PREFACE

Luminescent semiconductor nanocrystals (Quantum Dots or QDs) form an attractive alternative to organic molecules in the new generation displays, bio-labels and lasers due to their high luminescence quantum efficiency, spectral tunability, colour purity, high optical gain with lower threshold and high chemical stability. Doped counterpart of semiconductor nanocrystals have also attracted great interest due to their additional advantageous characteristics such as short luminescence lifetime, size independent emission, colour tunability, low voltage cathodoluminescence and alternate current electroluminescence. II-VI sulfide semiconductors such as CdS and ZnS are effective photocatalysts that decompose hydrogen sulfide ion (HS⁻) that is environmentally beneficial as it produces hydrogen, a clean source of energy. Also, CdS and ZnS meet the requirements for the core-shell formation namely (i) ZnS which forms the shell has higher band gap than the core CdS and (ii) there is sufficient lattice match between the two materials. Organic solvent approach for QD synthesis is complex and harmful to the environment because of pyrolysis of toxic organometallic reagents. There are only very few reports on the aqueous synthesis of CdS and ZnS quantum dots. This thesis deals with the aqueous synthesis and characterization of thioglycerol-stabilized CdS and ZnS quantum dots.

Chapter 1 gives an introduction to nanoscale materials, elementary idea of quantum size-effect, photoluminescence, stabilization of colloidal systems and review of earlier works on CdS and ZnS nanoparticles. The second chapter discusses the various diagnostic techniques used in the analysis of the samples. Characterization techniques like X-ray diffraction, high-resolution transmission electron microscopy (HRTEM), selected area electron diffraction (SAED), UV-visible and
photoluminescence (PL) spectroscopy techniques are used to characterize the samples.

Study on optical absorption and photoluminescence of thioglycerol stabilized CdS quantum dots synthesized using CdSO₄ and (NH₄)₂S precursors is given in Chapter 3. Nanoparticles of different size were obtained by adjusting the thioglycerol (T) to ammonium sulfide (A) ratio T:A from 1:25 to 1:3.3. The size of QDs obtained with T:A of 1:3.3 were determined using XRD, high-resolution TEM and dynamic light scattering and found to be ~ 4 nm. The UV-visible and PL spectra showed quantum size effects as shown by excitonic transition at 380 nm, blue-shift of absorption band edge upto 2.95 eV and blue-shift of PL from 628 to 556 nm when the ratio of T:A was varied from 1:25 to 1:3.3. Doping of CdS with 5 wt% Zn²⁺/Cu²⁺ is found to enhance PL intensity with blue-shift / red-shift. The UV-visible and PL spectral features of CdS/Au hybrid nanoparticles obtained by a physical mixing of CdS colloid and citrate reduced Au colloid in 1:1, 1:2, 1:3 and 1:4 volume ratio are also discussed. Au red-shifts and rapidly quenches the PL of CdS. An additional low energy band ~ 650 nm is observed in the UV-visible spectrum of the hybrid nanoparticles.

Chapter 4 gives a detailed account of the synthesis and characterization of CdS, CdS:Zn²⁺ and CdS:Cu²⁺ quantum dots prepared using CdSO₄ and Na₂S₂O₃ precursors with thioglycerol as catalyst and stabilizing agent. Nanoparticles of size in the range from 3 to 5 nm could be obtained by varying the precursor ratio during synthesis. The broad XRD peaks, high-resolution TEM, SAED pattern with bright circular spots and clear lattice fringes having a spacing of 0.32 nm indicate the formation of cubic CdS nanocrystals. The band gap observed in the range from 2.7 to 3.16 eV indicates quantum size effect. The corresponding PL
spectra show a blue-shift from 618 to 529 nm. The first excitonic transition was observed at 361 nm for the smallest particles. It is also found that capping action of thioglycerol is favoured at low concentrations and catalytic action predominates at higher concentrations of the thiosulfate ion. Effect of Cu$^{2+}$ and Zn$^{2+}$ doping at various weight percentage (wt%) on the PL spectrum is analyzed. In the case of Cu$^{2+}$, PL is red-shifted, intensity is maximum at 10wt% and is almost completely quenched at 15 wt% doping. On doping with Zn$^{2+}$, PL is blue-shifted and intensity of photoemission is found to be maximum at 2 wt% doping.

Studies on optical absorption and photoluminescence of thioglycerol stabilized ZnS quantum dots synthesized using ZnSO$_4$ and Na$_2$S$_2$O$_3$ precursors have been discussed in chapter 5. The XRD pattern, high-resolution TEM image and SAED pattern reveal that the nanoparticles are in well-crystallized cubic phase. The band gap of ZnS has increased from the bulk value of 3.7 to 4.11eV indicating quantum size effect. Excitonic transition is observed at 274 nm and PL emission at 411nm. Doping ZnS with Cd$^{2+}$ enhances the PL intensity and red-shift the PL band and absorption band edge of ZnS. ZnS:CdS hybrid nanoparticle system is also studied for various molar ratios and a red-shift of the band edge of CdS is observed. The PL band is red-shifted and the intensity is almost doubled in the 1:1 hybrid system of CdS/ZnS nanoparticles.

Chapter 6 gives a summary of the salient features, conclusions and future perspectives of the work.