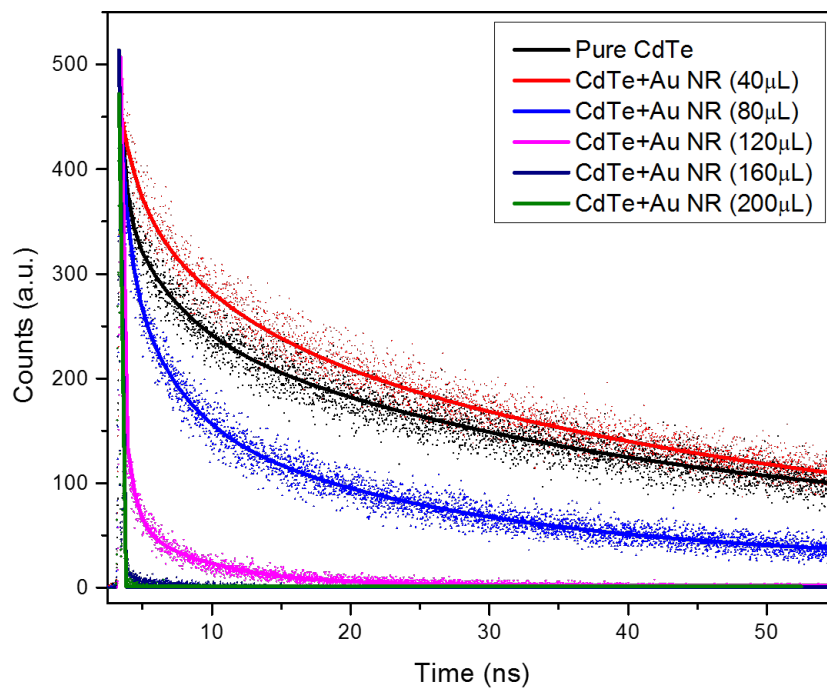


Figure 3.28: TCSPC plot for Pure CdTe (CdTe 6) and Au-CdTe hybrid nanostructures.

Similar result was found in another experiment performed with other CdTe aliquots (CdTe 5) for which TCSPC image is shown in 3.30 (a).

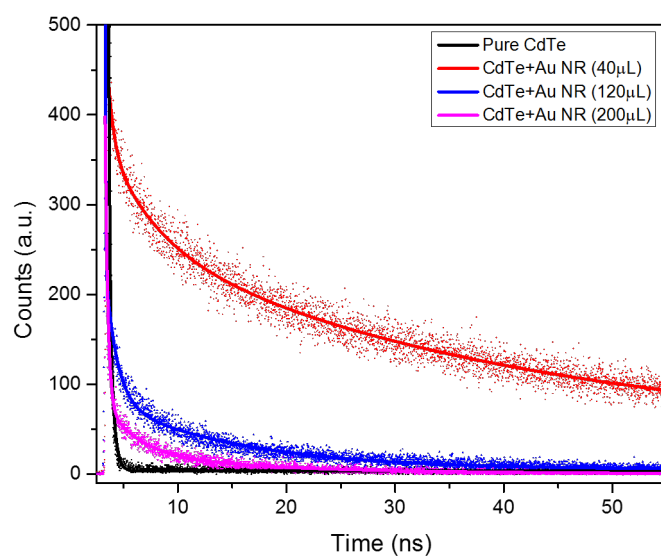


Figure 3.29: TCSPC plot for Pure CdTe (CdTe 5) and Au-CdTe hybrid nanostructures.

It can be seen from the calculations that, as the amount of Au NRs in the CdTe QR solution are gradually increased from zero, the average lifetime of the luminescent QRs first increases, and then decreases. This fact can be traced back to the PL study which also shows the initial increase in emission intensity followed by reduction and then complete quenching. Such an increase in emission can be due to two factors; increase in the amount of luminescent particles in the solution (which corresponds to increased number of emitted photons per unit time), or the increase in average lifetime of the particles. The first factor can be ruled out, as we have ensured to the best of our ability that the amount of CdTe QRs in each sample is the same. Hence, on a statistical basis, we can attribute this observation to the increase in average lifetime of the luminescent CdTe QRs due to coupled exciton-plasmon interactions.

3.5.2 Conjugation of Au nanostars with CdTe QRs

An attempt was made to conjugate gold nanostars with CdTe QRs using the same method used for conjugating Au NRs and CdTe QRs. The principle of attachment of these two nanoparticles remains same. Just as in the case of nanorods, CTAB layers may get removed from ends of the branches of a star shaped gold nanoparticle which can then be attached with CdTe QRs via Au-N weak covalent bond. A quick check up of fluorescence of conjugated nanoparticles was done under UV lamp enclosure which showed complete quenching of fluorescence of CdTe QRs upon exciton-plasmon coupling. This means that the energy emitted by CdTe QRs are being consumed in some kind of coupling consequences.

Figures 3.30 (a) and 3.31(a) show the UV-Vis absorption spectra of the synthesized Au nanostars (black) and CdTe QRs (red). The CdTe QRs show a characteristic excitonic absorption shoulder at 400 nm in 3.24 (a) while it's 408 nm in 3.25 (a), whereas the Au nanostars show two distinct absorption peaks, one at 588 nm and a bigger one at 710 nm with a shoulder at 530 nm, corresponding with the transverse and longitudinal surface plasmon resonances, respectively.

Figures 3.30 (a) and 3.31 (b) show the overlaid absorption spectra of the various Au-CdTe hybrid nanostructures. The spectra show three peaks, one corresponding with the excitonic absorption due to CdTe and the other two with the SPR modes of Au nanostars. It was observed that the curvature of excitonic shoulder changed due to addition of Au nanostars into CdTe solutions. It's also clearly visible from Figure 3.30 (b) that the position of longitudinal SPR shifted towards lower wavelengths.

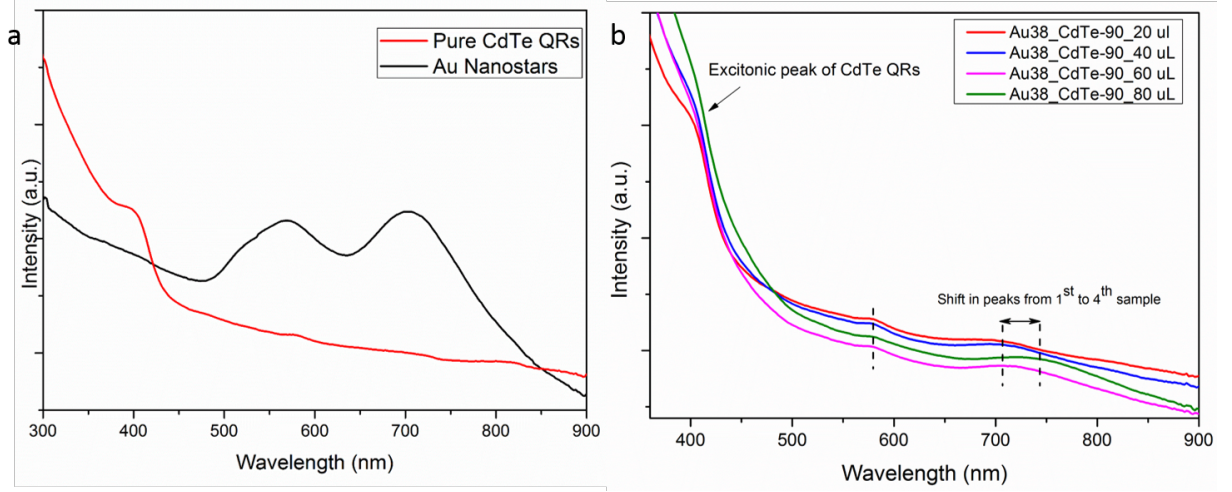


Figure 3.30: (a) UV-Vis absorption spectra of Au nanostars and CdTe QRs (with absorption peak at 400 nm). (b) UV-Vis absorption spectra of Au-CdTe hybrid nanostructures.

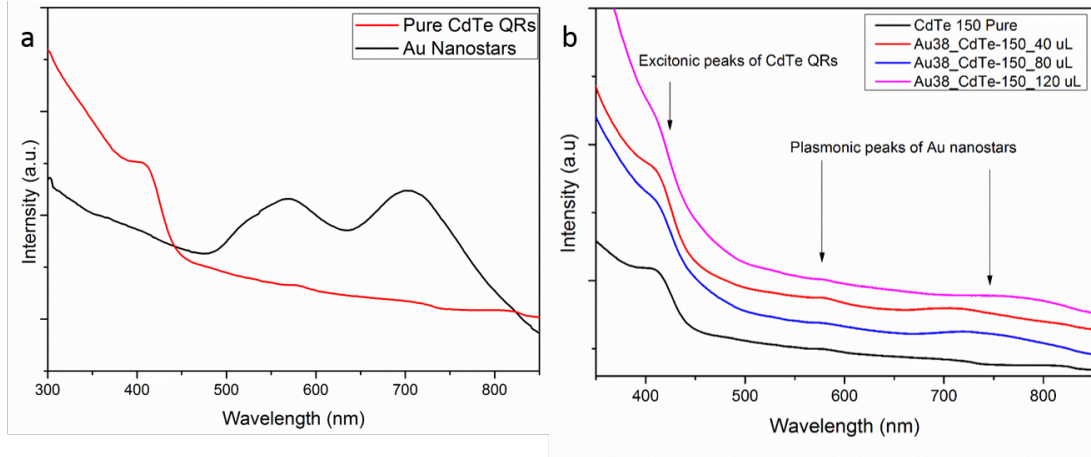


Figure 3.31: (a) UV-Vis absorption spectra of Au nanostars and CdTe QRs (with absorption peak at 408 nm). (b) UV-Vis absorption spectra of Au-CdTe hybrid nanostructures.

Figure 3.32 (a) shows the overlaid photoluminescence spectra of pure CdTe QRs and the Au-CdTe hybrid nanostructures, with increasing amounts of Au nanostars. These emission spectra were recorded at a fixed excitation wavelength of 400 nm, and the entrance/exit slit-widths equal to 1nm/4nm respectively. Care was taken to maintain same levels of sample dilution for the ease of comparing the emission intensities.

It was observed that due to exciton-plasmon coupling, the emission intensity of pure CdTe QR solution kept on reducing with increasing amount of Au nanostars, indicative of conjugation. In this case as it can be seen from Figure 3.32 (a) and 3.33 (a), there is no shift in emission peaks of CdTe –Au nanostars composites unlike the case of Au NR-CdTe conjugation and metal enhanced fluorescence has also not been observed. This can be seen from Figure 3.32 (b), which depicts the intensity maxima of emission versus increasing amount of Au NRs in the solution.

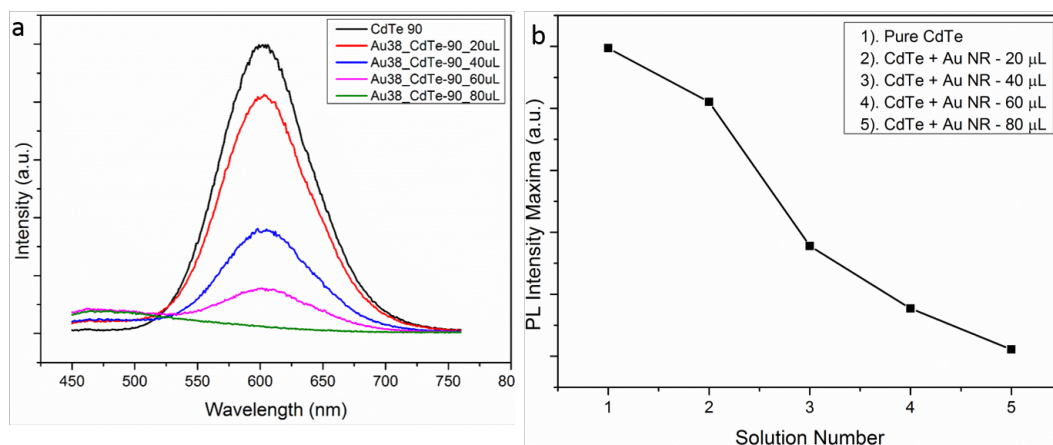


Figure 3.32: (a) PL spectra of Au-CdTe (CdTe 90) hybrid nanostructures. (b) PL Intensity maxima of Au-CdTe hybrid nanostructures.

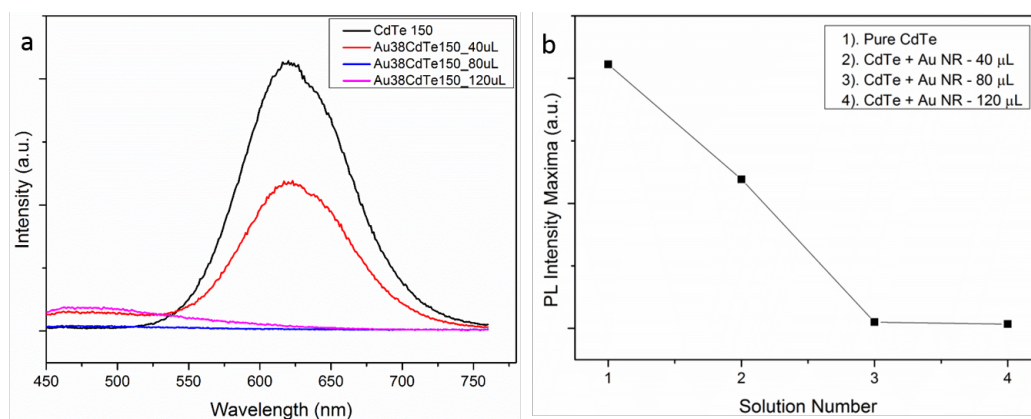


Figure 3.33: (a) PL spectra of Au-CdTe (CdTe 150) hybrid nanostructures. (b) PL Intensity maxima of Au-CdTe hybrid nanostructures.

FESEM images were taken for the Au nanostars and CdTe QRs conjugated heterostructures and EDAX was performed as well for compositional analysis of the heterostructures. Figure 3.34 shows a FESEM image and its EDAX analysis at a spot.

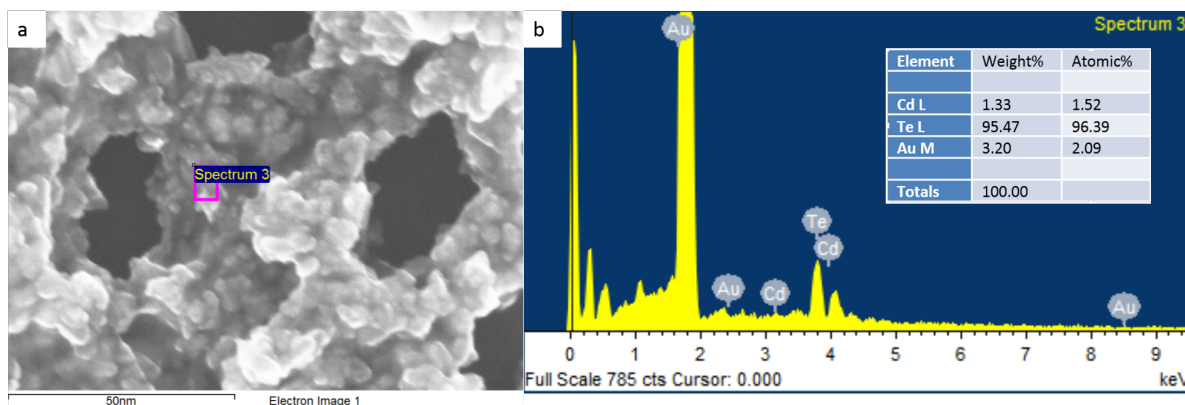


Figure 3.34: (a) FESEM image of Au nanostars and CdTe QRs. (b) EDAX analysis of same sample in a region shown in image (a).

3.6 Concluding Remarks

Gold nanorods and nanostars were synthesized by two-step seed mediated growth procedure in aqueous media. In order to conjugate Au NRs or Au nanostars with any other semiconductor nanoparticles, the media of solution has to be miscible as mostly in this work colloidal syntheses have been done. So, aqueous CdTe quantum rods were synthesized and a method has been successfully developed to chemically conjugate these nanoparticles. Various characterization methods were performed to validate the conjugation and thus exciton-plasmon coupling.

The result show that in case of Au NR-CdTe QR conjugation, as expected, fluorescence quenching has been observed successfully and besides that metal enhanced fluorescence has also been observed which shows that the CdTe QRs and Au NRs are brought closely when the concentration of Au NRs are less in the CdTe solution. Upon increased concentration of Au NRs more attachments result into total fluorescence quenching of the CdTe solution. In case of nanostars fluorescence quenching was achieved with very less amounts of Au nanostars in the CdTe solution and no enhancement was observed. As discussed in chapter one, excitation of surface plasmons is a resonant process with a resonance frequency dependent upon composition, size and shape of the metal nanoparticles and it's dielectric environment and because of this property metal nanoparticles are able to concentrate electromagnetic energy and enhance optical fields. Au NRs and Au nanostars, both are of different shapes and sizes and both show somewhat different absorption profile (stars showed a modified profile with a shoulder near transverse mode of LSPR) that may have led into the two kind of interaction with CdTe QRs (nanorods showed metal enhanced fluorescence^[8] followed by complete fluorescence quenching while nanostars showed only fluorescence quenching). Semiconductor quantum dots/rods are known to give high emission yields and light harvesting capabilities. Au-CdTe conjugated heterostructures have exciton-plasmon interactions in which electromagnetic field enhancements can be utilized in photodetectors and photovoltaic devices. The Au NRs have ability to localize the impinging light field that then can be absorbed by an appropriate light harvester (semiconductor nanostructures) which can be located in the proximity of the Au NRs. In such a case, a large fraction of the light can be absorbed by the excitonic structure and therefore such exciton-plasmon interactions can lead to an effective increase of absorption cross section of the semiconductor nanostructures which can be seen in Figure 3.30 (b) where excitonic peaks have continuously been shifting and the curvature of excitonic peaks are getting modified. Hence, metal-semiconductor nanostructures can increase the performance of photovoltaic devices. As it has been observed, Au NRs and CdTe QRs conjugated heterostructures showed enhanced emission property (Figure 3.23, 3.24, 3.25, 3.26) also besides fluorescence quenching. This property has been seen in absorption properties of Au-CdTe heterostructures also where the excitonic peak and transverse mode of LSPR got merged into a big envelope (Figure 3.19 (b)) as well as TCSPC (Figure 3.28 and 3.29) shows increased life time for the same sample which showed enhanced fluorescence. It has been suggested earlier that the spontaneous decay rate of a transition can be modified by coupling it to a resonant system.^[9] In such a case, metal nanostructures provide the resonators that couple to the excitons through near-field interactions when spectral overlap between emitter and surface plasmon energies and precise positioning of the emitter in the vicinity of the metal nanostructure is achieved.^[10,11] Such kind of interactions have earlier been found in cases of CdSe nanocrystals spin-coated with gold nanodisk arrays.^[12] The emission enhancement caused by exciton-plasmon interaction can

have potential applications in fluorescence based sensors.

3.7 Bibliography

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Chapter 4

Summary and Future Directions

In this work, gold nanoparticles (nanorods, nanostars, spherical-ended nanodumbbells and arrow-ended nanodumbbells) were synthesized via wet chemical route at room temperature and CdTe quantum rods were synthesized at 100°C with different times of refluxing resulting into different sizes. The nanodumbbells were synthesized by a one step end modification process using ascorbic acid and NaOH which resulted into spherical-ended dumbbells and arrow-ended dumbbells respectively. Addition of ascorbic acid or NaOH basically alters the pH of a nanorods solution and that causes removal of CTAB layers from the ends of the nanorods. Using this procedure with slight modification, conjugation of CdTe was done with gold nanorods as well as nanostars. The characterization of synthesized gold nanoparticles were done using UV-Vis spectrophotometer and FESEM while for CdTe quantum rods, apart from these, photoluminescence spectra were taken in addition to study emission properties. Au-CdTe heterostructures were characterized by taking UV-Vis absorption, PL-emission, FESEM imaging and TCSPC techniques. Results showed positive conjugation of CdTe quantum rods and gold nanorods.

This work can further be extended by considering silver nanostructures instead of gold nanostructures and investigating consequent changes in different properties. Similarly ZnO or other semiconductor nanoparticles or nanorods can be considered as excitonic counterpart. Silver is advantageous for plasmonics because of low intrinsic losses that result in narrow surface plasmon resonances with high oscillator strengths and large optical field enhancements. Instead of conjugation of two nanoparticles at a time, multiple conjugations can be done and their properties can be studied. That may lead to some new modifications in the properties of such hybrid heterostructures. Alloyed semiconductors can also be used to conjugate with metallic nanoparticles and their properties can be studied. In cases where the SPR of metallic nanoparticles can be tuned to be closer to the excitonic absorption peak of semiconductor nanoparticles, the absorption cross-section can be tuned to increase and then it can be made use in photovoltaics or solar cell applications.