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TITLE OF THE THESIS:

Group II-VI Semiconductor Nano-crystals for Photo and Electroluminescence Applications

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ABSTRACT

Luminescent properties of materials have been sustained area of research, which led to the development of various types of display devices like cathode ray tubes, plasma display panels, lighting applications, luminous paints, electroluminescent panels, etc. in the last many years. Semiconductor nano-crystals (NCs) and quantum dots (QDs) possess interesting and unusual optical and luminescent properties very different from those of their bulk counterparts, leading to novel applications. Luminescent properties exhibited by doped NCs are even more fascinating to the researchers due to their direct applicability in large area flexible displays and efficient lighting. These materials posses many attractive features e.g. size dependent band gap and discrete bands; quantum confinement effects and large surface to volume ratio for better applicability in various luminescent devices. The properties of luminescent NCs and QDs (nano-phosphors); colour of the emission spectrum, luminescence efficiency and radiative life times, may be tuned for their efficient use in various devices by carefully controlling the crystal size of the host lattice and effectively doping these NCs with the optically active ions (activators). This promises to meet the today's demand for energy efficient, white and cool/warm lighting; next generation, flexible, high definition, better resolution and contrast display systems driven at low voltage.

Large number of NCs and QDs have been synthesized, developed and explored for their luminescent properties, but group II-VI semiconductors NCs/QDs are efficient phosphors as they are wide and direct band gap materials, chemically stable and show high photoluminescence (PL) emission.

Motivated with these facts, research work in the thesis was mainly aimed at the development of zinc oxide (ZnO) and zinc sulphide (ZnS) NCs and QDs for their excellent luminescent properties and long term stability. Literature in the area provides enormous research on II-VI semiconductors especially on CdSe, CdS QDs but there are toxic issues with Cd related materials i.e. any leakage of Cd from the nano-crystals would be toxic and harmful to human being and environment. Keeping this in view, Cd free QDs, ZnO and ZnS, has been selected for study in the current thesis work. To achieve even better luminescence properties of ZnO and ZnS QDs/NCs than earlier reported, few novel synthesis methods have been developed which led to interesting and fascinating results. Variety of doped/undoped ZnO and ZnS NCs, QDs have been synthesized using wet chemical/modified methods and have been studied in detail for their Photo- and electroluminescence (EL) behaviour. Results obtained have been analyzed with the help of necessary characterizations and energy band diagram. The important findings out of thesis have been given below:

a. ZnO:Na QDs, with particle size ~ 2 nm, lying in strong quantum confinement (QC) region was found to have best luminescence property. Change over from strong to week QC effect exhibited variation in PL brightness, red shift in PL emission (535 nm to 542 nm) and excitation peaks (332 nm to 351 nm) and increase in the radiative decay times (35.4 ns to 1660 µs). The high luminescence efficiency and smaller decay time make it better applicable for ultra fast optical switches and modern displays.

b. ZnO:Li QDs having spherical shape and average particle size of the order of ~2 nm, lying in the QC region, exhibited strong and broad green PL emission centering at 445 nm and 480 nm. Optimized nucleation and growth time for this sample of ZnO:Li was obtained to be 12 h.

c. These ZnO:Na and ZnO:Li QDs exhibited tuning of PL emission colours in the range 480 nm and 562 nm with respect to the refractive index of the medium, in which they were dispersed. Quantitative study of this type on the sensitivity of PL wavelengths to the refraction of the medium, have been carried out for the first time**.**

d. Doped ZnS QDs in strong confinement region with average particle size ~ 4 nm have been synthesized to achieve three primary colour emitting phosphors in the blue (456 nm), green (515 nm), and red (600 nm) regions by doping them with Ag^{+}, Cu^{+} and Mn^{2+} respectively

e. ZnS:Ag QDs were prepared by co-precipitation technique. Treatment of ZnS:Ag by UV (365 nm) photolysis, improved the PL intensity to 170% as that of co-precipitated sample. Further a novel poly sulphide hydrothermal treatment on ZnS:Ag improved PL intensity to 250%.

f. Stable and efficient AC-EL from a non-EL (ZnS) material could be triggered by introducing very minimal amount of CNTs in ZnS/CNT hybrid material, at a low threshold voltage of 50 V. This was a great achievement in the current research work and could lead to the realization of novel flat lighting sources at low operating AC voltages, in future. The role of CNT has been understood as local electric field enhancer and facilitator in the hot carrier injection to produce EL in the ZnS/CNT hybrid material.

g. ZnS/Graphene nano-composite also exhibited AC-EL in ZnS:Mn NCs at AC voltage of ~ 10V, even smaller that ZnS/CNT. This can have application in the futuristic flexible, better contrast, resolution and low voltage driven display systems.

The study in Thesis work was to achieve efficient and stable ZnO and ZnS based luminescent material and has led to some useful conclusions. The experimental work, presented in the thesis, and the conclusions drawn from it, may be seen as a part of an ongoing extensive research in this area, all over the world, where researchers are drawing different possible variations in the experimental parameters in order to optimize the process of luminescence in the NCs and QDs of the material of choice. Work of the thesis on the ZnS/CNT hybrid material and ZnS/Graphene nano-composite was an initiative and leaves enormous scope for future research to achieve even better AC-EL. The method presented in this thesis can be used to develop low power driven and flexible EL lamps.