



## Full Length Article

Alloyed core/doped shell  $\text{Mn}_x\text{Zn}_{1-x}\text{Se}/\text{ZnSe}:\text{Mn}^{2+}$  nanocrystals: steady-state and time-resolved spectroscopySébastien Lamarre <sup>a,b</sup>, Anna M. Ritcey <sup>a,b</sup>, Claudine Nì. Allen <sup>a,\*</sup><sup>a</sup> Centre d'Optique, Photonique et Laser (COPL), Département de Physique, de Génie Physique et d'Optique, Université Laval, 2375 Rue de la Terrasse, Québec, QC, Canada G1V 0A6<sup>b</sup> Centre de Recherche sur les Matériaux Avancés, Département de Chimie, Université Laval, 1045 Avenue de la Médecine, Québec, QC, Canada G1V 0A6

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## ABSTRACT

Steady state and time-resolved optical properties of alloyed core/doped shell  $\text{Mn}_x\text{Zn}_{1-x}\text{Se}/\text{ZnSe}:\text{Mn}^{2+}$  nanocrystals with  $x$  between 0.2 and 1 were studied. The emission from  $\text{Mn}^{2+}$  ions at  $\sim 580$  nm is predominant for higher MnSe mole fractions in the core (higher  $x$ ). At lower fractions, the ZnSe excitonic emission is also present while the  $\text{Mn}^{2+}$  emission shifts to  $\sim 560$  nm. The ratio of photoluminescence intensity of these emission bands depends on the composition of the alloyed core. The excited state lifetime of  $\text{Mn}^{2+}$  ions is also strongly dependent on the core composition, ranging from 300  $\mu\text{s}$  for small MnSe mole fractions down to 65  $\mu\text{s}$  for  $x=1$ . This is attributed to the long-range strain caused by a lattice mismatch of more than 4% at the core/shell interface. For  $x \leq 0.6$ , an additional lifetime, depending on the presence of an extra electron within the nanocrystals, was measured in the hundreds of nanoseconds range. A 4-level dynamic model is proposed to explain this observation.

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## 1. Introduction

Colloidal quantum dots (cQDs) are widely studied for their tunable optical properties [1]. The properties of these semiconductor nanocrystals (NCs) can be further expanded by doping with optically active transition metal ions that add electronic states, paramagnetism [2], tunable excitonic lifetimes [3], and thermal resistance [4]. In particular,  $\text{Mn}^{2+}$  doped ZnSe NCs show intense luminescence from the  ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$  transition of  $\text{Mn}^{2+}$  crystal field states while retaining the broad and strong absorption of the semiconductor host. These NCs are interesting for their long photoluminescence lifetime and negligible self-absorption, common to phosphors, in conjunction with the processing flexibility of colloidal suspensions. Moreover,  $\text{Mn}^{2+}$ -doped ZnSe may exhibit interesting phenomena of diluted magnetic semiconductors, such as exciton magnetic polarons [5], giant Zeeman splitting [6–8], indirect control over dopant spins [9,10], carrier induced ferromagnetism [10] and high internal magnetic field [11].

Dual emission from  $\text{Mn}^{2+}$  localized transitions and excitonic recombinations has been observed for some semiconductor NCs. The first example has been described by Yu et al. [12] for ZnSe:  $\text{Mn}^{2+}/\text{CdSe}$  NCs, shortly followed by Vlaskin et al. [13] for ZnSe:  $\text{Mn}^{2+}/\text{CdZnSe}$  NCs with excitonic emissions from the CdSe and

CdZnSe shells, respectively. Both groups propose a thermo-activated energy transfer from the  $\text{Mn}^{2+}$  excited state  ${}^4\text{T}_1$  to the semiconductor excitonic state to explain the retarded fluorescence of the exciton and the temperature dependent dual emission. The back-transfer from the  $\text{Mn}^{2+}$  to the exciton has indeed a strong effect on relaxation dynamics. In particular, Beaulac et al. [3] observed exciton lifetimes retarded by three orders of magnitude while the  $\text{Mn}^{2+}$  relaxation rate was accelerated by a factor of at least 20 for small  $\text{Mn}^{2+}$ -doped CdSe NCs. However, dual emission has yet to be considered in semiconductors with wider band gaps, such as ZnSe. Furthermore, the dependence of the relative emission intensity on  $\text{Mn}^{2+}$  concentration, controlled by core alloy composition, has yet to be studied.

$\text{Mn}^{2+}$  crystal field states are not tunable in the way excitonic states are, but some research groups have partially overcome this issue by using interfacial strain. The strain caused by the lattice mismatch at the interface of a core/shell NC applies an anisotropic pressure around  $\text{Mn}^{2+}$  impurities, changing their local environments and thus their emission properties. Ithurria et al. [14] have modulated the strain with the distance between  $\text{Mn}^{2+}$  ions and core/shell interface of CdS/ZnS:  $\text{Mn}^{2+}$  NCs, and observed a shift of the internal  $\text{Mn}^{2+}$  emission transition maximum. Recently for the same NC system, Chen et al. [15] have described the effect of strain on the temperature dependence of the  $\text{Mn}^{2+}$  emission energy, finding it to become more pronounced with increasing strain.

Here, we present a study of  $\text{Mn}_x\text{Zn}_{1-x}\text{Se}/\text{ZnSe}:\text{Mn}^{2+}$  NCs with mole fractions of MnSe ( $x$ ) in the core between 0.2 and 1,

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controlling both the strength of local strain and the extent of  $\text{Mn}^{2+}$  ion diffusion in the shell. We observe photoluminescence from both  $\text{Mn}^{2+}$  and excitonic states for  $x \leq 0.6$ . This dual emission can be tuned by varying the NC core alloy: a greater MnSe fraction in the core promotes interdiffusion during shell growth yielding isolated  $\text{Mn}^{2+}$  ions in larger amounts. The  $\text{Mn}^{2+}$  emission in this system is centered either below 580 nm or at  $\sim 560$  nm. The former originates from the well-known  ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$  transition of  $\text{Mn}^{2+}$  and has a tunable lifetime in the hundreds of microseconds. The latter has a second distinct lifetime in the hundreds of nanoseconds. A thorough time-resolved analysis was performed and we propose a 4-level dynamic model to interpret these observations. We observe that strain caused by lattice mismatch of the core/shell interface may be used to reduce the radiative lifetime of the  ${}^4\text{T}_1 \rightarrow {}^6\text{A}_1$  transition.

## 2. Experimental section

The  $\text{Mn}^{2+}$ -doped NC synthetic method is based on the nucleation doping strategy developed by Pradhan et al. [4] Contrary to the common growth doping strategy, cores are first nucleated including the doping material, here  $\text{Mn}^{2+}$ , which diffuses into the shell as it is grown. By starting from pure MnSe cores, uniform and high dopant concentrations can be achieved in the ZnSe shells of all NCs. To vary the extent of doping in a controlled manner, we adapted this synthesis by including a zinc precursor to the core nucleation in order to prepare  $\text{Mn}_x\text{Zn}_{1-x}\text{Se}$  alloyed cores that are subsequently overcoated with a ZnSe shell in three injection steps. Although adding a second metal salt to the core synthesis made its composition and doping more variable from one NC to another, the variability is less drastic than in NCs with very low doping achieved by growth doping strategy. A detailed description of the synthetic methods and material characterizations is available in the [Supplementary material](#).

### 2.1. Characterizations

Optical characterizations were carried out on NC dispersions in chloroform. The steady state photoluminescence (PL) and photoluminescence excitation (PLE) spectra were acquired using a Jobin-Yvon Fluorolog. The NCs were excited at 350 nm for PL spectra and the detection window was set at the emission maximum for PLE spectra.

The transient behavior of the total PL signal was recorded with a custom setup exciting NCs with a pulsed 308-nm excimer laser, more details can be found elsewhere [16]. Different temporal ranges were needed to cover the whole PL decay. Each decay trace was fitted with a biexponential empirical model of decay:

$$I(t) = I_0 + A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}, \quad (1)$$

where  $I(t)$  is the time-dependent PL intensity trace,  $I_0$  the intensity offset,  $A_i$  the pre-exponential factor, and  $\tau_i$  the lifetime of the  $i$ th component. Only the intensity-weighted mean lifetime [17] was considered in our analysis and was calculated using:

$$\bar{\tau} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}. \quad (2)$$

Time-resolved spectra were acquired with a Jobin-Yvon Nanolog using 350-nm light from a flash lamp as excitation. The signal was acquired with a PMT and analyzed in the time domain by a Horiba Fluo-Hub acquisition module. The signal was summed in 68- $\mu\text{s}$  bins over a 1.4-ms acquisition window for each wavelength using the Datastation software.

Quantum yields were measured with an absolute method using an integrating sphere [18]. A 405-nm laser diode was used as the

excitation source in this case and an Ocean Optic USB-2000 spectrometer as detector. The two-measure method [18] was used and the signal was corrected for photon energy by multiplying the signal at each pixel by the corresponding wavelength. The 6-in. integrating sphere from SphereOptics with Optowhite coating ( $\text{BaSO}_4$ ) was equipped with a baffle at its exit port to eliminate the direct detection of the PL. This method is insensitive to light scattering and solution refractive index which facilitates accurate quantum yield measurements of colloidal dispersions. Combined to the quantum yield measures, PL decay traces recorded with the Jobin-Yvon Nanolog after a 405-nm excitation yield radiative lifetimes.

## 3. Results and discussion

### 3.1. Morphology and chemical composition

The synthetic method described above produces  $\text{Mn}_x\text{Zn}_{1-x}\text{Se}/\text{ZnSe}:\text{Mn}^{2+}$  NCs with a mean size between 6 and 7 nm. For some MnSe mole fractions, the NCs adopt tetrapodal shapes, as shown in [Fig. S2](#). This type of growth is common for NCs with a zincblende crystal structure such as ZnSe [19]. XRD patterns are independent of the composition of the core and always display the zincblende ZnSe pattern of the predominant shell ([Supplementary material, Fig. S3](#)). The molar ratios of Mn to Zn were determined using EDS and the results are presented in [Table 1](#). As expected, the Mn/Zn ratio varies with the amount of Mn precursor included in the core synthesis. However, it is impossible to estimate the amount of dopant incorporated within the shell lattice only, since whole NCs, including core, shell and surface, are analyzed simultaneously. Indeed, NCs have a tendency to self-purify and diffuse  $\text{Mn}^{2+}$  to the surface. These surface ions give rise to the same EDS signal than their incorporated counterparts and are thus indistinguishable.

### 3.2. Steady state PL from $\text{Mn}^{2+}$ ions and ZnSe excitons

Emission from isolated  $\text{Mn}^{2+}$  ions in the shell is observed in the PL spectrum of each sample. The energy of the  $\text{Mn}^{2+}$  transition changes as a function of the core composition, exhibiting a quasi-discrete jump near  $x=0.6$ , as shown in both [Figs. 1 and 2](#). For MnSe mole fractions between 0.2 and 0.6, the  $\text{Mn}^{2+}$ -related emission is centered at  $\sim 560$  nm and is hereafter referred to as the 560-nm band. For  $x \geq 0.6$ , this emission discretely shifts slightly below 580 nm, while maintaining its shape, and is hereafter denoted as the 580-nm band. The  $\text{Mn}^{2+}$ -related band near 560 nm is not fully assigned yet. It could originate from the change in  $\text{Mn}^{2+}$  concentration. Indeed, research groups have described the effect of the  $\text{Mn}^{2+}$  concentration in ZnSe NCs on their emission energy. Pradhan et al. [4], Mahamuni et al. [20] and Suyver et al. [21] have observed an emission band at  $\sim 580$  nm for high

**Table 1**  
Quantum yield, lifetimes and elemental composition of  $\text{Mn}_x\text{Zn}_{1-x}\text{Se}/\text{ZnSe}:\text{Mn}^{2+}$  NC samples.

Sample x	Quantum yield (Dimensionless $\pm 5\%$ )	Excited state lifetime ( $\mu\text{s}$ $\pm 5\%$ )	Radiative lifetime ( $\mu\text{s} \pm 10\%$ )	Non- radiative lifetime ( $\mu\text{s}$ $\pm 10\%$ )	Composition Mn/Zn (mol/mol)
1.0	0.58	62	110	150	0.06 $\pm$ 0.01
0.9	0.25	94	370	130	0.07 $\pm$ 0.02
0.8	0.40	330	800	550	–
0.7	0.63	580	900	1600	0.11 $\pm$ 0.05
0.5	0.10	–	–	–	0.03 $\pm$ 0.01

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