



# Manifested luminescence and magnetic responses of stoichiometry dependent $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ quantum dots



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## ABSTRACT

We report on stoichiometry dependent manifested physical properties of thioglycolic acid (TGA) coated  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  QDs. While possessing a wurtzite phase, with increasing  $x$ , the QDs exhibited a notable blue-shifting of the onset of absorption. Attributed to  $V_{\text{Cd}}-V_{\text{Se}}$  di-vacancies, the QDs describe an intense deep-defect related emission response at smaller values of  $x$  ( $=0$  to  $0.3$ ). Due to the facilitation of magnetic  $\text{Mn}^{2+}$  ion migration from the core to the QD surfaces,  ${}^4T_1-{}^6A_1$  transition based  $\text{Mn}^{2+}$  orange emission get suppressed at a higher  $x$  ( $=0.6$  to  $1$ ). While the FT-IR spectra of the alloyed QDs display characteristic Mn–OH stretching mode at  $\sim 644\text{ cm}^{-1}$ , the peak located at  $\sim 703\text{ cm}^{-1}$  is assigned to Cd–Se bending. Furthermore, the QDs with a low  $x$  ( $=0.3$ ), exhibit paramagnetic characteristics owing to the presence of uncorrelated, isolated  $\text{Mn}^{2+}$  spins. The collective luminescence and magnetic features would find immense scope in bio-labeling and imaging applications, apart from solid state luminescent components.

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## 1. Introduction

Semiconductor nanocrystals are known for their bright emission response with size dependent color tunability between the ultra violet (UV) and near infra-red (NIR) region of the electromagnetic spectrum. Of particular interest, the magnetic impurity doped systems (magnetic semiconductor nanocrystals/quantum dots, *ms*-NCs/QDs), such as, nanoscale  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  systems, have received growing interest owing to their immense potential in magneto-optics, nonlinear optics, nano-photonics and nano-biotechnology. This is because, these QDs exhibit special properties, like localization of magnetic ions that result in free electron and hole carriers [1,2], size-dependent sp-d exchange interaction [3,4] along with introduction of new energy levels within the forbidden gap. The strong sp-d exchange interaction may result in enhanced spin relaxation [5], giant Zeeman splitting

of the electron and hole states when subjected to a magnetic field [6], along with the formation of excitonic magnetic polarons [3,7]. These interesting characteristics occurring in *ms*-NCs ensure their potential applicability in various fields including spintronics [8], tunable lasers [9], solar cells [10], magneto-optic elements [11], quantum computing etc.

Over the years, magnetic semiconductor systems of the form  $A^{II}_{1-x}M_xB^{VI}$ , (with cations  $A^{II}=\text{Cd}^{2+}$ ,  $M=\text{Mn}^{2+}$ , anion  $B^{VI}=\text{Se}^{2-}$ ) have drawn significant research interest owing to the strong dependence of sp-d exchange interaction on the amount of doping (mole fraction,  $x$ ). Moreover, highly fluorescent II–VI semiconductor systems, mostly Cd-based ones (e.g., CdSe, CdTe, CdS, CdSe/ZnS core shell QDs etc.), have been investigated in great detail including their extensive deployment in biolabeling and bioimaging studies [12]. In this work, we demonstrate a simple, user-friendly approach for synthesizing  $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$  QDs, using thioglycolic acid (TGA) as the capping agent. Although TGA in excess amount is somewhat toxic, but due to its ability to provide effective surface functionalization and extra-photostability to the fluorescent QDs, the TGA capped QDs are found to be extremely

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useful in practical situations [13,14]. Here, we discuss and compare structural, optical, vibrational and magnetic responses of the synthesized QDs in conjunction with stoichiometry variation.

## 2. Experimental: materials and methods

### 2.1. Production of $Cd_{1-x}Mn_xSe$ quantum dots

The step-by-step synthesis protocols, for obtaining various QD systems with varying stoichiometric parameter  $x$ , are as detailed below.

#### 2.1.1. QD synthesis for $x=0$

The procedure of synthesizing CdSe QDs ( $x=0$ ) can be found elsewhere [14]. Here, we employ a modified method along with inclusion of an anionic surfactant as coating element. At first, 0.93 g of cadmium nitrate-tetra hydrate [ $Cd(NO_3)_2 \cdot 4H_2O$ ] was dissolved in 100 mL of deionized (DI) water followed by stirring ( $\sim 250$  rpm) at a temperature of  $60^\circ C$ , for 20 min. Then, 0.5 ml of TGA was added to the  $Cd^{2+}$  solution under stirring. The pH of the solution was adjusted to  $\sim 11$  by adding aqueous sodium hydroxide (NaOH) in a drop-wise manner. Then, 0.22 g of  $SeO_2$  was taken along with the 0.2 g sodium borohydride ( $NaBH_4$ ), added as a reductant. Finally, the mixture was kept under stirring for 1 h and at a temperature of  $80^\circ C$ . The precursor extract was then subjected to centrifugation ( $\sim 5000$  rpm) followed by adequate filtration using a Whatman

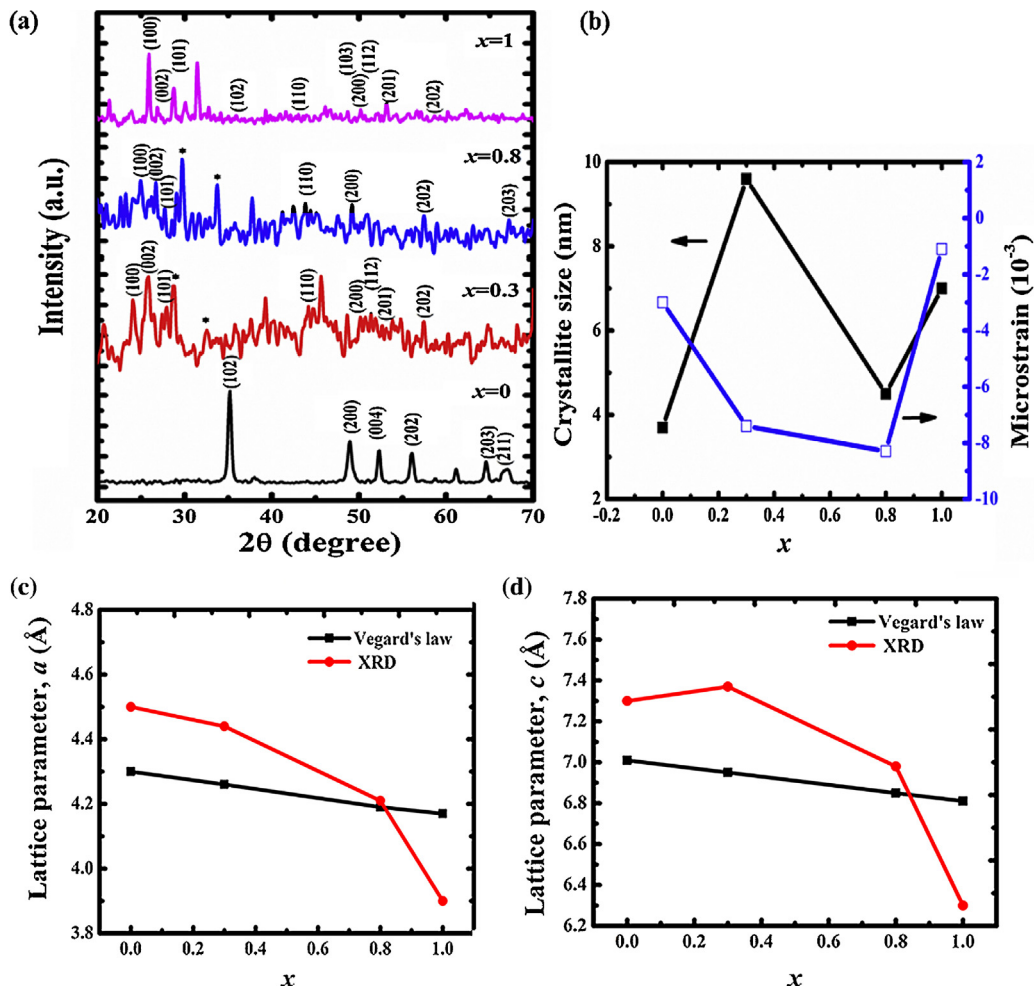
filter<sup>®</sup>. The precipitate was washed with DI water several times and finally, cleansed with ethanol.

#### 2.1.2. QD synthesis for $x=1$

In a typical procedure, 0.62 g of manganese chloride-tetra hydrate [ $MnCl_2 \cdot 4H_2O$ ] and 0.11 g  $SeO_2$  were dissolved in 22 ml DI water followed by the addition of 0.1 g  $NaBH_4$ . The pH of the solution was adjusted to  $\sim 11$  by adding aq. NaOH. The stirring ( $\sim 250$  rpm) was maintained at  $60^\circ C$ , for 5 min. Following the addition of 10% TGA, the whole mixture was transferred to a teflon-lined stainless steel autoclave of 50 ml capacity. The autoclave was sealed properly and kept under oven at  $180^\circ C$ , for 6 h. On completion of the reaction, the autoclave was cooled down to room temperature naturally. The extract was subjected to centrifugation ( $\sim 5,000$  rpm) and subsequently, filtration. The residual content was washed away with DI water repeatedly and finally, with ethanol. The whole process was believed to facilitate homogeneous growth of the MnSe QDs [15].

#### 2.1.3. QD synthesis for $x=0.3$ to $0.8$

A suitable stoichiometric variation was considered in order to make a comparative account on manifested properties of the synthesized QDs. The ternary QDs of  $Cd_{1-x}Mn_xSe$ , with  $x=0.3, 0.6, 0.8$  were prepared following the aforesaid procedure but with a little alteration. Here, considering a fixed amount of  $SeO_2$ , and  $NaBH_4$  as reductant, the  $Cd^{2+}$  to  $Mn^{2+}$  molar concentration was



**Fig. 1.** (a) XRD patterns of different  $Cd_{1-x}Mn_xSe$  systems, (b) variation of average crystallite size and microstrain with  $x$ . The sub-figures (c) and (d) depict variation of effective lattice parameters  $a$  and  $c$  with  $x$  considering XRD analysis (red label) and Vegard's law (black label). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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