Summary of Thesis

Colloidal semiconductor nanocrystals have attracted great fundamental and technical interest because of their unique optical and electronic properties, such as photostability, continuous absorption band, narrow photoemission, strong fluorescence, broad photoexcitation. An overcoating nanocrystal with higher band gap inorganic materials has been shown to improve the photoluminescence quantum yields by passivating surface nonradiative recombination sites. These Core-shell composite NCs exhibit novel properties making them attractive from both an experimental and a practical point of view.

This thesis presents a comprehensive study of preparation, characterization and device fabrication of II-VI (CdSe/CdS and CdSe/ZnSe) Core/Shell Nanostructures dispersed in PVA matix. The Core (CdSe) and Shell (ZnSe, CdS) are also separately dispersed in PVA matrix and studied to account the proper effect of each materials in Core/Shell system. The structural and optical characterization is performed on all the samples. In structural chacterization, X-ray diffraction measurements are done using PANalytical X'Pert PRO diffractometer. Transmission Electron Microscopy [Hitachi H7500] is used to study the morphology of as-prepared sample to confirm the formation of shell. The UV/Vis spectra have been using the Perkin Elmer Lambda 750 to acquire the information about optical gap and optical transparency of the materials. The Photoluminescence measurements [Perkin Elmer LS55] are done on to determine nature of emission and efficiency of materials. The nonlinear optical properties of these samples are studied by Z-scan technique at low by Z-scan technique using low power CW He–Ne laser light of wavelength 633 nm.

The nature of Core PVA:n-CdSe is found to have a mixture of cubic and hexagonal phase. The particle size of as-deposited PVA:n-CdSe thin films from XRD measurements comes out to be 4.1 nm. TEM images show the morphology of PVA:n-CdSe is of nanorods type. The optical band gap calculated from the UV/Vis spectra is 2.69 eV. The observed values of E_g are higher than the value of bulk optical gap of CdSe (1.74 eV). The blue shift in the band gap energy of chemically deposited PVA:n-CdSe thin films, confirms the quantum confinement effect. The PL measurements show the emission peak at wavelength 541 nm at the excitation wavelength 350 nm. The emission peak does not vary with the excitation wavelength only there is enhancement in PL intensity. The optical microscopy of PVA:n-CdSe shows the green light emission wavelength. The nonlinear refractive index is negative,

indicating self-defocusing effect and nonlinear absorption coefficient is showing reverse saturabale absorption. PVA:n-CdSe show larger third order susceptibility ~10^{-5} esu which is due to presence of quantum confinement effect and dielectric confinement effect.

PVA:n-ZnSe nanocrystals show sphalerite cubic structure. The particle size of as-deposited PVA:n-ZnSe films from XRD comes out to be ~ 6.1 nm. TEM image shows that PVA:n-ZnSe nanoparticles are homogenously dispersed in PVA matrix and spherical in shape. The range of diameter of PVA:n-ZnSe nanoparticles are from 10 nm to 15nm. The optical band gap calculated from the UV/Vis spectra is 2.74 eV. The observed values of E_g are higher than the value of bulk optical gap of ZnSe (2.58 eV) due to the quantum confinement effect and PVA matrix effect. The PL measurements show the emission peak at wavelength 526 nm at the excitation wavelength 350 nm. The optical microscopy of PVA:n-ZnSe shows the green light emission wavelength. The nonlinear refractive index is negative, indicating self-defocusing effect and nonlinear absorption coefficient is showing reverse saturabale absorption following the multiphonon absorption. Origin of the large optical nonlinearity in PVA:n-ZnSe films is presented on the basis of photo-induced modification of surface states and dielectric confinement effect.

The XRD of PVA:n-CdS nanocrystals dispersed in polymer matrix show sphalerite cubic structure. The particle size of as-deposited PVA:n-CdS films from XRD comes out to be ~ 5.3 nm. TEM image shows that PVA:n-CdS nanoparticles are homogenously dispersed in PVA matrix and spherical in shape. The range of diameter of CdS nanoparticles are from 5-10 nm. The absorption spectra of PVA:n-CdS nanocomposite show the optical band gap ~ 2.86 eV. The observed values of E_g are higher than the value of bulk optical gap of CdS (2.42 eV) due to the quantum confinement effect and PVA matrix effect. Room temperature PL spectrum of PVA:n-CdS nanocomposite shows a strong emission band centered at about 497 nm is observed, which show the blue-shift behavior in comparison to bulk CdS. This blue shift is due to the quantum confinement effect resulting from the decrease in size of the nanoparticles. The factor which has a great effect on the size of PVA:n-CdS nanoparticles is the PVA matrix. The observed emission is due to band to band recombination. These nanoparticles exhibit strong and well-defined green photoluminescence indicating that the PVA:n-CdS nanocomposites has endowed with luminescence features. The nonlinear refractive index is negative, indicating self-defocusing effect and nonlinear absorption coefficient follows two photon absorption mechanisms and larger third order susceptibility is due to presence of quantum confinement effect and dielectric confinement effect.

CdSe/CdS Core/Shell nanorods dispersed in PVA are synthesized by Chemical method at room temperature. X-ray diffraction (XRD) measurements show mixed structure i.e. cubic and hexagonal structures. The XRD spectra of CdSe/CdS core/shell nanorods show higher intensity peaks as compared to CdSe core. The value of average crystallite size obtained from XRD spectra for CdSe/CdS core/shell nanorods is 4.5 nm. TEM images shows that CdSe/CdS core/shell is of nanorods type but due to very small size, individual CdSe/CdS core/shell nanorods are clustered together or are agglomerated or/ and coalesced. The average diameters of CdSe/ZnSe core/shell NCs, as measured by TEM, are 4-5 nm. TEM image clearly shows the formation of CdS shell over the CdSe core. The thickness of CdS shell is using the Superposition of Quantum Confinement Energy (SQCE) model. The FTIR spectrum of CdSe/CdS core/shell nanorods is showing a decrease in the wave number as compared to CdSe spectra. The red shift of CdSe/CdS core/shell nanorods shows the attachment of sulphur precursor on CdSe core. The effect of shell thickness on UV/Vis spectra and PL spectra is studied to confirm the formation of Shell. The UV/Vis spectra and PL spectra of CdSe/CdS core/shell nanorods shows red shift as compared to CdSe core showing the formation of Core/Shell. The PL intensity and Quantum Yield (QY) is improved from 29% for the pure CdSe core to 50-60% for the samples passivated with CdS shell. The PL spectra of CdSe/CdS core/shell nanorods show two main peaks at 548 and 556 nm which indicates the presence of two sized particles. The PL emission peaks are red shifted with variation of thickness of CdS shell. CdSe/CdS core/shell nanorods has demonstrated to exhibit strong and well-defined green and yellow photoluminescence indicating that the solution has endowed with luminescence features. The higher value of nonlinear susceptibility of CdSe/CdS core/shell nanorods indicates as a suitable material for nonlinear optical devices.

CdSe/ZnSe Core/Shell NCs dispersed in PVA are synthesized by Chemical method at room temperature. X-ray diffraction (XRD) measurements show mixed structure i.e. cubic and hexagonal structures. The XRD spectra of CdSe/ZnSe core/shell NCs show higher intensity peaks as compared to CdSe core. The value of average crystallite size obtained from XRD spectra for CdSe/ZnSe core/shell NCs is 3 nm. TEM image shows that CdSe/ZnSe core/shell is homogenously dispersed in PVA matrix and spherical in shape. It is observed that the NCs have a narrow size distribution. The average diameters of CdSe/ZnSe core/shell NCs, as measured by TEM, are 3-4.5 nm. TEM image clearly shows the formation of ZnSe shell over the CdSe core. The thickness of ZnSe shell is not estimated from TEM measurements. The FTIR spectrum of CdSe/ZnSe core/shell NCs is showing a decrease in the wave number as compared to CdSe spectra. The red shift of CdSe/ZnSe core/shell NCs shows the attachment of zinc precursor on CdSe core. The effect of shell thickness on UV/Vis spectra and PL spectra is studied to confirm the formation of Shell. The UV/Vis spectra and PL spectra of CdSe/ZnSe core/shell NCs shows red shift as compared to CdSe core showing the formation of Core/Shell. The PL intensity and Quantum Yield (QY) is improved from 25% for the pure CdSe core to 50% for the samples passivated with ZnSe shell. CdSe/ZnSe core/shell NCs has demonstrated to exhibit strong and well-defined green photoluminescence indicating that the solution has endowed with luminescence features.

We have also fabricated and characterized the Schottky and MOS diodes of the II-VI semiconductor nanocrystals (CdSe, CdS, ZnSe, CdSe/ZnSe and CdSe/CdS). The Current-Voltage $(I - V)$ characteristics have been measured at different temperatures in the forward bias. The performance of the diodes are measured from the barrier height(ϕ_b) and ideality factor (n). The I-V parameters such as series resistance(R_s), the ideality factor (n), the effective barrier height(ϕ_b), the Richardson constant (A^*) and the leakage current with the temperature have emphasized an inhomogeneity of the barrier height and a tunneling mechanism assisted by traps in the Schottky barrier diode. In Capacitance-Voltage $(C - V)$ measurements, in the reverse bias, have been performed as a function of temperature. The values of barrier height (ϕ_{C-V}), the built-in–voltage (V_{bi}) and carrier concentration (N_D) and depletion layer width (W) have been calculated at different temperatures in reverse bias. The barrier inhomogeneities of metal-semiconductor contact have been explained on assumption of a Gaussian distribution of barrier heights by using potential fluctuation model. The introduction of Alumina layer into metal-semiconductor contact results into the improvement in the ideality factor.

Our studies show that II-VI semiconductor nanocrystals show good optical and electronics properties. The CdSe/ZnSe and CdSe/CdS Core/Shell photostability and light emission properties as compared to core materials. This effect is a fundamental prerequisite for the use of nanocrystals in applications such as biological labelling and light-emitting devices, which rely on their emission properties. Thus, an interesting step forward from this developed work would be a designed system with the choice of chemical functionality in PVA to be utilized as a 'linker' or "coupling agent" for posterior bioconjugation. Alternatively, by the addition of some transition metals ion into the these materials can be helpful in using it as a electrolumniescence devices.