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Effect of manganese (Mn) doping on the optical properties of zinc sulfide (ZnS) semiconductor nanocrystals

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In this research, we report the synthesis of ZnS nanocrystals with a size range of 1-10 nm in diameter with varying manganese (Mn) concentrations. Various samples of Zn_{1-x} Mn_xS, with x = 0.0001, 0.007, 0.02, 0.03, 0.055, 0.09 and 0.13, have been prepared from a quaternary W/O microemulsion system. It is observed that by adding Mn to ZnS nanoparticles, the emission intensity changed and by using 5.5% magnesium for total Zn⁺², a maximum emission were achieved. A photoluminescence (PL) study was carried out by band-to-band excitation ($\lambda_{ex} = 293$ nm and 321 nm) upon ZnS : Mn, which results in two emission peaks corresponding to surface states and Mn⁺² emission. Also, we observe orange emission from Mn²⁺ ions in the doped ZnS nanocrystals, apart from the blue emission characteristic of the ZnS defect states. The relative intensity of the orange emission compared with the blue varies with the manganese concentration in a nonmonotonic way. For analyses of the quality and quantity of this product, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDS), inductive coupled plasma (ICP), and spectrograph techniques were used.

Key words: Nanocrystal, Zinc sulfide, Manganese, Microemulsion.

Introduction

In recent years significant research effort has been devoted to developing inorganic nanocrystalline particles because of their potential application in biology, electronics, optics, transport and information technology. Although several approaches have investigated ways of making these nanocrystalline particles, controlling the size, shape and crystallinity and various parameters affecting the size and shape of these materials still need to be found [1].

Over the last few years, a considerable interest in the novel optical and electrical properties of doped semiconductor nanocrystals has emerged [1-3]. These structures are interesting from a physical and chemical point-of-view mainly because several of their properties are very different from those of bulk materials [1]. In particular, the significant sizedependent change in the band gap has attracted much attention.

ZnS, a typical II-VI semiconductor, has been commercially used as a phosphor as well as in thin film electroluminescent devices, especially if doped with divalent manganese ions [4]. A few studies have been carried out on the doped nanoparticles which mainly include Mn-doped ZnS [5-11]. This allows us to study the evolution of various physical properties of such doped nanoclusters as a function of only the dopant concentration; this is all the more important in view of the fact that any variation in the size of the host nanoclusters is known to strongly affect the observed physical properties. Most of these samples have been either prepared by aqueous colloidal methods [5, 7, 8] or by reacting metalorganic complexes with hydrogen sulfide in a suitable solvent and then passivating the surface with a surfactant such as methacrylic acid [6]. We have synthesized Mn-doped ZnS with varying Mn concentrations in ZnS nanoclusters with a fixed size using a microemultion system [12].

We have employed a wide array of techniques such as fluorescence emission and excitation. In the case of Mndoped ZnS, excitons, formed by the photo-excitation of electrons across the bandgap of the host nanoclusters, deexcite predominantly via the defect states in the host, giving rise to a blue emission or through the Mn *d* states leading to an orange fluorescence. Present results show that the orange/ blue emission ratio changes with the Mn concentration.

In the literature various mechanisms have been proposed to explain the luminescence of ZnS : Mn^{2+} . In the literature on nanocrystalline ZnS : Mn^{2+} it is often suggested that first an electron is captured by Mn^{2+} . However, in the literature on the luminescence of bulk ZnS : Mn^{2+} careful high-resolution measurements have been reported which indicate that the Mn^{2+} center is attractive for holes [13, 14]. In view of the known oxidation states of manganese (2+, 3+, 4+ and 7+ are well known, whereas 1+ is not stable) it seems indeed more likely that Mn^{2+} is hole attractive. Based on the measurements several possible excitation mechanisms for Mn were suggested. In one mechanism the Mn^{2+} ion first traps a hole and the subsequent recombination with an electron results in Mn^{2+} in an excited state.

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Alternatively, an exciton may be bound to Mn^{2+} and recombination of the bound exciton promotes the Mn^{2+} to the excited state. Both mechanisms may be active in bulk and nanocrystalline ZnS : Mn.

To date there are many methodologies available for synthesizing ZnS nanocrystals (QDs), such as laser ablation, chemical, electrochemical fabrication, solvo-thermal and solgel methods [12, 15-20]. However, water-in-oil (w/o) microemulsions or the reverse micelles technique is one of the most recognized methods due to its several advantages, for instance, soft chemistry, demanding no extreme pressure or temperature control, ease of handling, and requiring no special or expensive equipment. In general, micro-emulsion or ME is an isotropic, thermodynamically stable dispersion of oil, water, surfactant and often co-surfactant, which is normally alcohol. A micro-emulsion can be characterized as oil-in-water (O/W), water-in-oil (W/O) or a bi-continuous system. Oil-in-water is a micro-emulsion containing an excess oil phase with surfactant molecules existing in the aqueous phase in the form of normal micelles. On the other hand, a water-in-oil (W/O) micro-emulsion is the coexistence of an excess water phase and the surfactant molecules which aggregate in the oil phase in the form of a reverse micelle. It is well known that these micelles could act as nano-scaled reactors [12]. QD conjugation to biotinylated antibodies subsequently is readily achieved. Fluoroimmunoassays utilizing these antibody conjugated QDs were successful in the detection of protein toxins (staphylococcal enterotoxin B, cholera toxin) [21].

In this paper, we mainly focused on preparing and investigating Mn-doped ZnS with varying Mn concentrations in ZnS nanocrystals using a reverse micellar microemulssion method. ZnS : Mn biotinylated was used with avidin bioconjugated antibodies. This handed over in such an easy manner permits their use as a common diagnosis reagent. But it was found that biological components were coupled with nanocrystals which can reduce the final emission of nanocrystals during diagnostic recognition. To this end, we should find a suitable dopant concentration such that the resultant emission is higher enough. Finally, their photo luminance characteristics were studied.

Materials and methods

Powder synthesis

All reagents were used as received without any further purification from the Merck Company.

First, the solution of cyclohexane (using less than half of the existing water in this system), Triton X-100 and n-hexanol (whose amounts are the same and equal to four times the ZnS : Mn which was finally produced) were prepared and mixed in two accurate beakers. Then aqueous solutions of ZnSO₄.7H₂O and Mn(NO₃) with different concentrations (Table 1) were added into the first beaker and Na₂S was added into the micro-emulsion solution in another beaker. Finally, the emulsions were vigorously agitated by a magnetic stirrer.

After mechanical agitation for about 15-120 minutes, the two separate micro-emulsion solutions were mixed together and agitated for about 15 minutes. The resulting mixture was then kept for 2 days at room temperature. Thus, we used a reverse micelles technique. In this method, water drops that surrounded the nanocrystals were imprisoned in the bulk of the oil and these micelles could act as nano-scaled reactors.

Powder characterization X-ray diffraction

The resulting samples were analyzed by X-ray diffraction (XRD) with a Rigaku-Dmax 2500 diffractometer. This instrument was used with voltage and current settings of 40 kV and 200 mA, respectively and used Cu-K α radiation (1.5405 Å). For qualitative analysis, XRD diagrams were recorded in the interval $20^{\circ} \le 2\theta \le 60^{\circ}$ at a scan speed of 2° /min.

Scanning electron microscope

The powders were coated with a thin layer of gold (Au) by sputtering (EMITECH K450X, England) and then the microstructure of the powders were observed on a scanning electron microscope (Sterio Scan S360 Cambridge) that operated at the acceleration voltage of 15 kV.

Transmission electron microscope

The morphology of powders was characterized by transmission electron microscopy (Hitachi H-800 electron microscope). Carbon-coated 200 mesh copper grids were dipped in a dilute suspension of the powders. The particles were deposited onto the support grids by from a dilute suspension in acetone or ethanol.

Energy dispersive X-ray spectroscopy

The chemical composition of the samples were studied by the X-ray microanalysis, using energy dispersive spectroscopy (EDS) on a LED 14550.

Table 1. The amounts of reactants added to prepare nanoclusters with different manganese concentrations

Chemicals	Amounts added in mmol for % Mn						
	0.01 %	0.7 %	2 %	3 %	5.5 %	9 %	13 %
ZnSO ₄ .7H ₂ O	4×10^{-2}	4×10^{-2}	4×10^{-2}	4×10^{-2}	4×10^{-2}	4×10^{-2}	4×10^{-2}
Mn(NO ₃)	4×10^{-6}	2.8×10^{-4}	8×10^{-4}	1.2×10^{-3}	2.2×10^{-3}	3.6×10^{-3}	5.2×10^{-3}
Na_2S	3.92×10^{-2}	3.92×10^{-2}	3.92×10^{-2}	3.92×10^{-2}	3.92×10^{-2}	3.92×10^{-2}	3.92×10^{-2}

Inductive coupled plasma

A Perkin-Elmer Optima-3000 was used to determine the chemical composition of the sample by inductively coupled plasma analysis (ICP).

Photoluminescence spectroscopy

For photoluminescence spectral studies, the sample was excited by 200-400 nm ultraviolet light. The emitted light was studied using a CDS spectrograph to which IP 21 photomultiplier tubes was coupled (PerkinElmer Model LS5) which was capable of measuring the intensity of the emitted light in the range of 250-600 nm. The luminescence intensity was measured over the wavelength range 250-700 nm.

Results and Discussion

Fig. 1 shows the XRD patterns of the as-prepared ZnS (a) and ZnS : Mn^{2+} (b).

Vertical bars indicate standard cubic bulk ZnS peak position from JCPDS No. 77-2100. It is obvious that all of the XRD peaks of the nanocrystals can be indexed as the cubic zinc blende structure, which is consistent with the values in the standard card. It can be seen that the XRD peaks are broadened with three main peaks corresponding to the (111), (220), and (311) planes. It is noticeable that for lower Mn contents, all the peaks in this figure can be indexed to the known zinc blende structure of ZnS, revealing that the doping of Mn does not change the zinc blende structure of ZnS, and that the manganese has doped into the crystal structure. Because no diffraction peaks corresponding to Mn precipitates or Mn-related impurity phase were observed, this further confirms the formation of a ZnS : Mn solid solution instead of Mn precipitation or a second phase. However, Yuan et al. [20] demonstrated that a higher doping content of Mn in ZnS results in the segregation of Mn atoms out of the ZnS matrix.

In addition, the broadening of the diffraction peaks of all the ZnS : Mn^{+2} samples were obvious, which is a charac-



Fig. 1. XRD patterns of ZnS and ZnS : Mn nanocrystals.

teristic of nanocrystals. The mean crystallite sizes D was determined according to the Scherrer equation $(D = k\lambda/\beta)$ $\cos \theta$, where k is a constant (shape factor, about 0.9), λ is the X-ray wavelength (1.5405 Å as mentioned before), β is the full width at half maximum (FWHM) of the diffraction line, and θ is the diffraction angle). Based on the full width at half-maximum of the reflection from the (111) plane in the zinc-blend structure, the mean crystallite size of ZnS : Mn⁺² was estimated as 3.2 nm. It is worth mentioning that the calculated lattice constant of pure ZnS nanocrystals, a = 0.5414 nm, is the same as the value from the standard card a = 0.5415). However, as for ZnS : Mn²⁺ nanocrystals, we observe a slight increase in the lattice constant, that is, a = 0.5420. This is probably caused by the substitution of Zn^{2+} by Mn^{2+} since the ionic diameter of Mn^{2+} (0.83 nm) is larger than that of Zn^{2+} (0.74 nm) [21].

As observed in the experiments, nanocrystals were made within the first few minutes, but after a few minutes, these particles aggregated and their size became larger, because of their large surface-to-volume ratio (due to the increase in the large ratio of surface area to volume, the attractive force between the nanoparticles will increase, and agglomeration of nanoparticles will take place, as seen in Fig. 2, so, the size of the particles became larger).

To avoid these problems, we used a reverse micelles technique. In this method, water drops that surrounded the nanocrystals were enclosed in the oil bulk phase and these micelles could act as nano-scaled reactors.

SEM allows imaging of individual crystallites and the development of a statistical description of the size and shape of the particles in a sample. SEM micrographs of the ZnS dry powder showed that the particle size was less than 100 nm in diameter (Fig. 2).

TEM high magnification imaging allows the determination of the individual crystallite morphology. TEM micrographs of the ZnS : Mn powder showed that the diameter of zinc sulfide particles is less than 5 nm (Fig. 3(a) and (b)) which is consistent with the particle size determined using XRD analysis.

In order to identify the constituents of these synthesized products, typical EDS analysis was conducted to demonstrate that these products are ZnS : Mn nanocrystals (Fig. 4). The X-ray fluorescence peaks at 1.0 and 2.3 keV exhibit a combination of Zn and S. Meanwhile, the smaller peaks at 8.6 and 9.6 keV correspond to the transition of Zn k α and k β , respectively.

Comparison of these results with the study by Charinpanitkul *et al.* [10], it is observed that peak boundaries were the same as that reported in [10]. However, in our study the peak height was less than that in [10]. In addition, our powder has another peak that showed a small amount of Mn in the ZnS nanocrystals. Thus, this peak can be related to the replacement of some Zn^{+2} by Mn^{+2} in ZnS : Mn.

The actual doping concentration of Mn^{2+} ions should be determined because the actual concentration is different from the initial concentration. Using the ICP analysis, Effect of manganese (Mn) doping on the optical properties of zinc sulfide (ZnS) semiconductor nanocrystals



Fig. 2. SEM micrograph of ZnS : Mn nanocrystals at (a) low magnification and (b) high magnification.



Fig. 3. TEM micrograph of ZnS : Mn nanocrystals at (a) low magnification and (b) high magnification.



Fig. 4. EDS diagram from synthesized nanocrystals.

the actual concentrations of Mn^{2+} ion doped into the ZnS : Mn samples was determined (see Table 2).

In fact, Mn^{2+} ion in a ZnS nanocrystals has two choices of its nearest cations: (i) Zn^{2+} and (ii) Mn^{2+} . Since the actual Mn^{2+} concentration is low in the sample, it is found that these Mn^{2+} ions may be isolated by Zn^{2+} ions and no Mn^{2+} pairs are formed [22]. It is notable that the results obtained which were reported by ICP examination confirm the EDS results with a low concentration of Mn^{2+} ions in the sample.

When Mn^{2+} ions are incorporated into the ZnS lattice and substituted for host cation sites, the mixing between the s-p electrons of the host ZnS and the d electrons of Mn^{2+} occurs and makes the forbidden transition of ${}^{4}T_{1} \rightarrow {}^{6}A_{1}$ to be partially allowed, resulting in the characteristic emission of Mn^{2+} [23]. Sooklal *et al.* studied the effect of the

Material	Percent (%)
Na	8.42
S	16.15
Zn	20.80
Mn	0.235

Table 2. ICP analysis of the synthesized powder

location of Mn^{2+} on the photophysics of ZnS nanocrystals [6]. They found that Mn^{2+} incorporated into the ZnS lattice leads to the Mn^{2+} -based orange emission while ZnS with surface-bound Mn^{2+} yields ultraviolet emission. Thus, it can be concluded that the Mn^{2+} ions in our samples are indeed incorporated into the host ZnS nanocrystals.

It is worth mentioning that concentration quenching has been mainly attributed to the migration of the excitation energy between Mn^{2+} ion pairs in the case of Mn^{2+} doping. Thus, the existence of Mn^{2+} pairs is important for the occurrence of the concentration quenching effect. During the concentration quenching process, the excitation energy is transferred from one Mn^{2+} ion to its nearest Mn^{2+} ion by nonradiative transitions and via a number of transfer steps, finally to a quenching site (e.g. defect state).

A room-temperature excitation spectrum of ZnS : Mn nanocrystals is shown in Fig. 5 and an emission spectrum in Fig. 6.



Fig. 5. Excitation spectrum of ZnS : Mn nanocrystals ($\lambda_{ex} = 294$ and 321 nm).



Fig. 6. Emission spectrum of ZnS : Mn nanocrystals ($\lambda_{em} = 296$ and 602 nm).

The emission spectrum showed a small broad peak at 602 nm which appeared at a slightly greater wavelength as compared with the other group. Photoluminescence in this region is due to the presence of sulfur vacancies in the lattice, as previously found for ZnS colloids. The peak at 602 nm is not shifted even at higher Mn percentages. The luminescent intensities (shown in Fig. 7) gradually increased with an increase of Mn up to 5.5 percent and decreased beyond 5.5 percent in the microemulsion solution.

It is also observed from Fig. 8 that the highest-energy peak of the PL spectra has the highest luminescent intensity, suggesting that the smallest particles are contributing most of the Mn^{+2} emissions.

Conclusions

ZnS : Mn nanocrystals with a distinguishable morphology were synthesized in quaternary w/o micro-emulsion systems. According to the above mentioned experimental results, it could be clearly shown that the size and the morphology of the ZnS : Mn nanocrystals are dependent upon the oil-to-water ratio.

We found that it is better if Zn^{+2} and S^{-2} are prepared individually and mixed efficiently. By using this condition ions have a good chance to connect with each other.

Also it is better if one of the amount of reactants is a



Fig. 7. The fluorescence (PL) spectra for different Mn concentrations (Ml = Microliter).



Fig. 8. Emission intensity for different Mn concentrations in ZnS.

little more than the other one.

The fluorescence (PL) spectra for different Mn concentrations show that by altering the concentration of Mn^{+2} ions, there is a maximum emission at the optimum doping (~5.5% of Mn). The fluorescence spectra of the doped crystals consist of orange-red emissions.

The photoluminescence results indicate that Mn^{+2} ions replace Zn^{+2} at the tetrahedral sites and at sites with axial symmetry with a well defined hyperfine structure at low Mn concentrations. The Mn-Mn dipolar interaction increases upon increasing the Mn^{+2} ion concentration, wiping out the hyperfine structure at higher Mn concentration.

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