

## **ABSTRACT**

Quantum dots of II-VI semiconductors display excellent properties compared to bulk semiconductors by confining the motion of conduction band electrons and valence band holes or excitons in all three spatial directions. The properties of the quantum dots purely depend on size and they hold promise for numerous optoelectronic materials, sensors, photo detectors, biological labels and photonic applications. Cadmium sulfide is the most promising candidate owing to its tunable band gap which makes it most attractive material for nonlinear optical applications such as optical limiters, data storage, quantum computing and in photovoltaics.

The properties of the CdS semiconductor nanoparticles are influenced mainly by their size effect. Several synthetic approaches are being developed to tune the size of the particles and to understand their influence on the optical properties including photoluminescence and UV-Vis absorption. The decrease in particle size increases the surface to volume ratio and this drastically affects the electronic structure of the material resulting in the increased band gap. The electronic states in nanoparticles become discrete and are located at higher energy compared to the bulk, leading to significant changes in the optical properties. In general, quantum dots do not exhibit good optical properties due to their poor crystallinity and the presence of surface traps. One of the key approaches to improve the optical performance of CdS nanoparticles is by providing a protective surface layer encapsulation by using an organic capping layer that prevents nanoparticle aggregation and modify the surface trap. The agglomeration can be effectively prevented by steric means. Many polymers serve as steric stabilizers for the incorporated

particles. It is now well established that polymers are excellent host materials for semiconductor nanoparticles. When semiconductor quantum dots are reinforced in organic polymer, they exhibit better optical properties because of its homogeneous distribution inside the polymer. The synthesis of CdS nanoparticles in polymer matrix with sterically stabilizing surfactant such as poly (ethylene Oxide) (PEO) and poly (methyl methacrylate) (PMMA) are studied extensively, due to their efficient photoluminescence property, enhanced change in thermal behavior of the matrix and their electrical conductivity.

The aim of the doctoral work is to synthesize and analyze the properties of CdS:PEO and CdS:PMMA nanocomposite solid films of high transparency for device applications using cost effective novel insitu solution casting technique. The solid films should have the minimum thickness with high transparency. The solid films are prepared by dissolving the polymers in the common solvents and in both the polymers,  $\text{Cd}(\text{NO}_3)_2$  is used as the cadmium source. The concentration of  $\text{Cd}^{2+}$ : polymer is varied in both the composites. The films are formed out of  $\text{Cd}(\text{NO}_3)_2$  : PEO and  $\text{Cd}(\text{NO}_3)_2$  : PMMA. The formed films are exposed to  $\text{H}_2\text{S}$  gas to convert  $\text{Cd}^{2+}$  ions to CdS. The solid films are yellow in colour which is the indication of the formation of CdS. The thickness of the solid films are found using interferometric method and the thickness of CdS:PEO and CdS:PMMA films are  $\sim 10 \mu\text{m}$  and  $\sim 5 \mu\text{m}$  respectively. The maximum transmittance of the solid films of CdS:PEO is around 87% and for CdS:PMMA solid films, the transmittance is around 92%. The XPS studies are carried out for the composite solid films to verify the presence of CdS in the host polymer and to know the composition of Cd:S. The results reveal the presence of CdS in the matrices. 1:1 stoichiometry is achieved in both the composites (CdS:PEO and CdS:PMMA) having lower CdS concentration.

The XRD pattern resulted in the change in shape and nature of the PEO related peaks which implies the strain induced in the polymer matrix due to the incorporated CdS particles. The XRD pattern for the higher concentration of CdS:PMMA matrix (1:20) shows the peak related to the cubic phase CdS in the matrix. The lower CdS concentration in PMMA matrix results in broad amorphous PMMA peaks. The TEM images of CdS:PEO composites shows the uniformly distributed particles in the polymer matrix and the minimum particle size is around 5-10 nm for lower CdS concentration. In CdS:PMMA matrix, the minimum particle size from TEM images having lower CdS concentration is around 2-5 nm. The AFM image illustrates the uniformly distributed nanosized CdS particles in both PEO and PMMA matrix. But in PMMA matrix, narrow particle size distribution is achieved.

The functional group analysis using FTIR-ATR spectra reveals the bonding mechanism that exists between CdS and PEO. The relative intensity ratio of the peaks increases before H<sub>2</sub>S treatment which is the indication of the complexation of Cd<sup>2+</sup> ions with the ether oxygen of the PEO. The peaks came back nearly to the position of pure PEO after H<sub>2</sub>S treatment which reveals the lost in influence of charge neutralized CdS particles over ether oxygen. The relative intensity ratio with respect to C-O-C bond of CdS:PMMA nanocomposites also shows the increase in intensity before and after H<sub>2</sub>S treatment, the peaks approaches the position of pure PMMA. This may be attributed to the contribution of both ether oxygen and carbonyl functional group of PMMA matrix over Cd<sup>2+</sup> ions and CdS particles. The Raman spectra of CdS: PEO nanocomposites show the 1LO and its overtone 2LO around 301.9 cm<sup>-1</sup> and 607.48 cm<sup>-1</sup> for 1:100 concentration and the longitudinal optical modes are shifted slightly towards higher wavenumber side for decrease in CdS concentration. The results reveal the confinement of optical phonon with decrease in particle size. For CdS:PMMA

nanocomposites, the 1LO and its overtone 2LO is observed around  $308\text{ cm}^{-1}$  and  $604\text{ cm}^{-1}$ . Both the polymer environment is different and the peak positions of 1LO and 2LO slightly differs.

The thermal studies of CdS:PEO nanocomposites reveal the decrease in the percentage of crystallinity of the polymer with increase in CdS concentration. But the position of melting peak shows small shift for different concentrations before and after  $\text{H}_2\text{S}$  exposure. The glass transition temperature of PMMA increases with addition of CdS in the matrix. This indicates the increase in hardness of the material due to the incorporated CdS particles. The optical properties using UV-Visible absorption spectra for CdS:PEO nanocomposites shows the existence of absorption shoulder around 489 to 505 nm. The band edge of the nanocomposite is shifted towards blue region with decrease in CdS concentration which in turn decreases the particle size. This results in increase in band gap. In CdS:PMMA nanocomposites, the band gap varies from 2.58 eV to 3.23 eV. The band edge values lies between 489 to 409 nm for the nanocomposites. The photoluminescence spectra displays the broad defect state emission for different concentrations of CdS:PEO nanocomposites and is shifted towards blue region with decrease in particle size. The emission spectra of CdS:PMMA shows the near band edge emission in addition to the broad emission which lies in the blue region of the visible spectrum and the broad emission is related to the green emission of the composites. The maximum room temperature dc conductivity obtained for CdS:PEO nanocomposites is  $2 \times 10^{-10}\text{ S/cm}$ . The ac conductivity of the nanocomposites increases with increase in frequency. Similarly, for CdS:PMMA nanocomposites, the maximum room temperature dc conductivity obtained is around  $1.5 \times 10^{-13}\text{ S/cm}$  and it is very less compared to CdS:PEO nanocomposites.

The properties of the CdS:PEO and CdS:PMMA nanocomposites are compared to find their suitability for device applications. Though high transmittance is observed in both the nanocomposite solid films, uniform and narrow distribution of particles is observed in CdS:PMMA nanocomposites from the AFM and TEM images which is one of the prerequisites for optoelectronic applications. The DSC analysis of CdS:PMMA nanocomposites reveals the thermal stability of the composites which makes it suitable for high temperature applications. The optical properties of both the composites shows the quantum confinement effect and the nanocomposites of CdS:PEO and CdS:PMMA can be used for optoelectronic applications. CdS:PEO nanocomposite can be utilized as a better polymer electrolyte material compared to CdS:PMMA, since the room temperature dc conductivity of CdS:PEO pronounced much.