



## Excitation energy dependence of the life time of orange emission from Mn-doped ZnS nanocrystals

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### ABSTRACT

Mn-doped ZnS nanocrystals were prepared by co-precipitation method. X-ray diffraction analysis indicates pure cubic zinc blende structure. We report for the first time experimental observation of the dependence of the decay time of Mn<sup>2+</sup> emission from Mn-doped ZnS nanocrystals on excitation energy. Photon energy smaller than the ZnS bandgap induces faster decay time compared to the one equal to the bandgap energy. In addition, while the decay spectra of orange emission indicate both sub  $\mu$ s and ms, the time-resolved luminescence measurement suggests that the sub  $\mu$ s component belongs to the tail of the blue emission.

### 1. Introduction

Semiconductor nanocrystals exhibit peculiar properties, which are totally different from their bulk counterparts [1–3]. The size-dependent characteristics make nanocrystalline semiconductors promising materials for optoelectronic applications [4,5]. Despite of the fact that doped semiconductor nanocrystals were studied early in 1980's [6], they actually did not attract attention until the publication by Bhargava et al. [7] in 1994. This paper reported on Mn<sup>2+</sup> doped ZnS nanocrystals with remarkable luminescent efficiency of 18% and short lifetime of the order of nanoseconds. As proposed in this work, the d – electrons of Mn<sup>2+</sup> acts as a luminescent center, and the strong interaction between these d – electrons and s-p states of the host matrix provides a highly effective energy transfer path that results in the shortening of the lifetime and an increase in the emission efficiency. This publication has inspired many other papers that studied various doped nanocrystals with different dopants [8–19]. The incorporation of rare earth (Tb, Eu, Er) or other elements (Fe, Ni, Co, Cu, Ag, Mn, etc.) to ZnS has been studied for visible light emission and photoluminescence enhancement. Among these dopants, Mn has attracted much attention because of its efficient doping, biocompatibility, and high-resolution bioimaging capability [20,21]. Bhargava's report additionally has been discussed in the recent luminescent spectroscopy textbooks and is considered as the

start of the research on doped semiconductor nanocrystals [22,23]. Besides ref. [7], some other groups also observed the life time shortening of the Mn<sup>2+</sup> emission due to strong quantum confinement in nano-scaled crystals, for example, ref. [16] and ref. [9] reported ns lifetime in ZnS:Mn<sup>2+</sup> nanoclusters.

On the opposite viewpoint, Bol and Meijerink [24,25] showed that the luminescent lifetime in ZnS:Mn<sup>2+</sup> nanocrystals was around 1.9 ms, which is comparable to that in bulk ZnS. It also raised some questions about the work of ref [7]. For example, the hybridization of sp-d states should result in the shift of Mn<sup>2+</sup> energy levels, which was not observed [4,7]. Moreover, the assumption about the hybridization as well as the reduction of forbidden transitions in such doped nanocrystals needs more concrete evidence from a quantitative theoretical model. More importantly, the details about lifetime measurement were still lacking. Bol and Meijerink came to the conclusion that the lifetime shortening of Mn<sup>2+</sup> emission with respect to crystal size reduction is incorrect. The as-reported nanosecond decay time most likely originated from the tail of broad defect-related (blue) emission that overlaps the Mn<sup>2+</sup> (orange) emission at around 590 nm. From lifetime and time-resolved measurements, they showed that the Mn<sup>2+</sup> emission possesses a decay time in the ms range, comparable to that in bulk ZnS:Mn<sup>2+</sup>.

In this work, we synthesized Mn<sup>2+</sup> doped ZnS nanocrystals with average dimensions 2 – 4 nm by a co-precipitation method. From both

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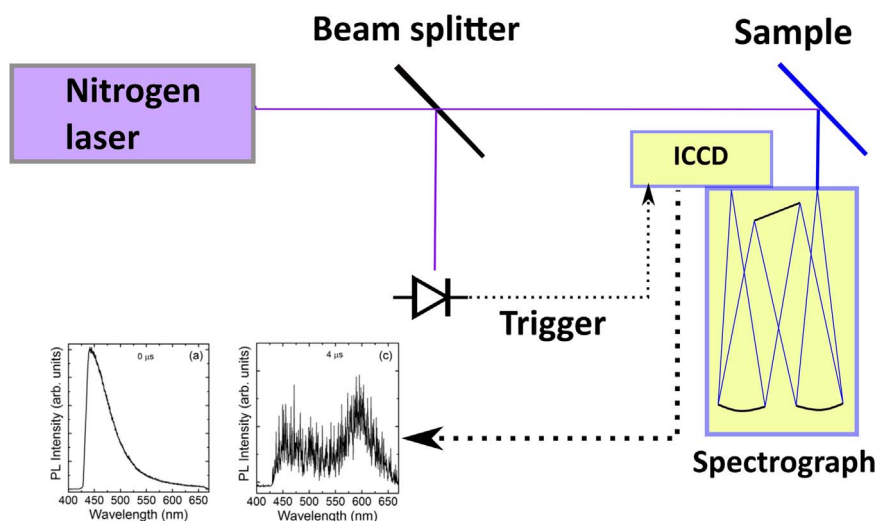


Fig. 1. A schematic diagram of the experiment apparatus used in time resolved measurement.

decay time and time-resolved measurements we conclude that there is no lifetime shortening of orange emission from  $\text{Mn}^{2+}$  incorporated in ZnS nanocrystals in comparison with the bulk counterpart and the previously reported ns lifetime comes from the tail of ZnS related photoluminescence. Furthermore, we report on the dependence of  $\text{Mn}^{2+}$  emission lifetime on excitation energy. Specifically, it is shorter for photon energies smaller than the ZnS bandgap.

## 2. Experimental

$\text{Zn}(\text{CH}_3\text{COO})_2$  and  $\text{MnCl}_2$  were used as precursors while  $\text{Na}_2\text{S}$  was the sulfur source. Initially, 10 ml  $\text{Zn}(\text{CH}_3\text{COO})_2$  1 M was dissolved with different amounts of  $\text{MnCl}_2$  0.1 M (0.5 – 10 ml) and 10 g  $\text{Na}(\text{PO}_3)_n$  (sol stabilizer). Deionized water was then added to the reaction flask and the mixture was stirred for 30 min at room temperature. After that 10 ml  $\text{Na}_2\text{S}$  1 M was injected into the flask and the solution was continuously stirred for 30 min. We received white suspensions, which subsequently were separated out of the solution by extensive centrifugation (8000 – 12,000 rpm), and then rinsed many times with deionized water. The washed powder was finally dried and sintered in inert gas (Argon 99.99%) environment.

The structure and crystallinity of the samples were characterized and analyzed by X-ray diffraction (XRD SIEMENS D5000) using  $\text{CuK}\alpha$  radiation ( $\lambda = 0.154$  nm) at a step of  $0.02^\circ$  ( $2\theta$ ) at room temperature. The morphology of the ZnS nanoparticles were recorded on JEM 1010 (JEOL, Japan) transmission electron microscopes (TEM) operating at 80 kV. Size distribution was calculated using the Gwyddion v. 2.49 software (Czech Metrology Institute, Czech Republic).

The emission spectra and the excitation spectra of the samples were measured on a Jobin-Yvon Nanolog spectrofluorometer equipped with a photomultiplier detector. A Xenon (Xe) lamp was used as an excitation source. The decay of phosphorescence of the samples was also recorded using either 370 nm excitation with a NanoLED at 0.5 MHz (Jobin Yvon Nanolog system at Hanoi University of Science and Technology, Vietnam) or 1 MHz (Jobin Yvon Nanolog system at Beijing University, China), 337 nm excitation with a pulsed  $\text{N}_2$ -laser (1–2 Hz) (Ghent University, Belgium), or a flash Xenon lamp (30 Hz) (Beijing University).

Time resolved spectra were measured using a nitrogen laser as the excitation source ( $\lambda = 337$  nm; pulse frequency 1–2 Hz; pulse duration < 1 ns). The emitted light from the sample was measured using an intensified CCD (Andor Instruments IStar ICCD DH720) coupled to a 500 mm grating spectrograph. Using a variable delay between the laser excitation and opening the electronic shutter from the CCD image intensifier, it was possible to acquire full emission spectra at specific

times after the excitation, with a time resolution of a few ns. For easy of reading, a schematic diagram of the experiment apparatus used in time resolved measurement is shown Fig. 1.

## 3. Results and discussion

In order to examine the phase composition and crystallography of samples, an X-ray Diffraction (XRD) pattern was taken. As shown in Fig. 2a, all peaks are well indexed as cubic zinc blende modification of ZnS structure with three typical diffracted planes of (111), (220) and (311). No peaks of any other phases or impurities were detected. The dimension of the nanocrystals as calculated quantitatively from the full-width at half-maximum (FWHM) of diffraction peaks and Scherrer equation [27] is about 2–4 nm.

The nanocrystals' size was verified again by direct measurement from TEM images, Fig. 2b. The particle size distribution has been calculated from TEM image Fig. 2b using the Gwyddion V.2.49 software and the result is shown in the inset of Fig. 2b. As shown in the inset of Fig. 2b, the  $\text{ZnS}:\text{Mn}^{2+}$  crystals exhibit nearly spherical shape and quite uniform dimension of 4 – 10 nm on average. The discrepancy in size of the ZnS nanoparticles between XRD and TEM measurements can be attributed to the fact that the dimension measured in TEM images is for agglomerates of several crystals.

The optical properties of  $\text{ZnS}:\text{Mn}^{2+}$  were examined under excitation with a monochromated Xe lamp. Fig. 3a shows the emission (PL) and excitation (PLE) spectra of ZnS nanocrystals doped with 0.5 at%  $\text{Mn}^{2+}$ . The emission spectrum is characterized by two peaks at 417 (blue) and 589 nm (orange). While the blue emission is known to originate from intrinsic defects in ZnS such as sulfur vacancies on the nanocrystal surface or zinc vacancies inside the structure [28,29], the orange emission is ascribed to the  ${}^4\text{T}_1 - {}^6\text{A}_1$  transition of  $\text{Mn}^{2+}$  ions in the ZnS host matrix [30–32]. Despite the fact that the concentration of surface defects is very large due to the high surface to volume ratio in nanoscale structures, the intensity of such orange emission is dominant, even at rather low concentration of  $\text{Mn}^{2+}$ , which suggests the effective transfer of electron-hole pairs into  $\text{Mn}^{2+}$  states, followed subsequently by the d-d emission in  $\text{Mn}^{2+}$ . According to previous studies [33,34], if the  $\text{Mn}^{2+}$  ions are located on the surface of the ZnS crystal, ultraviolet emission at around 350 nm is observed. Therefore, the strong orange emission at 589 nm is indicative of the successful incorporation of  $\text{Mn}^{2+}$  into the ZnS matrix. The PLE spectrum recorded when monitoring the 589 nm emission revealed two peaks at 341 nm and 282 nm whereas peaks at essentially the same positions were observed for the 417 nm emission. Since the position of the PLE peak indicates the band edge of the host (in the direct bandgap semiconductor), the PLE peaks at 342 and

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