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Synthesis and Characterization of Mn doped ZnCdS Core Shell Nanostructures QDs using a Chemical Precipitation Route

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Abstract. With advancement in time, researchers has drawn great attention in the synthesis and characterization of mono dispersed alloyed nanocomposites of II-VI compounds. Ternary semiconductor alloyed ZnCdS quantum dots (QD's) exhibit properties intermediate between those of ZnS and CdS. It shows high absorption coefficients, a composition tunable and size tunable band gap. Moreover, ZnCdS alloyed NC's display unique composition dependent properties distinct from those of their bulk counterparts. The most striking feature of the alloyed NC's nanocrystals is their unusual long time stability in emission wavelength. ZnCdS alloyed QD's at room temperature has been synthesized using chemical precipitation method. Undoped and Mn^{2+} doped ZnCdS QDs have been synthesized and studied. UV-visible absorption spectrum shows absorbance in the visible region and photoluminescence (PL) emission spectra of the doped ZnCdS QD's shows orange emission in comparison to weak blue emission from undoped QDs. The crystallite size is calculated from the XRD patterns. The experimental results indicate that this easy synthesis route would prove a versatile approach for the preparation of doped and undoped ZnCdS QD's.

Keywords: ternary semiconductor, photoluminescence, chemical precipitation.

INTRODUCTION

Colloidal semiconductor nanocrystals (NCs), are of great interest and have been widely investigated because of their unique optoelectronic properties. These properties arises due to quantum confinement effect and large surface to volume ratio. These properties varies along with their size and composition possess potential applications in light emitting diodes (LEDs)[1], displays[2],bioimaging [3], and solar cell [4]. Ternary semiconductor ZnCdS NCs have combined properties of ZnS and CdS i.e. they exhibit direct band gap, high absorption coefficient in blue and UV region. They show composition tunable as well as size tunable bandgap from 2.4 to 3.7 eV. Recently, doping of semiconductor NCs yields a wide range of interesting properties. Doped semiconductor NCs possess additional advantages. Dopants strongly influence the optical behavior of Quantum dots (QDs) as they form deep trap levels and act as luminescence centers. While retaining the intrinsic advantages of undoped QDs, they possess large stoke shift to avoid self-absorption/energy transfer, greatly enhance thermal and chemical stability and longer excited state lifetime [5-10]. Variety of transition metal ions, including Mn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Ag^{+} have been doped into semiconductor NCs, making NCs attractive for diverse applications. Band gap tuning of colloidal QDs can additionally be controlled by the alloy formation since control of size is difficult. The QD core coated with a wide band gap inorganic material shell have significantly improved photoluminescence quantum yield due to passivation of surface nonradiative recombination sites. In this paper, ZnCdS:Mn/ZnS nanoparticles (NPs) are synthesized by using a chemical precipitation route and characterization has been done. Then the luminescent properties of synthesized nanoparticles are studied.

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EXPERIMENTAL SECTION

A chemical precipitation route has been used to synthesize ZnCdS doped nanoparticles [5, 6]. ZnCdS particles were synthesized using cadmium acetate dehydrate (Cd $(COOCH_3).2H_2O$) and zinc acetate dehydrate (Zn $(COOCH_3).2H_2O$) instead of metal chlorides. Sodium sulfide was used as sulfur source. 3-Mercaptopropane-1, 2-diol, also known as thioglycerol was used as an organic stabilizer. Zinc cadmium sulphide (ZnCdS) nanoparticles were obtained with different compositions, by appropriately changing the Cd/Zn ratio in the starting solution. Doping of particles were done by adding appropriate amounts of manganese acetate. Then the zinc and sodium precursors were added successively to make shell. Then the mixture was stirred for 3 hrs at 80ºC. The precipitate was separated by centrifugation and washed several times with ethanol. Then the washed precipitate was dried to collect the finally prepared QDs.

RESULTS AND DISCUSSION

Figure 1 shows the UV-visible absorption spectra of $Zn_{1-x}Cd_xS$ doped with Mn. The excitonic absorption peak was observed at 360 nm. This explains the formation of ZnCdS alloyed QDs via intermixing of wider bandgap ZnS with narrower band gap CdS. Moreover with increasing Cd concentration, the excitonic peak which is characteristic of QDs gradually shifts towards a higher wavelength.

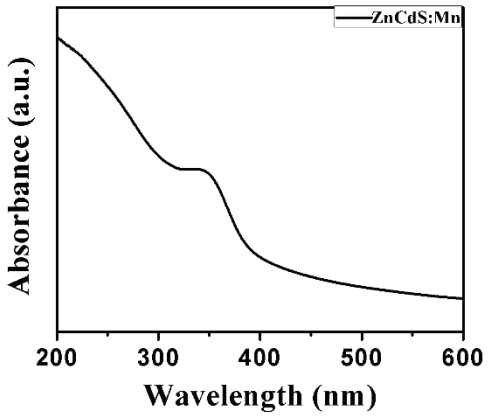

FIGURE 1. UV-visible spectrum of Mn Doped ZnCdS nanoparticles.

The PL emission spectra for ZnCdS doped with Mn is shown in figure 2. It shows broad emission when excited at 400 nm due to dopant (Mn^{2+}) related transition $^4T_1 - {}^6A_1$. The formation of shell passivates the defects as satisfies the anionic and cationic dangling bonds results in blockage of nonradiative transitions. Thus the relative increase in intensity as well as red shift in peak has been observed.

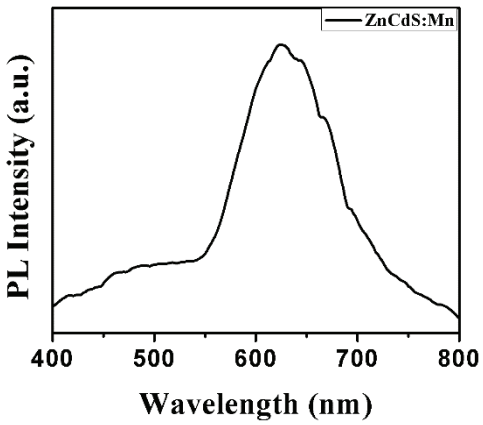

FIGURE 2. PL Spectrum of Mn doped ZnCdS nanoparticles.

When shell is formed around the core, the emission enhances in core shell QDs as demonstrated in figure 3, compared with that of the core QDs. This indicates that forming shell around the core QDs can also improve the photoluminescence quantum yield of core shell structures.

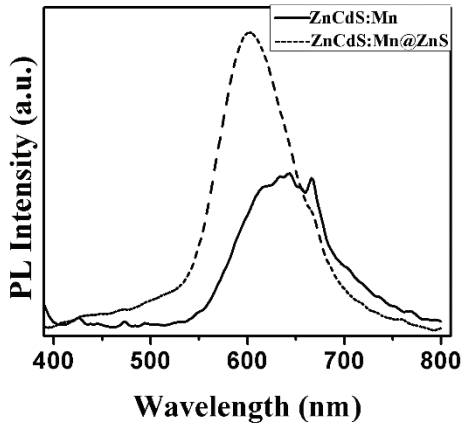

FIGURE 3. PL emission spectrum of ZnCdS: Mn and ZnCdS:Mn/ZnS.

Figure 4 demonstrate the XRD pattern of ZnCdS QDs doped with Mn. XRD results shows cubic structure with broad diffraction peaks of (111), (220), (311). We have calculated the average crystallite size from XRD peak broadening by using Scherrer formula i. e. ($d=0.9\lambda/\beta\cos\theta$), where d is the calculated particle size in angstrom, β is the full width at half maximum (FWHM), λ is the wavelength of the X rays used i.e. 1.54 A°. From this, particle size of 2.9 nm have been obtained. Mn doping has not changed crystal structure of host ZnCdS which is evident from XRD pattern of Mn doped QDs. The texture coefficients are calculated as 0.0934, 0.0976, 0.1486 for (111), (220), (311) planes.

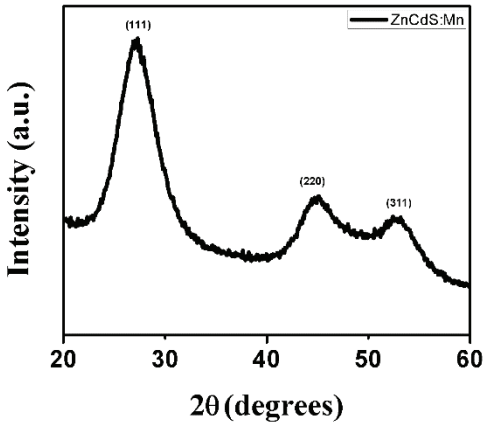

FIGURE 4. XRD pattern of ZnCdS QDs doped with Mn.

CONCLUSION

Water soluble ZnCdS QDs doped with Mn have been synthesized via a simple aqueous route at room temperature. The ZnS shell is formed around the Mn doped ZnCdS core. Mn doped QDs shows stokes shifted orange emission in comparison to blue emission from conventional undoped QDs. The synthesis mechanism have been studied and results have been discussed. Further studies are underway for application of these synthesized QDs as color conversion LEDs.

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