Synthesis of biotin caped Mn\textsuperscript{2+} activated ZnS quantum dots with their structural stability and modulation of opto-electronic properties

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Abstract. Mn\textsuperscript{2+} activated ZnS (ZnS:Mn\textsuperscript{2+}) nanoparticles biotin matrix have been synthesized by chemical co-precipitation route. X-ray diffraction (XRD) results confirmed single phase zinc blend structure with crystallite sizes ranging from 1.5 to 1.9 nm. The small particle sizes are believed to have single domain crystallites because of quantum confinement of particles in the biotin matrix. Scanning electron microscopy (SEM) analysis shows smooth and polygon shape potato like morphology having cluster size varying from 77\textmu m to 182\textmu m. Optical measurement shows the band gap of 3.85 eV which has been blue shifted and is accredit to the quantum size effect. The particle size estimated for this gap is to be 2.03 nm and is good agreement with sizes obtained from XRD. The luminescence feature of the as synthesized sample was also reported. The photoluminescence (PL) spectra shows two wide peaks centred at 408 nm and 520 nm respectively. The first emission at 408 nm with short time is attributed to the defects of ZnS while another peak at 520 nm attributed in green emission due to the elemental sulphur species on the surface of zinc sulphide. The both emissions are blue shifted and are attributed to the small particle sizes. The well known manganese related orange-red emission peak centered at 590 nm has not been observed and is completely quenched that confirmed that the Mn\textsuperscript{2+} ions have been allocated outside the ZnS crystals. A new emission at 338 nm appears to have radiative transitions from the defect level to the acceptor levels. Thus, by using suitable activator and capping molecule, we are able to stabilize the growth of nanoparticles at room temperature, thereby enhance the structural and opto-electronic properties.

Keywords: Quantum dots, biotin, luminescence, ZnS:Mn\textsuperscript{2+}

1. Introduction

During the past few years, researcher has made its attention to the preparation and characterization of semiconductor materials in the nanometres size scale which are a new kind of condensed matter in reduced dimensions that could provide materials with novel characteristics. For example, size dependent band gap tuning in semiconductor nanoparticles [1], melting temperature [2], phase transition temperature in solid to solid [3] and pressure [4]. Besides to their fundamental interest, these novel nanoscale materials like CdS: Mn\textsuperscript{2+} [5], ZnS:Mn\textsuperscript{2+}/Eu\textsuperscript{2+} [6] and Y\textsubscript{2}O\textsubscript{3}: Eu\textsuperscript{3+}/Tb\textsuperscript{3+} [7], ZnO [8-9] and ZnMgS: Mn\textsuperscript{2+} [10] are expected to have remarkable inherent applications in fields like solid-state lighting technology, opto-electronics device, photo catalyst fabrication and drug delivery system [11-14]. These materials are important because they show exceptional physical and chemical properties from their bulk counter parts. Furthermore, their high surface area provides unique platforms for binding...
different kinds of ligand which could be used for sensing and other applications. Modification of nanoparticles surfaces by inorganic or organic materials has been studied by several groups [15-16].

The controlled growth of nanoparticles with desired sizes and properties in an organic matrix for various applications has been attracted in recent years [17-20]. In this method, the synthesized nanoparticles are stabilized against environmental attacks and avoiding coarsening due to its surface passivation. This group of recent materials have not only exhibited novel optical and luminescence properties but also demonstrate exclusive opportunities for the study of physics in small dimensions which are inherently useful for scientific applications. In doped (ZnS: Mn\(^{2+}/\) Eu\(^{2+}\)) semiconductor nanocrystals, the impurity (Mn/Eu) levels has rendered a particular role in modifying the electronic configuration and transitional probabilities of the nanocrystals as compared with the undoped (ZnS) nanocrystals. Such a system is referred to have the quantum confined atom which exhibits numerous captivating phenomenon’s like radiative life-time reduction, electroluminescence, photo-blinking effects and effective short-voltage cathodoluminescence leading to several tremendous inherent applications in field described above [6].

ZnS is wide band gap semiconducting material having large band gap of 3.68 eV [21] and Bohr excitons radius of 2.5 nm which driven many researchers to synthesized doped and undoped quantum dots in the past, [22] and such synthesis with narrow size distribution is relevant today. ZnS nanoparticles doped with manganese are most studied doped nanoparticles systems even though the formation of ZnS:Mn\(^{2+}\) is a facile process, making them in high quality is a challenging task. There have been numerous reports in former years which demonstrate the systematized exploration of changes in properties and consequent uses and usages of doped ZnS nanoparticles by growing in the emulsifier system to manage the particle size. Wei Chen et al. [23-24] for instance, examined the size dependent luminescence features of ZnS:Mn\(^{2+}/\)Eu\(^{2+}\) nanoparticles.

Furthermore, some polymers capping could participate in the energy transfer from absorbing groups to near-surface Mn\(^{2+}\) ions of ZnS:Mn\(^{2+}\) so that those groups and ZnS can be excited simultaneously. This energy transfer process contributes to the enhancement of the photoluminescence of ZnS: Mn\(^{2+}\) nanoparticles. Besides the passivating action of polymer on the surface of nanoparticles, they could undergo polymerization upon irradiation with UV light or thermal treatment which results in better passivation on the surface of the nanoparticles. Also some authors have proposed that photo oxidation at surface of ZnS nanocrystals in the existence of water and oxygen results in the evolution of ZnSO\(_4\) and Zn (OH)\(_2\), which could contribute as passivating barriers on ZnS nanoparticles surface. The response of capping agent on nanoparticles size is being investigated further.

The objective of the present study is to synthesized the biotin caped ZnS: Mn\(^{2+}\) nanoparticles by chemical co-precipitation route and make use of the inherent advantages of surface passivating agent biotin in governing/regulating the particle sizes and band gap of the nanoparticles and thus their opto-electronic properties for device fabrication. Definite regulation of particle density for regular size distribution (monodispersity) of nanoparticles is also attempted which is necessary for better device performance. Impression of clinching/capping on optical, luminescence properties, and affinity with the nanoparticles was also studied.

2. Materials and Method

In biotin matrix, ZnS:Mn\(^{2+}\) nanoparticles were synthesized using well known co-precipitation method which is a conventional method of producing nanoparticles from colloidal solution. We have chosen this method because of its various supremacy including simple processing at ambient situations, different kinds of impurities doping at room temperature with large doping concentration, better management over the system of doping, ease of surface capping with a multiplicity of different steps used in the formation of nanoparticles.

Materials used are zinc acetate dehydrate \([\text{Zn(CH}_3\text{COO)}_2.2\text{H}_2\text{O}\] (cationic solution), manganese acetate tetrahydrate \([\text{Mn(CH}_3\text{COO)}_2.4\text{H}_2\text{O}\], sodium sulphide-\(\text{Na}_2\text{S}\) (anionic solution), biotin (capping
agent), double distilled water and ethanol. The chemicals procured of analytical reagent grade and used without any further purification. All glassware’s utilized in this experiment were washed with acetone and dried in oven at 80°C. For all dilutions purpose and sample preparations, double distilled water was used. In this method, 0.5M zinc acetate was mixed to 60 ml double distilled water with the addition of 20 ml of manganese acetate (5% M) solution in this. After that 20 ml of 0.5M sodium sulphide along with capping agent biotin was added drop wise in the mixture and kept for 2 hrs vigorous stirring. A white colour precipitate was attained which was filtered by using whatman filter paper. The obtained precipitate was washed with ethanol and water for several times. Then precipitate was dried in drying oven at 110°C to achieve the white powder samples as shown in figure 1. The synthesis of biotin caped ZnS:Mn$^{2+}$ occurred as follows:

\[
n(Zn(CH_3COO)_{2}.2H_2O + Biotin + n(Mn(CH_3COO)_{2}.4H_2O) \rightarrow \text{Biotin} - (Zn^{2+} + Mn^{2+})_n
\]

\[
\text{Biotin} - (Zn^{2+} + Mn^{2+})_n + n(Na_2S) \rightarrow \text{Biotin} - (ZnS:Mn^{2+})_n
\]

**Figure 1:** Synthesized biotin caped ZnS:Mn$^{2+}$ nanopowder.

The as synthesized sample was further characterized by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), PL spectroscopy and UV-Visible spectroscopy.

3. Results and discussion

XRD spectra of the nano-structured biotin capped ZnS:Mn$^{2+}$ system were recorded using RIGAKU ULTIMA IV X-Ray Diffractometer operated at 40 kV/20 mA using CuK$_{α1}$ radiation with wavelength of 1.54 Å in a wide-angle region from 10° to 80° on 2 theta scale and is shown in figure 2 which confirmed single-phase zinc blend (cubic) structure with space group of F43m. No evidence for phase formation of MnS was recorded. The XRD pattern shows wide peaks at positions of 28.980, 48.240, and 57.00 corresponding to (111), (220), and (311) reflections respectively and in agreement with standard pattern (JCPDS file # 800020) and with data available in literature also [25]. The present phase recorded reflections have been made fit to Gaussian distribution. The XRD line broadening (also called as Scherrer’s broadening), is accredit to the nano-crystalline feature of the samples, which can further be used for calculating the crystallite size ‘d’ of the nanoparticles using Debye-Scherrer’s formula $d = \frac{0.9\lambda}{\beta\cos\theta}$, where $\lambda$ is termed as wavelength of X-rays, $\beta$ is known as full width at the half maximum i.e. (FWHM) in the XRD pattern of ZnS:Mn$^{2+}$ for a particular crystal plane and $\theta$ is the Bragg angle. Average crystallite size calculated is of the order of 1.7 nm. The small particle sizes are believed to have single domain crystallites because of quantum confinement effect in the particles under the biotin matrix.
Figure 2: X-ray diffraction spectrum for biotin capped ZnS:Mn$^{2+}$ nanoparticles.

The investigation of particle morphology of the prepared materials has been proceeded by Scanning electron microscopy. The SEM micrographs has been recorded from Hitachi TM3000 electron microscope operating at 5000V with magnification 500X and are presented in figure 3. The micrograph analysis shows smooth and polygon shape potatoes like morphology having cluster size varying from 77$\mu$m to 182$\mu$m.

Figure 3: Scanning electron micrographs of ZnS:Mn$^{2+}$ at different magnifications showing potatoes like morphology.

Ultraviolet-Visible spectroscopy is an important technique for the invigilation of changes in the optical properties due to quantum size effect. The UV-visible absorption spectra of biotin passivated ZnS:Mn$^{2+}$ nanoparticles were recorded using DR 6000 UV-visible spectrophotometer from wavelength range 200 to 800 nm to measure the band gap of the ZnS:Mn$^{2+}$ nanocrystals. The absorption spectrum is shown in figure 4(a). The absorption peak observed at 328 nm is blue shifted in comparison of bulk band gap of 3.7 eV [26]. The quantum size effect induces blue-shift in the excitonic absorption and has
resulted due to consequent variation of band gap of nanoparticles while defects like distortions in lattice and vacancies, which may be presented near the surface in small particles induces broadening.

The band gap of the prepared materials are estimated from tauc’s plots by fitting the absorption data to the equation \((\alpha h\nu) = A(h\nu - E_g)^m\) where \(\alpha = \frac{4\pi k}{\lambda}\), \(k\) is the absorbance or absorption index and \(\lambda\) is wavelength in nm) is the absorption coefficient, \(h\nu\) is the photon energy and \(E_g\) is the band gap., where \(m=1/2\) for allowed direct transition. The Tauc plot for biotin caped ZnS: Mn\(^{2+}\) system is shown figure 4(b).

The relationship \(\alpha = \frac{2.303 A}{t}\), where ‘A’ is the absorbance and ‘t’ is the thickness through which the radiation is being transmitted. Since all the other quantities are constant so we can directly plot the Tauc plot by taking the coefficient of absorption directly proportional to the absorbance. The band gap thus obtained from the Tauc plot has been found to be 3.85 eV. By the following Brus equation, a quite well first-order approximation of energy band gap in electron volts as a function of particle radius \(r\), in nanometres for nanocrystalline ZnS can be estimated [27]

\[
r(E_g) = \frac{0.32 - 2.91 \sqrt{E_g - 3.49}}{2(3.50 - E_g)}
\]

The particle size for biotin caped ZnS:Mn\(^{2+}\) nanoparticles from the absorption spectrum using above equation is calculated to be 2.03 nm corresponding to band gap of 3.85 eV obtained from absorption spectra. The size obtained from the absorption spectra is in excellent agreement with the size attained from XRD.

\[\text{Figure 4: (a) Absorption spectra of biotin caped ZnS: Mn}^{2+}\text{ (b) Related Tauc plot for estimation of the band gap.}\]

The PL Spectra of biotin caped ZnS:Mn\(^{2+}\) nanoparticles were recorded by using Edinburgh instruments FLS920 with the excitation wavelength of 325 nm and is shown in figure 5. The spectra shows three broad peaks centred at 338 nm, 408 nm and 520 nm respectively. A new peak at 338 nm occur to have radiative transitions from the defect level to the acceptor levels and the emission at 430 nm of ZnS is blue shifted to 408 nm which has accredited to the quantum size effect. The second peak at ~ 408 nm has been entitled “self-activated”. According to K. Sooklal et al., [28] this emission results due to vacancies of sulphur in the lattice which results in the production of ionized donor sites in locality at room temperature and increases the population of conduction band. So, the emission results due to band-gap or from near the band gap recombination. However the emission is more likely to be due to shallow traps as recombination centres for photogenerated charge carriers in the case of ZnS nanoparticles. The well-known luminescence related to ZnS due to vacancies of Zn (at ~ 480 nm) is not detected in these nanocrystals, which indicates that the related emission is totally quenched due to transfer of energy to the Mn\(^{2+}\) ions. Due to relatively long life time of the ~ 480 nm luminescence,
radiative decay cannot complete with transferring the energy to the Mn$^{2+}$ ions [29]. On the other hand, the short life time of the ~ 408 nm luminescence allow it to complete with this transfer of energy and is quietly observable, a little bit fragile than in undoped ZnS.

Figure 5: Photoluminescence spectrum of biotin caped ZnS:Mn$^{2+}$ nanoparticles.

Another peak at 520 nm attributed to the green emission of the visible spectrum due to the elemental sulphur species on the surface of zinc sulphide. The well known efficient radiative transition $^4T_1 \rightarrow ^6A_1$ related to orange-red luminescence at 590 nm corresponding to Mn$^{2+}$ is not observed and is completely quenched that confirms the distribution of Mn$^{2+}$ ions outside the ZnS crystals, which in turns induces the defects related emission at 338 nm and 520 nm. Further the field near the surface of ZnS:Mn$^{2+}$ nanoparticles modified by the capping molecules that depends on the defects density on the nanoparticles surface. The biotin coating minimize the density of unsaturated bonds and passivate the surface by reducing the quantity of surface trap sites for the occurrence of non-radiative recombination processes, which in turn increases the luminescence intensity.

4. Conclusion

In conclusion, Mn$^{2+}$ activated ZnS nanoparticles passivized with bio-molecule “biotin” have been successfully synthesized. From results, it has been concluded that capping is inescapable and the potential of biotin as a capping agent results in the better structural stability and opto-electronic properties of ZnS:Mn$^{2+}$ nanoparticles. By using biotin, the size has been retained; distribution against growth and agglomeration has been done and also provides protection from any environmental invasion. We have successfully retained the size of the particles minimum to 1.5 nm in the biotin matrix which is consistent with the size obtained from absorption measurement. SEM results show beautiful polygon shape potato like morphology having cluster size varying from 77µm to 182µm. It has been further observed that biotin is a powerful passivation agent for the unsaturated bonds presents on the surface of particle which leads to not only efficient luminescence efficiency but also results in the stabilization of luminosity of the Mn$^{2+}$ doped ZnS nanoparticles. Thus capping and doping successfully alter the defects related emissions. Thus, by using suitable activator and capping molecule, we are able to sustain the production of nanoparticles at room temperature, thereby enhance the structural and opto-electronic properties.
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6. References

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