Journal of Luminescence 202 (2018) 157–162

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Thermally stable luminescence of Mn^{2+} in Mn doped $CsPbCl_3$ nanocrystals embedded in polydimethylsiloxane films

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ARTICLE INFO

Keywords:
Luminescence
$Mn:CsPbCl_3$
Perovskite
Nanocrystals
Light emitting diodes
Polydimethylsiloxane

ABSTRACT

Mn^{2+} doped $CsPbCl_3$ nanocrystals (NCs) have exhibited promising applications in the field of solid state lighting. Their thermal stability at elevated temperature should be particularly considered when they come into commercial use. Here, we reported the thermally stable luminescence of Mn^{2+} in Mn doped $CsPbCl_3$ NCs embedded in polydimethylsiloxane (PDMS) films. The luminescent properties of $Mn:CsPbCl_3$ NC/PDMS films under various heat treatment temperatures for different time were studied by steady-state and time resolved photoluminescence (PL) spectroscopy. It was found that the $Mn:CsPbCl_3$ NC/PDMS films had more thermally stable PL of Mn^{2+} at temperatures of 80 and 100 °C than the pure NC films. The embedding of $Mn:CsPbCl_3$ NCs into PDMS was considered to significantly avoid the growth of the NCs, resulting in reduced nonradiative recombination centers. The $Mn:CsPbCl_3$ NC based light emitting diodes were fabricated by combining with green emitting Cu:ZnInS/ZnS NCs to obtain a white emission.

1. Introduction

Recently, all-inorganic cesium lead halide ($CsPbX_3$, where X is Cl, Br, and I) perovskite nanocrystals (NCs) have attracted much attention due to their unique characteristics of high photoluminescence quantum yields (PL QYs), narrow linewidths, tunable emission bands for potential applications in fields such as light emitting diodes (LEDs), lasers, photodetectors and solar cells [1–16]. Many novel functionalities have been realized in traditional II-VI and III-V semiconductor materials by impurity doping. It is noted that manganese ions (Mn^{2+}) doped NCs, such as $Mn:CH_3NH_3PbX_3$ [17], $Mn:(C_4H_9NH_3)_2PbBr_4$ [18] and $Mn:CsPbX_3$ [19–25], have shown distinguished luminescent properties. Generally, Mn^{2+} doping was found to manipulate the optical and magnetic mechanisms in $CsPbCl_3$ NCs, displaying broad orange to red emission band which is from the Mn^{2+} $^4T_{1g} \rightarrow {}^6A_{1g}$ d-d transition [24]. Besides, undesired reabsorption losses can be avoided because of the large stokes shift and bicolor emissions located at ~400 nm and ~600 nm can thus be acquired, demonstrating potential applications in high color rendering white LEDs due to Mn^{2+} doping caused crystal lattice stabilization [17–25].

It is well known that the biggest obstacle for perovskite NC-based devices in application is their severe instability which is, in part, accused of the low formation energy of lattices [19]. In terms of the lattice structure, considering the radius reduction when Pb^{2+} (~1.33 Å) is substituted by Mn^{2+} (~0.97 Å), the crystal lattice of $Mn:CsPbCl_3$ NCs is prone to shrink, leading to a high formation energy of Mn-Cl bond and a thermally stable situation [19]. However, if exposed to air, the doped NCs can be seriously degraded because their surface will suffer from water, oxygen and ultraviolet light [14,19]. The surface modification methods, including surface chloride doping [26], low flux X-ray irradiation [27], and inert mesoporous silica coating [9,28–30] are used to improve the stability. However, there are more or less deficiencies when they were applied for $Mn:CsPbCl_3$ NCs because surface chloride doping was devoted to stabilizing other halide (i.e. I or Br) based perovskite from phase transformation, X-ray irradiation was inclined to change the surface ligands in formation of C=C bonds, and silica coating decreased the output emission light. Encapsulated polymers with good chemical compatibility and transparence, on the other hand, can act as the barrier between NCs and the surrounding to improve the stability. Unluckily, the most commonly used polymethyl methacrylate and silicone resin would quench PL in $CsPbX_3$ NCs. Recently, polydimethylsiloxane (PDMS) has been extensively used as a good free-standing dispersing agent in colloidal semiconductor NCs due to its excellent compatibility and intrinsically hydrophobic surface [30–35]. Lee et al. reported the use of PDMS as a tailorable encapsulation film for enhancing thermal stability of dichromatic white LEDs by blocking

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https://doi.org/10.1016/j.jlumin.2018.05.061
Received 12 January 2018; Received in revised form 12 May 2018; Accepted 24 May 2018

water and oxygen. The textured structures on the soft surface of PDMS layer improved not only the light extraction efficiency but also the color rendering index (CRI) [32]. It is clearly shown that perovskite NCs can be embedded in the PDMS to obtain stable composite films. For instance, Li et al. successfully incorporated green $CsPbBr_3$ NC-based silica/alumina monolith powders into PDMS films. Polychromatic LEDs were fabricated by coating the composite film on a blue LED chip, having a very high luminous efficacy of 80.77 lm W^{-1} [34]. However, to our best knowledge, research about the thermal effects of PDMS agent on Mn^{2+} emission in Mn:$CsPbCl_3$ NCs has not been comprehensively reported yet.

In this work, we studied the PL thermal stability of Mn^{2+} in Mn:$CsPbCl_3$ NCs embedded in PDMS agent by steady-state and time resolved photoluminescence (PL) spectroscopy. The Mn:$CsPbCl_3$ NCs with various Mn^{2+} doping concentrations were synthesized by regulating the Mn/Pb molar ratios. Stable emissions of Mn^{2+} were observed for Mn:$CsPbCl_3$ NCs in PDMS at 80–100 °C, in contrast to a significant thermal quenching of PL in pure NC films. Moreover, the doped NC based white LEDs with high CRI of over 83 were fabricated.

2. Material and methods

2.1. Materials

Lead chloride ($PbCl_2$, 99.99%), manganese chloride ($MnCl_2$, > 99%), trioctylphosphine (TOP, 90%), 1-octadecene (ODE, 90%), cesium carbonate ($CsCO_3$, 99.99%) were purchased from Alfa Aesar. Oleylamine (OAm, 70%), oleic acid (OA, 90%) were purchased from Aldrich. All chemicals were used without further purification.

2.2. Synthesis of Mn:$CsPbCl_3$ NCs

The Mn:$CsPbCl_3$ NCs were synthesized by a facile one-pot injection approach reported previously [24]. In brief, a mixture of 2 mmol of $PbCl_2$ and 5 mmol of $MnCl_2$ was added to a 50 mL three-necked flask containing 1 mL of TOP, 1.5 mL of OAm, 1.5 mL of OA, and 5 mL ODE and degassed at room temperature for 30 min. The reactants were then heated up to 108 °C under argon flow, and degassed again for removing bubbles. When the temperature was elevated to 190 °C under argon, the Cs-oleate precursor was rapidly injected into the mixture, maintaining for 1 min to grow Mn^{2+}:$CsPbCl_3$ NCs, followed by an ice bath to terminate the reaction. The Mn:$CsPbCl_3$ NCs with Mn/Pb feed molar ratio of 1:1 and 5:1 were also synthesized, maintaining the total molar amount of Pb^{2+} unchanged. The obtained NCs were collected by centrifugation at 7000 rpm for 5 min and dispersed in hexane.

2.3. Fabrication of Mn:$CsPbCl_3$ NC films with/without PDMS

For fabrication of pure NC films, 0.2 mL (25 mg/mL) of the as-synthesized Mn:$CsPbCl_3$ NCs with Pb^{2+}/Mn^{2+} molar ratio of 2.5:1 were dropped on a silicon substrate, and heated at 50 °C for 30 min. The NC based PDMS films were fabricated by the same procedure by adding 0.25 mL (200 mg/mL) of PDMS (in hexane) to 0.2 mL Mn:$CsPbCl_3$ NC solution. These films were named as NC and NC/PDMS films, respectively.

2.4. Fabrication of NC/PDMS based white LEDs

The white LEDs were fabricated by combining Mn:$CsPbCl_3$ and Cu:ZnInS/ZnS NC PDMS films on InGaN-based blue-emitting chip (Sanan Optoelectronics, China). Briefly, a solution of Mn:$CsPbCl_3$ NCs (2 mL) was mixed with Cu:ZnInS/ZnS NCs (1.5 mL, 10 mg/mL) in hexane and added slowly to 0.3 g of the PDMS agent (Sylgard184, Dow Corning, China). The mixture was stirred vigorously until homogeneous and kept at 50 °C in vacuum for 10 min to increase the viscosity. The obtained LEDs were put into a vacuum oven at 60 °C for 2 h and finally cooled down to room temperature.

2.5. Characterization

A Shimadzu UV-2700 spectrophotometer was used to measure the UV–vis absorption spectra of Mn:$CsPbCl_3$ NCs. The steady-state and time-resolved PL spectra as well as PL QYs were recorded by a Horiba Jobin Yvon Fluorolog-3 spectrometer with a QY accessory and a time-correlated single-photon counting (TCSPC) system. A pulsed xenon lamp or a NanoLED (N-405L or N-300) was utilized as the excitation source for time-resolved PL spectrum measurement. A 150 W ozone-free xenon arc-lamp was employed as the continuous excitation source. Transmission electron microscopy (TEM, JEM 2010, 120.0 kV) was used to observe the morphology of the NCs. High-resolution scanning electron microscopy (SEM, JSM 7401F, 15.0 kV) was used to measure the thickness of doped NC films. XRD patterns were acquired by a Rigaku D/max-2500 diffractometer with Cu Kα1 radiation (λ = 0.154187). The temperature-dependent PL measurements were carried out by mounting the samples on a vacuum liquid nitrogen cryostat (Janis VPF-500) with a temperature controller. The chromatic and photometric properties of white LEDs were studied by an Ocean Optics USB-4000 spectrometer.

3. Results and discussion

The used Mn:$CsPbCl_3$ NCs were obtained with different Mn^{2+} nominal concentrations by selecting Mn^{2+}/Pb^{2+} feed molar ratios of 1:1, 2.5:1, and 5:1. Fig. 1 shows the absorption and PL spectra of Mn:$CsPbCl_3$ NCs with various Mn^{2+} doping concentrations. Their first excitonic absorption peaks located at around 402, 398, and 378 nm, respectively. The blue-shift of absorption peaks with higher Mn^{2+} concentrations might be attributed to the lattice contraction when Pb^{2+} is substituted by Mn^{2+} and the effect of Mn^{2+} alloying with the host $CsPbCl_3$ [36].

Upon UV excitation at 365 nm situated above their band-gap absorption, two featured luminescence peaks centered at ~ 400 nm and ~ 600 nm are observed in each PL spectrum as shown in Fig. 1, in line with previous report about Mn:$CsPbCl_3$ NCs [24]. The former dominant narrow emission can be ascribed to the excitonic luminescence, which is shifted to the blue with increasing the Mn^{2+} doping. While the later broad emission band is considered to originate from the parity- and spin-forbidden ${}^4T_{1g}{\rightarrow}{}^6A_{1g}$ d-d transition of Mn^{2+} with a red-shift from 598 to 615 nm, accounting for the formation of Mn^{2+}-Mn^{2+} pairs at higher doping level [37–42]. The red-shift in PL emissions was also observed in organometallic perovskites and traditional II-VI NCs by increasing the Mn^{2+} doping concentration [43]. Apparently, the

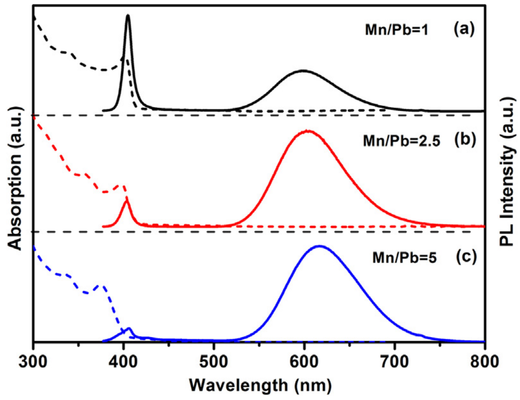

Fig. 1. The absorption (dashed black, red, and blue lines) and PL (solid black, red, blue lines) spectra of Mn:$CsPbCl_3$ NCs with Mn/Pb molar ratios of 1:1 (a), 2.5:1 (b) and 5:1 (c), respectively, in hexane at room temperature. The excitation wavelength is 365 nm.