

Synthesis and photoluminescence enhancement of PVA capped Mn^{2+} doped ZnS nanoparticles and observation of tunable dual emission: A new approach



R. Viswanath^a, H.S. Bhojya Naik^{a,*}, G.S. Yashavanth Kumar^a, P.N. Prashanth Kumar^a, K.N. Harish^a, M.C. Prabhakara^b, R. Praveen^c

^a Department of Studies and Research in Industrial Chemistry, School of Chemical Sciences, Kuvempu University, Shankaraghatta, Karnataka, 577451, India

^b Department of P.G. Studies and Research in Industrial Chemistry, Sir. M.V. Government Science College, Bommanakatte, Shimoga, Bhadravathi, Karnataka, 577302, India

^c Department of Technical Education, Automobile Technology Branch HMS Polytechnic (Government Aided), Tumkur, Karnataka, 572102, India

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ABSTRACT

This paper reports the enhanced photoluminescence (PL) property of polyvinyl alcohol (PVA) capped Mn^{2+} doped ZnS nanocrystals prepared by chemical precipitation method. The surface-modified Mn^{2+} doped ZnS nanocrystals resulted in the multi-color property. The morphology and crystallite size were characterized by field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD) techniques. The crystallite size was estimated to be 5 nm from HRTEM and calculated as 2–4 nm from peak broadening of the X-ray diffraction (XRD) pattern with cubic zincblende structure. Increase in the band gap with decrease in the crystallite size was observed from the UV–visible absorption spectrum, which confirms the quantum confinement effect. The room temperature photoluminescence (PL) emission measurements revealed the presence of blue (427 nm) and near IR reddish–orange (752 nm) emission bands in addition to the typical yellow–orange (585 nm) bands in all the Mn^{2+} doped samples, which were attributed due to transition within the 3ds configuration of Mn^{2+} ions incorporation in ZnS host under UV excitation at 320 nm. As far as we know, the reddish–orange bands at 752 nm near IR region along with the blue and yellow–orange colored PL are reported for the first time. In this way, the PL color from these ZnS nanocrystals can be tuned from UV to near infrared region (IR). The synthesized ZnS:Mn NPs can be further functionalized for using them as biolabels.

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1. Introduction

In the recent years, transition-metal-doped nanocrystals have come up as a new class of light-emitting materials that retain all of the advantages of undoped nanocrystals and also overcome some of the intrinsic disadvantages. Luminescent semiconductor nanocrystals, especially II–VI semiconductors, have attracted great interest in the past two decades due to their unique properties and potential applications. The optical properties of the nanocrystal can be tailored by judicious control over the crystallite size and size distribution or by doping with luminescent ions. Over the past two decades, there have been extensive experimental and theoretical studies of optical and electrical properties of zinc semiconductor

nanoparticles in their different forms as an important optoelectronic device material for use in the violet and blue region because of its wide band gap [1,2]. Especially Mn doped ZnS nanoparticles ($ZnS:Mn^{2+}$) are non-toxic systems known for their attractive light emitting properties and were extensively investigated. Mn dopants can introduce new luminescence properties to nanocrystals, resulting in particles with dual emission properties [3]. The doping ions act as recombination centers for the excited electron–hole pairs and result in strong and characteristic luminescence. These luminescent nanocrystals have a narrower emission band, broad excitation band and better photochemical stability in comparison to the traditional organic dyes. These advantages make them ideal candidates as fluorescent labeling agents, especially in biology [4].

After the first publications on the influence of quantum size effects on the luminescence of Mn^{2+} doped in ZnS, many articles from different groups have appeared on the luminescence and the potential applications of these doped nanocrystals [5]. This was due

* Corresponding author. Tel.: +91 8282 256228; fax: +91 8282 256255.
E-mail address: hsb.naik@rediffmail.com (H.S. Bhojya Naik).

to the fact that doped Mn^{2+} ions provide good defect states for the excited electrons.

At high Mn concentrations, ZnS:Mn^{2+} may also be written as $(\text{Zn,Mn})\text{S}$. In general, by varying the Mn concentration until its solubility limit, it is possible to tailor its band gap and other optical properties of compound semiconductor alloys. However, in bulk ZnS:Mn , this has not been possible. This could be possible because the band-gap values of bulk ZnS and MnS, the two constituent binaries of $(\text{Zn, Mn})\text{S}$ are of the same order [6].

Recently, several researchers have focused and reported the red emission along with the blue and orange emission band in case of Mn doped ZnS nanocrystals, which have created an interesting feature in their photoluminescence properties. Karar et al. [6] observed the PL emission peaks in the red region at 640 and 680 nm, which were attributed due to higher-order d–d transitions of Mn^{2+} ion in ZnS due to the relatively higher Mn^{2+} concentrations. More recently, Alessia Le Donne et al. [7] have observed red PL emission peaks at about 635 nm, which were associated, respectively, to Mn^{2+} located at crystallattice nodes, according to Daisuke Adachi et al. [8] the PL spectra of NS ZnS:Mn showed a emission peak at 700 nm, as a Mn–Mn pairs of highly Mn-doped ZnS along with regular orange emission at 588 nm. Yang et al. [9] also have observed the PL emission bands in the green (520 nm) and red region (635 nm). It is still a challenging task to synthesize and understand the origin of these different emission bands.

This article will discuss the synthesis and PL studies of PVA capped ZnS:Mn nanocrystals using chemical precipitation method based on doping concentration of Mn^{2+} ions in ZnS nanocrystals, to achieve deliberate color modulation from blue to red via orange yellow emission under single-wavelength excitation. However, red light emission was rarely reported from ZnS:Mn^{2+} nanocrystals. In this paper, we have reported the strong red light PL emissions with high color purity from ZnS:Mn^{2+} nanoparticles along with the blue, green and orange bands. The emission mechanism was also discussed. To date we are not aware of any reports on the PL emission of Mn doped ZnS at 752 nm near IR region. These types of materials provide another objective of using them as nanoscale fluorescent probes for potential pharmaceutical, biological and medical applications, such as targeted drug delivery and labeling of biological cells in different biomedical applications after functionalizing them with suitable materials, which makes them bioactive [10].

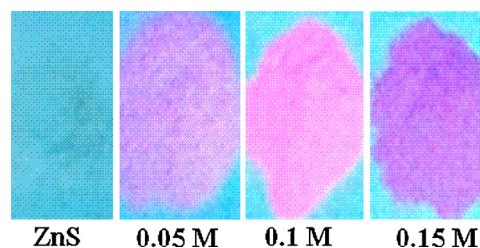
2. Experimental

2.1. Materials

To synthesize ZnS and ZnS:Mn^{2+} nanoparticles, we have used the following materials. Analytical grade zinc acetate $(\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O})$, manganese acetate $(\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O})$, sodium sulfide $(\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O})$ and ethanol were purchased from Aldrich chemical company Ltd and were used without further purification. All glassware used in this experimental work was acid washed. Ultrapure de-ionized water was used as the reaction medium in all the synthesis steps for dilution and sample preparation.

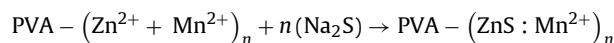
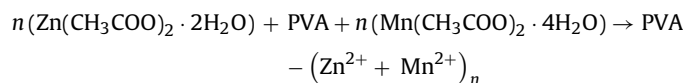
2.2. Synthesis of ZnS:Mn nanocrystals

The Mn doped ZnS nanoparticles (called ZnS:Mn nanoparticles) with different Mn contents were synthesized by the chemical precipitation method according to the following process. In a typical procedure, aqueous stock solutions of 0.1 M of Zinc acetate $(\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O})$ and the surfactant polyvinyl alcohol (PVA) at constant molar ratio i.e. 0.1 M where dissolved in 50 ml double distilled water and stirred vigorously for 15 min, then



Scheme 1. Reaction mechanism and digital images of pure ZnS and ZnS:Mn nanocrystals with different concentration of Mn^{2+} under excitation at 350 nm with a UV lamp.

different concentrations (0.05, 0.1 and 0.15 M) of manganese acetate $(\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O})$ were added to the above solution. Under continuous stirring 0.05 M of 50 ml Na_2S solution was slowly dropped into the above solution. During the whole reaction process 80°C was maintained and finally the reaction mixture was stirred at this temperature for 1 h and then after continuously stirring for 1 h a white precipitate was deposited at the bottom of the flask, which was cooled to room temperature. The obtained precipitate was washed systematically five times in double distilled water and ethanol, which was then separated by centrifugation to remove the remaining sodium particles, if any. Finally, the wet precipitate was dried at 80°C under vacuum for 2 h for further measurements. The reaction takes place as followed:



Scheme 1 shows the reaction mechanism and digital photographs of the ZnS:Mn nanoparticles along with pure ZnS nanoparticles under 350 nm UV light. Samples shows light pink to dark pink and then light blue color as doping concentration of Mn^{2+} increases. This establishes that Mn^{2+} is responsible for color emission in ZnS:Mn nanoparticles.

2.3. Characterization

The crystal structure was studied by the X-ray diffraction method (XRD) on Phillips X'PERT XRD powder diffractometer (Phillips, PW-1800) using a radiation $\text{Cu-K}\alpha$ with 1.54 \AA wavelength (40 mA, 45 kV), with 2θ range from 20° to 70° . These nanoparticles were washed thrice with ultrapure water and air-dried into carbon-coated copper grids for characterization by transmission electron microscopy (TEM) on a JEOL JEM-2010 transmission electron microscope operated at 200 kV. Further FESEM analysis was carried out to study the surface morphology on field emission scanning electron microscopy (FESEM-Carl Zeiss, Supra 40VP). A few drops of the sample solution were pipetted out onto MCE filter paper (5 mm), which were air-dried. Portions of the stained MCE filter paper were then cut out and mounted on SEM sample stubs with double sided tape. The optical absorbance measurements of these samples were taken by UV–visible spectrophotometer (Shimadzu-Pharmaspec-1600) after ultrasonification in ethanol. The photoluminescence spectrum of the prepared samples was recorded using a spectrofluorimeter (F-2500 FL Spectrophotometer, Hitachi). Spectra were recorded using monochromator slit widths of 5.0 nm on both excitation and emission side. All the observations were taken at room temperature.

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