

Bright White-Light Emitting Manganese and Copper Co-Doped ZnSe Quantum Dots**

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White-light emission (WLE) from semiconductor nanostructures is presently a research area of intense interest, especially where the primary objective is to replace conventional light sources in order to minimize energy costs and therefore global energy consumption for lighting.^[1–8] Presently the general methods to achieve white-light emission are either by coating a yellow phosphor or by combining green and red phosphors on a background consisting of a blue-light emitting diode (LED) or by employing nanocrystals (NCs) of the three primary colors (red, green, blue) using multilayer structures in LEDs. However, when one simply mixes these nanocrystal quantum dots (QDs) of different colors together to generate white light, the efficiencies are often observed to decrease due to the re-absorption of light and subsequent undesired energy transfer (ET). This may lead to undesirable changes in the chromaticity coordinates and photometric performance due to the different relative temporal stabilities of the components. Hence the use of a single-emitting component offers many advantages over multiple component systems for white-light emitting sources such as LEDs, amongst which are: greater reproducibility, low cost preparation, ease of modification, and simpler fabrication processes. Therefore, it is of great importance for many applications to find high-quality single source white-light emitters through low-cost chemical synthesis approaches that will allow the production of white light while meeting the needs of industry, such as satisfactory Commission International d'Eclairage (CIE) coordinates.

One route that offers the possibility by which such materials may be accessed is that of the colloidal synthesis of doped semiconductor nanocrystals, which has already proven itself to be an interesting field for future nanotechnologies as it can presently provide highly efficient emission sources for various applications.^[9–12] Although

various attempts have been made towards the growth of doped QDs in solution, it still remains a challenge to dope all of the nanocrystals present in the reaction mixture simultaneously with the different dopants, as the host matrix tends to expel the dopant ions from the internal crystal lattice to the surface, in a sort of “self-purification” process.^[13] Therefore, even in the most favorable cases of the dopant ions having the same valence state and similar ionic radius as those of the corresponding host, successful doping remains difficult to achieve by the simple addition of a small amount of dopant precursors during the synthesis of the host NCs. To overcome this, a number of doping strategies, such as nucleation–doping and growth–doping, where the doping is decoupled from the nucleation and/or growth, provide ample possibilities to selectively introduce dopants at desired positions within the host materials to generate different emission centers inside of a single quantum dot.^[14] Usually, in a Mn^{2+} -doped ZnSe system there is a dominant yellow/orange emission present at 585 nm which results from the ${}^4\text{T}_1\text{--}{}^6\text{A}_1$ transition of the Mn^{2+} impurity excited by energy transfer from the host lattice.^[15,16] Therefore, if one can supply a source of blue and/or green emission within such a system, then white-light emission is likely to result. In fact, Mn^{2+} -doped CdS ^[17] and ZnS ^[18,19] NCs with white-light emission have been successfully prepared by the combination of the orange emission of the Mn^{2+} impurity and the blue and/or green emission of the surface defect states of the NCs. There are also a number of reports which describe the synthesis of semiconductor NCs with white-light emission such as “magic-sized” CdSe NCs,^[1] trap-rich CdS -QDs and onion-like CdSe/ZnS/CdSe/ZnS -QDs,^[2] alloyed $\text{Zn}_x\text{Cd}_{1-x}\text{Se}$ quantum dots,^[3] ZnS:Pb ,^[4] ZnS incorporated into porous Silicon,^[5] and ZnSe .^[6] However, all the above-mentioned systems rely on the manipulation of surface-state emission from the NCs, which is notoriously difficult to control and/or reproduce and, in addition, the temporal stability of these states varies with the environmental conditions in a manner which is presently still not fully understood. Also the intrinsic toxicity of cadmium and lead sheds a doubt on the future applicability of these NCs, particularly in view of recent environmental regulations.

Herein we report a method which overcomes these difficulties through the successful synthesis of doubly doped QDs using a versatile hot-injection colloidal synthesis to produce Mn and Cu co-doped ZnSe QDs (Cu:Mn-ZnSe), where white-light emission can be readily realized and its characteristics tuned. The two dopants have been introduced into the host material in a two-step process such that the dopants retain their individual emission properties which cover most of the visible spectral range. Also we demonstrate versatility of the tuning of the white-light generation with

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respect to its adjustable tristimulus coordinates, correlated color temperature and color rendering index. The synthesized doped QDs also fulfill the potential of semiconductor QDs without the toxicity limitations encountered by II–VI QDs, therefore this material may offer the opportunity for future-generation WLE materials. To achieve co-doping of the ZnSe host with Mn and Cu, the dopants were introduced at different times of the host growth. Details of a typical synthesis are provided in the Supporting Information.

Figure 1 shows the photoluminescence (PL) and optical absorbance spectra of the samples obtained at different stages of the synthesis. In the first step core-doped Mn–ZnSe QDs were synthesized by a nucleation–doping strategy, and in the second step subsequent incorporation of the Cu ions into the doped QDs was achieved. The initial MnSe nanoclusters were synthesized by the reaction of manganese stearate, $\text{Mn}(\text{St})_2$, and seleniumtributylphosphine in an amine-rich solution, the reaction mixture being kept at 280 °C for 30 to 45 min due to the low reactivity of the manganese precursor. The use of larger amounts of amine was also found to be advantageous for the growth of ZnSe as it controls the reactivity of the zinc fatty acid/salt fatty acid mixture in the reaction mixture. Upon addition of the Zn precursor to the synthesized MnSe nanocrystals, the appearance of a yellow emission was observed under UV illumination.

From Figure 1a it can be seen that three distinct peaks may be observed for the Mn–ZnSe doped QDs. The highly intense yellow emission at 585 nm results from the ${}^4\text{T}_1\text{--}{}^6\text{A}_1$ transition of the Mn^{2+} impurity excited by energy transfer from the host ZnSe.^[15,16] The peak at 410 nm and the broad peak at 470 nm are due to band-edge emission and surface defects, respectively, which emanate from the host ZnSe. It was possible to observe these ZnSe related peaks due to the low Mn^{2+} dopant concentration present.^[18] However, it was observed that the presence of these surface defects during the synthesis of the Mn–ZnSe doped QDs appears to favor the generation of white light after the incorporation of the Cu ions into the host lattice in the later step. The emission intensity at 585 nm is observed to first increase gradually during annealing and then gradually decreases. This indicates the diffusion of the Mn ions from the center towards the surface of the nanoparticles (see Supporting Information Figure S1). In the second step, the temperature is lowered to

180 °C so as to arrest the growth of the Mn–ZnSe doped QDs and to this the required amount of Cu precursor is injected. Subsequently, due to the gradual increase of the temperature, Cu ions were adsorbed onto the surface of the previously grown Mn–ZnSe doped QDs, which act as small hosts for the adsorption of the Cu ions.

The adsorption of the Cu ions onto the surface of the Mn–ZnSe nanocrystals is confirmed by the appearance of the highly intense blue-green peak at 485 nm (Figure 1a), which is 15 nm red-shifted with respect to the pure ZnSe QD defect related emission. This peak is assigned to the recombination of an excited electron in the conduction band/defect states of the ZnSe host nanocrystal with the d-orbital hole of a Cu ion.^[14,20,21] A decrease in the band-edge emission peak intensity of the host ZnSe is also observed, which is a further indication for the adsorption of the Cu ions onto the surface of the host Mn–ZnSe nanocrystals, where the loosely adsorbed dopant ions can easily act as surface traps to quench the host PL. Interestingly, there is an accompanying decrease in the PL intensity of the 585 nm peak observed. The partial quenching of the highly intense Mn^{2+} dopant emission and appearance of the broad emission at 490 nm after the introduction of Cu ions indicates the successful adsorption of these ions onto the Mn–ZnSe doped QDs surface, which displays the opening of the more favorable optical relaxation path through the Cu states for the photophysical processes.

There are a number of different transition mechanisms involved in the emission of the co-doped ZnSe system. In Mn–ZnSe, after electrons have been excited from the valence band to the conduction band, a number of electrons may relax to the defect states, from where they can recombine with holes in the valence band, with the resultant emission of photons in the 470 nm spectral region. When the copper ions are present, they are adsorbed on the surface of the doped QDs and hence populate these surface sites. Therefore radiative recombination between electrons in the defect states and holes in the d orbitals of the copper ions is expected to increase in dominance. Hence significantly, the peak intensity of the copper-related PL increased by many-fold compared with both the defect- and Mn^{2+} -related d–d emissions. Finally, when the ZnSe shell is synthesized on the surface of the doped QDs, it can act to reduce the concen-

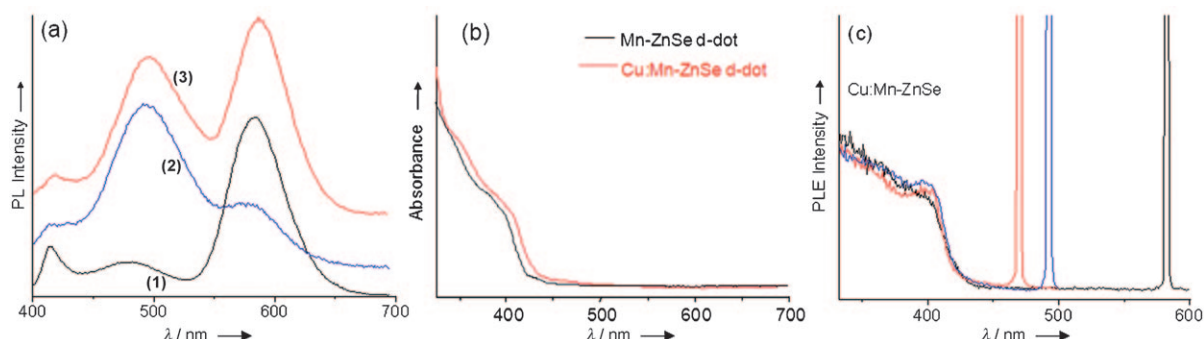


Figure 1. a) PL spectra of the samples at different steps of synthesis: 1) Mn–ZnSe doped QDs, 2) Mn–ZnSe doped QDs after Cu injection, and 3) Cu:Mn–ZnSe white-light emitting doped QDs. b) UV/Vis absorbance spectra of Mn–ZnSe and Cu:Mn–ZnSe doped QDs. c) Photoluminescence excitation spectra of the Cu:Mn–ZnSe sample taken at the different peak emission positions.

tration of surface states and hence favor the energy transfer from the ZnSe host to the Mn centers.

Successful formation of the ZnSe shell is confirmed by the Cu related PL emission being red shifted (Figure 1a) after the shell formation due to the accompanying increase in the size of the doped QDs. From the optical absorbance spectra (Figure 1b) a red shift in the spectrum for the Cu:Mn-ZnSe sample is observed which is additional support for the formation of the ZnSe shell. Photoluminescence excitation (PLE) spectra (Figure 1c) for the WLE-doped QDs taken at the different emission peak positions were found to mirror the UV/Vis absorption spectrum of the ZnSe host matrix remarkably well, indicating that all emissions originated from the same particle set and not from extraneous species or undesired secondary growth of quantum dots formed during the synthesis.

From the TEM observation (Figure 2a,b) the size of the Mn-ZnSe doped QDs and the Cu:Mn-ZnSe doped QDs were measured to be $4.0\text{ nm} \pm 10\%$ and $5.2\text{ nm} \pm 10\%$, respec-

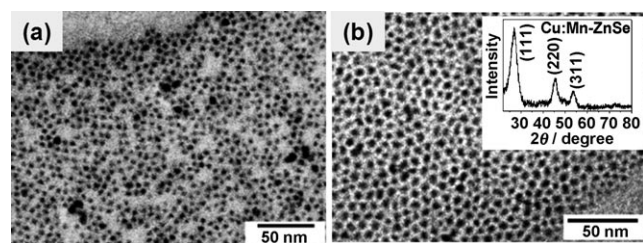


Figure 2. TEM images of a) Mn-ZnSe doped QDs, b) Cu:Mn-ZnSe doped QDs. Inset: XRD spectrum of Cu:Mn-ZnSe doped QDs.

tively, which is also in good agreement with the sizes as calculated from the absorbance spectra. A HRTEM image of the Cu:Mn-ZnSe doped QDs is provided in the Supporting Information (Figure S2). The X-ray diffraction (XRD) pattern of a typical Cu:Mn-ZnSe doped QD sample (inset of Figure 2b) displays the peak broadening, which is characteristic of a nanocrystalline material and exhibits a number of well-resolved peaks that can be indexed to the (111), (220), and (311) planes of zinc blende ZnSe (JCPDS 37-1463) and the diffractogram is devoid of any signatures which may be assigned to other phases. The size of the nanocrystals was calculated using Debye–Scherrer formula using the (111) reflection of the XRD pattern and the average particle size estimated was 5.5 nm, which is also in good agreement with the optical study.

To further establish the inclusion of both the dopant ions in a single nanoparticle, a number of contrastive experiments were undertaken. When separately prepared Mn-ZnSe and Cu-ZnSe doped QDs were mixed together, no quenching of the Mn related emission at 585 nm is observed (see Figure S3). When this mixed Mn-ZnSe/Cu-ZnSe doped QD solution was annealed at 260 °C for few minutes, no drastic quenching in the Mn-ion related PL peak is observed. In contrast, after Cu injection during a normal synthesis, it was observed that the Mn-related emission is almost completely

suppressed after 10 min when the temperature is increased gradually to 240 °C (see Figure S4). This may be due to the migration of the Mn ions towards the surface of the doped QDs at this higher temperature, giving rise to a photophysical interaction between the two different ions due to the increase in their proximity. From this observation it may be postulated that the different ions are required to be separated by a minimum distance if they are to emit their individual colors. When they are close enough the Cu emission is observed to be dominant and the Mn-related emission is almost suppressed. Further study on this aspect will provide a better understanding of the interaction between two emitting ions occupying the same nanosized host matrix with respect to their relative positions. This also provides additional weight to previous reports that the two different dopants are not homogeneously distributed throughout the doped QDs but rather that the core may be Mn-rich^[22] and the surface rich in Cu ions, and migration of the ions to within close proximity of each other is to be avoided if one is to achieve WLE.

The quantum yield (QY) of the samples at different stages of the synthesis was measured. In the first step, the QY of the Mn-ZnSe is observed to be 22 %. When the Cu ions were adsorbed on the surface of the Mn-ZnSe doped QDs the QY is decreased to 8–10 %. This may be due to the generation of the surface defect states and so also the observed quenching of the highly intense Mn^{2+} -related emission. As the emission from d–d transitions of Mn^{2+} are largely affected by the crystal field and sensitive to the environment,^[23,24] these studies also give a clear indication for the interaction of the optical active channels due to the different dopant ions inside a single crystal. After adding the ZnSe shell in the third step, the QY was observed to increase to 13–17 % under suitable conditions. Hence, in this rather complex photophysical system, the inorganic capping leads to a reduced escape possibility for the charge carriers with a consequent increase in the emission QY.

The doped QDs so obtained were also observed to be soluble in a number of organic solvents such as toluene and hexane. A white powder could be obtained by precipitating the doped QDs with acetone and drying under a nitrogen flow and was found to be stable under normal atmospheric conditions for days or for months under inert atmosphere. To further explore the photostability of the doped QDs, a solution in toluene was exposed to irradiation from the 365 nm line (intensity approximately 1 mWcm^{-2}) of a UV lamp. Upon exposure to UV-light, the PL intensity of the dopant emission peaks decreased gradually and the ZnSe emission band increased. After 3 h of exposure the Cu-related emission peak is observed to be diminished (Figure S6) which may be due to the photooxidation of Cu ions close to the surface of the doped QDs and also to possible gradual lattice ejection of some of the dopants from the host material under irradiation.^[25] When the doped QDs were transferred to a 5 % PMMA solution in toluene and spin-coated, the resulting thin films were found to be stable (inset of Figure S5) suggesting that for applications, encapsulation methods can provide a greater degree of stability. In Figure 3a the white-light emission from the powders under the 365 nm excitation line of a UV lamp can be seen.

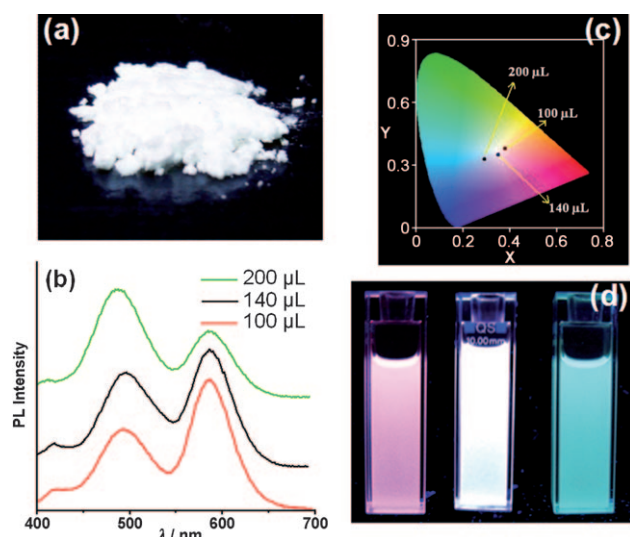


Figure 3. a) Cu:Mn-ZnSe doped QD powder showing white-light emission under a UV lamp with a 365 nm excitation. b–d) Cu:Mn-ZnSe doped QDs samples with different amount of Cu precursors: b) emission spectra, c) CIE coordinates, and d) photographs under a UV lamp with a 365 nm excitation.

A number of large-scale syntheses have also been successfully carried out and gram quantities of high-quality WLE doped QDs could be supplied from a single batch. The spectral properties of the white light could also be controllably adjusted, by systematically varying the ratio of the dopant concentrations. Figure 3b presents the emission profiles recorded for the samples obtained after different amounts of the Cu precursor were injected. Figure 3c shows the corresponding CIE coordinates and Figure 3d photographs of the emission under UV light for the same samples. For these samples the CIE coordinates, color rendering index, and correlated color temperature have been included in tabular form in the Supporting Information. This therefore demonstrates the added possibility to tune the photometric properties of WLE for different specific commercial applications as may be so required. In Table S3 the shades of WLE are shown to be conveniently spanned using varying amounts of the Cu precursor. When the emission colors from the doped QDs are compared with the different color temperatures (warm vs. cold white) of commercial white-light LEDs,

the emission from the doped QDs presented here belongs to the cold white-light classification.

Time-resolved spectroscopy measurements were undertaken in order to gain insight into the various mechanisms involved in the emission process. Figure 4 shows the photoluminescence decay profiles of the different emission centers in the Mn-ZnSe and Cu:Mn-ZnSe materials. The lifetimes associated with the various decay processes have also been presented in tabular form in the Supporting Information. By the introduction of the Cu d-states, it is observed that the band-edge emission is quenched and thus a faster decay results, while the trap-associated recombination becomes slower as is apparent at the tail end of the decay profiles. This is attributed to the enhanced efficiency of the trap-state population in the presence of the Cu ions. For both samples the exciton emission and trap emission are fast processes compared to the emission from the doped sites. The emission collected from Cu:Mn-ZnSe at 470 nm most probably contains a contribution which may be associated with trap emission, as indicated by the shorter component in the lifetime fitting parameters observed for the Mn-ZnSe doped QDs (see Supporting Information, Tables S1 and S2). However, the emission recorded at 495 nm displayed a dominant decay channel of ca. 100 ns in the lifetime profile, which may be attributed to the Cu d-states, as it is unlikely to be due to either excitonic or purely trap emission, both of which are intrinsically much faster processes.

The decay profile of the Mn-related emission at 585 nm is presented in Figure 4c, and shows the mono-exponential nature of both the samples. The lifetime measured for the Mn-ZnSe sample is calculated to be 264 μ s and that for the Cu:Mn-ZnSe sample is 324 μ s. The Mn^{2+} ion emission in the Cu:Mn-ZnSe doped QDs displayed a longer lifetime due to the thicker ZnSe overcoating layer, which also supports the successful formation of a thicker shell of ZnSe around the doped QDs encapsulating both the Mn and Cu ions. Based on these results, the energy level diagram for the doped QDs may be depicted as shown in Figure 5. This system of multiple dopants, which are very close to each other and have lifetime values differing by three orders of magnitude, also raises certain questions concerning the relative emission efficiency between two emission bands and future studies providing such insights will be helpful in explaining the complex nature of the energy states.

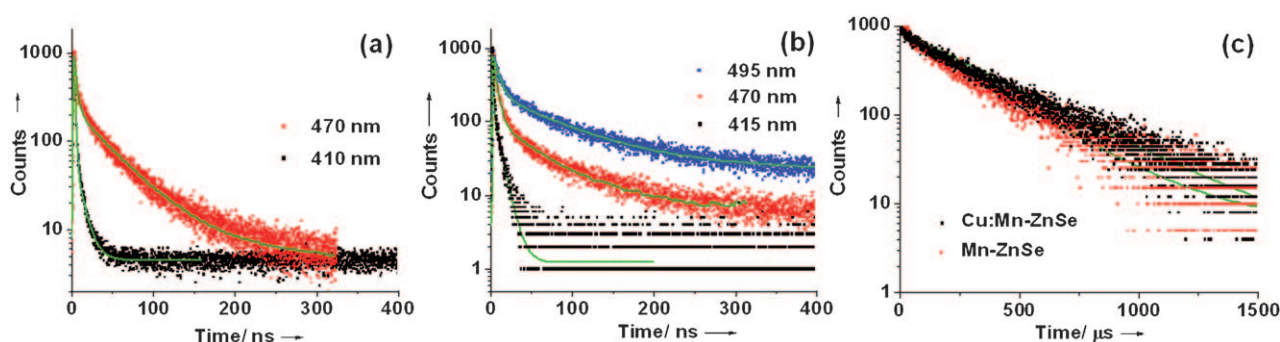


Figure 4. Photoluminescence (PL) decay traces of a) Mn-ZnSe doped QDs, b) Cu:Mn-ZnSe doped QDs at different peak positions, and c) of Cu:Mn-ZnSe and Mn-ZnSe doped QDs at 585 nm.

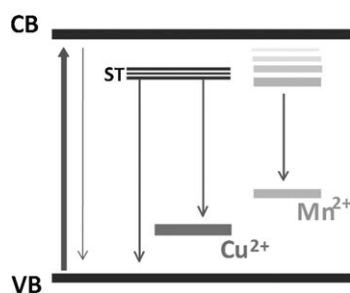


Figure 5. Energy level diagram for the Cu:Mn-ZnSe doped QDs. (VB: valence band, CB: conduction band, ST: surface trap states).

In conclusion, we report the generation of doubly doped QDs by a hot-injection colloidal synthesis approach that possess high-quality white-light emission in both the colloidal solution and solid-state powder with photoluminescence efficiencies as high as 17%. This protocol has proven to be robust and offers the possibility of being extended to other host materials allowing co-doping with different dopants to obtain high quality emitters that have the potential to cover most of the visible and NIR spectral window for future optoelectronic applications. The WLE-doped QDs may facilitate simple device implementation and hold great promise for the future of solid-state lighting. In addition, these doped QDs may offer high-performance emissive materials without the inclusion of any of the highly toxic class-A elements (Cd, Hg, and Pb) and therefore may be used in place of the current workhorse of intrinsic quantum dot emitters which are based on these materials.

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