Stable near white light emission in CsPbCl$_3$ perovskite quantum dots by incorporating Al$^{3+}$/Mn$^{2+}$ ions

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Abstract

All inorganic cesium lead halides (CsPbX$_3$, X = Cl, Br, I) are promising materials and have been developed in recent years for various optoelectronic devices and applications because of their excellent optoelectronic properties. Regardless of their excellent characteristics their stability is still uncertain and it is a challenging task to obtain stable emission in CsPbX$_3$ perovskite quantum dots (PQDs), hence limiting their practical optoelectronic application. In this context, several approaches have been used like an-ion exchange, ion doping, and core–shell structure to enhance PQDs stability. Herein, we synthesized dual ion co-doped Al$^{3+}$/Mn$^{2+}$ CsPbCl$_3$ PQDs for stable light emitting diodes through traditional hot injection method for the first time. By adjusting molar concentration of Al$^{3+}$/Mn$^{2+}$ CsPbCl$_3$, co-doped PQDs were successfully prepared. The co-doped PQDs exhibit tunable emission, covering a wide range under UV excitation. Moreover, these high luminescent co-doped PQDs were used to fabricate WLEDs, displaying stable near white light emission with the chromaticity coordination at (0.35, 0.28). Some new evidence has emerged, although some aspects of Mn$^{2+}$/Al$^{3+}$ doping are considered to be consistent with previous conclusions. This viewpoint incorporates all of these details and focuses on the path of transition metal ion doping to perovskite nanostructures and offers an overview for possible potential studies.

1. Introduction

Recent research has proven that all inorganic cesium lead halide PQDs become a kind of novel material for optoelectronic devices and gain much attention for its remarkable properties such as narrow bandgap, adjustable emission and excellent photoluminescence quantum yields (PLQYs) [1]. The focal point of CsPbX$_3$ PQDs is that their bandgap can be very easy to switch through adjusting their ions [2–4]. These outstanding features provide a way for possible applications in the field of lighting equipment’s and devices [5–7]. Despite of all these advantages, there are still some drawbacks such as poor stability and toxicity is also an important issue. It is still a challenging task to attain stable multi-color and white light emission [8, 9]. In order to attain stable white light emission, red, orange and blue emissions are crucial, but CsPbBr$_3$/I$_3$ PQDs emit very weak red light under extreme circumstance, and their structure weaken due to the presence of water and oxygen in surroundings which causes photo oxidation [10–13]. Impurity ions doping and alteration is known to be an efficient and practical way for protecting PQDs structure from photo oxidation which will help in extending and enhancing the PQDs optical properties [14]. Recent studies on PQDs have proven that doping of transition metal ions into perovskites semiconductor can effectively regulate the optical properties of PQDs [15–19]. In this context Mn$^{2+}$ doping in PQDs showed an extensive potential due to their minimum self-quenching emission characteristics [20]. Mn$^{2+}$ emission in doped PQDs give red-orange color, which is driven from the Mn$^{2+}$ d–d transition states by energy transfer from excitons in the host to Mn$^{2+}$ dopants [20–24]. The wavelength emission...
of Mn$^{2+}$ can be from 590 nm to 630 nm by regulating the doping ratios [20, 23, 25, and 26]. Yang group successfully substituted Pb$^{2+}$ ions with Mn$^{2+}$ ions in CsPbCl$_3$ PQDs. The PQDs show red emission at 600 nm which was driven from the intrinsic transition of Mn$^{2+}$ ions and also exhibit enhanced PLQYs from 5% to 54%. Another group, Klimov’s, stated that the PQDs doped with Mn$^{2+}$ ions and its perovskite NC host band gap differed regularly [27, 28]. Moreover, the effect of doping on the charge transfer of perovskite has also been studied by incorporation of Bi$^{3+}$ ions in CsPbBr$_3$ PQDs through ultrafast spectroscopy investigation [29]. De et al suggested that the CsPbCl$_3$ PQDs PLQYs were tremendously enhanced from 92%—98% by doping of CuCl$_2$ [30]. Mondal et al states that the PLQYs of CsPbCl$_3$ PQDs were improved by post treatment of CdCl$_2$ to near-unity [31]. The PLQYs and stability of CsPbX$_3$ (X = Cl, Br, or I) NCs were improved together by incorporation of ZnX$_2$ [32]. Doping and post-treatment with metal halide salts also taken the exciton PLQYs with CsPbX$_3$ PQDs to near-unity [12]. It is obvious that the passivation of the number of traps/defects as non-radiative recombination centres could effectively enhance the effectiveness of the energy transfer from the host exciton to Mn$^{2+}$ with the exciton relaxation pathways and increase the performance of the Mn$^{2+}$ emission in the doped PQDs. Whereas, aluminium is known as the one of earth-abundant elements belonging to IIIA group in periodic table, typically it can used in GaN-based blue light emission diodes. Generally, aluminium loses its three outermost electrons and becomes aluminium (III) ions Al$^{3+}$ to a stable oxidation state [33]. It is important to investigate the improved luminescence and stability of CsPbCl$_3$ PQDs by incorporation of transitional metal ions.

Taking advantage of Mn$^{2+}$ and Al$^{3+}$ herein, we are reporting a facile way to achieve stable white emission in CsPbCl$_3$ PQDs through incorporation of Al$^{3+}$/Mn$^{2+}$, for the first time in the best of our knowledge, through traditional hot injection method. The PL spectra, UV Absorbance and PL decays with different molar concentration were studied. Obvious transition in optical performances was observed. As a result of the low intensity levels in these co-doped ions, the emitting peaks were restricted to move in a few particular wavelength regions [3]. The collaboration between the exciton transition of the host CsPbCl$_3$ PQDs and the intrinsic emissions of the doped metal ions has successfully achieved white light emission, and an effective energy transfer has also been observed between them [1]. This viewpoint incorporates all of these details and focuses on the path of transition metal ion doping to perovskite nanostructures and offers an overview for possible potential studies.

2. Experimental section

2.1. Materials and chemicals

Cesium carbonate (Cs$_2$CO$_3$, 99.995%), lead (II) chloride (PbCl$_2$, 99.999%), Manganese (II) chloride (MnCl$_2$, 99.999%), Aluminium chloride (AlCl$_3$, 99.999%), Oleic acid (OA, 90%), Oleylamine (OLA, 98%), 1-Octadecene (ODE, 90%), TOP (Tri-n-octylphosphine, 90%) were purchased from Aladdin. Ethyl acetate, n-hexane from Shanghai Chemical Industrial Company. All reagents were used without further purification.

2.2. Preparation of Cs-oleate

0.4 mmol Cs$_2$CO$_3$, 1.25 ml OA and 10 ml ODE were mixed into a 100 ml three-neck flask and magnetic stirring continues until the reaction mixture became transparent. The whole process was done under Ar gas environment.

2.3. Synthesis of Un-doped CsPbCl$_3$ PQDs

0.105 g of PbCl$_2$ and 10 ml of ODE were added in a 100 ml three-neck flask and stirred in vacuum condition at 120 °C for approximately 1 h, then 1 ml of OLA, 1 ml of OA and 0.5 ml of TOP were added in to the flask. The temperature was risen to 200 °C. Subsequently 0.8 ml of Cs-oleate were added in to the system, and the resulting PQDs solution was cooled in ice-water bath.

2.4. Synthesis of Mn$^{2+}$ ion doped CsPbCl$_3$ PQDs

Various amount of MnCl$_2$ (0.05 g, 0.1 g, 0.2 g and 0.3 g) and 0.105 g of PbCl$_2$ were added with 10 ml of ODE in a 100 ml three-neck flask and stirred at 120 °C. Then, 1 ml of OLA and 1 ml of OA 0.5 ml of TOP were injected into the system and then the temperature was risen to 200 °C. Lastly, 0.8 ml of hot Cs-oleate solution was injected, and then PQDs solution was cooled down using water bath was finally stored in different bottles for further characterization.

2.5. Synthesis of Co-doped Al$^{3+}$/Mn$^{2+}$ ion doped CsPbCl$_3$ PQDs

Fixed amount i-e 0.1 g of AlCl$_3$, 0.105 g of PbCl$_2$ and particular amount of MnCl$_2$ (0.5 g, 0.1 and 0.2 g and 0.3 g) was mixed with 10 ml of ODE in a 100 ml three neck flask and degassed under vacuum at 120 °C. Next, 1 ml of OLA and 1 ml of OA, and 0.5 ml of TOP were added into the system and temperature was increased to 200 °C.
When solution became transparent, 0.8 ml of hot Cs-oleate was added into the system and the reaction mixture was cooled down using water bath. Finally stored PQDs in different bottles for further characterization.

2.6. Purification

The crude of all as-prepared PQDs was purified by using centrifugation machine at 6500 rpm for 8 min with n-hexane (1:1 v/v) and ethyl acetate (1:2 v/v), followed by re-dispersion in n-hexane for further analysis.

2.7. Characterization

X-ray diffraction (XRD) patterns was performed using a D/Max 2400 x-ray diffraction meter with Cu Kα (40 kV, 100 mA) irradiation (\(\lambda = 1.5406 \text{ Å}\)). Absorbance spectra were measured using Jasco V-570 UV/vis/NIR spectrophotometer, which has a wavelength ranging from 190 to 2500 nm. Photoluminescence (PL) spectra of the samples were calculated with Gilden Photonic Sens-9000 with xenon lamp as the excitation source. For time-resolved PL (TRPL) measurements, the samples were excited by 375 nm dye laser with pulse width of 0.8 ns and equivalent power of about 1 mW. Intensities were normalized, and all curves were fitted by using bi-exponential function to calculate average lifetimes. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were observed on a JEM-2100F transmission electron microscope with an accelerating voltage of 200 kV. EDS mapping was also performed using same equipment. X-ray photoelectron spectroscopy (XPS) was measured by Kratos Axis Ultra DLD, using mono Al Kα operated at 150 W. The emission spectra of the WLEDs were tested by the Micro Fibre spectrometer HRUSB2000+.

3. Results and discussion

3.1. Optical properties

Mn\(^{2+}\) has an electronic state of d\(^5\), and its luminescence emissions is referred to the transition of d-d parity that is strongly influenced by crystal state. The photoluminescence of Mn\(^{2+}\) is due to the transformation of 4T\(^1\) (4G) to 6A\(^1\) (S) and its crystal field mainly depends on the photoluminescence magnitude and wavelength \[12, 34, 35\]. The condition of co-doping with other cations in CsPbCl\(_3\) PQDs can be determine by the coordination numbers of elements which are Cs\(^+\) = 12, Pb\(^{2+}\) = 6 and Cl\(^-\) = 6, respectively. The tolerance factor \(t\) can be calculated by given equation (1) \[12, 36\]

\[
t = \frac{R_{\text{Cs}} + R_{\text{Cl}}}{\sqrt{2} \times (R_{\text{Pb}} + R_{\text{Cl}})}
\]

Similarly, Cs ionic radius is equal to 1.88 Å, Pb ionic radius is calculated as 1.19 Å and for Cl\(^-\) it is equal to 1.81 Å, and ionic radius of CsPbCl\(_3\) is equal to 0.87 Å. Whereas Mn\(^{2+}\) has Ionic radius of 0.83 Å and Al\(^{3+}\) has 0.54 Å. To get stable perovskite structure tolerance factor \(t\) should be closer to 1, hypothetically \(t\) should be in between 0.8 to 1.1 otherwise, cation is crucial to be doped into CsPbCl\(_3\) PQDs, since \(t\) (CsPbCl\(_3\)) is 0.87 which is less than 1 and close to 0.8, the cation smaller than Pb\(^{2+}\) is more suitable to incorporate such as Al\(^{3+}\) and Mn\(^{2+}\) in CsPbCl\(_3\) PQDs \[36\]. In order to get more stable PQDs structure, we incorporated Mn\(^{2+}\) ions in CsPbCl\(_3\) and then Co-doped Mn\(^{2+}\)/Al\(^{3+}\) ions. Firstly, optical properties of as-prepared un-doped samples were investigated. It can be shown in (figure 1(a)) un-doped CsPbCl\(_3\) PQDs emit bright blue light with the strong emission spectrum and FWHM is 15 nm, which was consistent with the previous findings \[37\]. Figure 1(b) shows a precise absorption peak with shortened wavelength and PL emission, which can be analysed on the basis of the exciton binding strength. The un-doped CsPbCl\(_3\) PQDs shows an extreme absorption band centred at 409 nm and energy bandgap is equal to 2.48 eV.
significantly which suggests that the energy of the band-edge excitonic energy and size of NPLs are maintained in all samples [14]. Mn-doped CsPbCl₃ PQDs show an apparent shift from blue towards orange color in band-edge emission peaks at an increased concentration ratio of Mn²⁺ in CsPbCl₃ PQDs.

The emission of the perovskite exceeds the max wavelength of about 422 nm, when the Mn²⁺ ion concentration increases. Further increasing molar concentration of Mn²⁺ does not significantly alter the wavelength. Whereas, Mn emission wavelength is independent of the Mn²⁺ ion doping concentration in the perovskite host, while the emission intensity depends on it. The PL time decay curves are calculated by bi-exponential function given in equation (2) and the average lifetimes are calculated by equation (3). B(t) is the PL intensity, B₁ and B₂ are the weight of slow decay and long decay, τ₁ and τ₂ are the time constant respectively [37].

$$B(t) = \frac{B_1 e^{-t/\tau_1} + B_2 e^{-t/\tau_2}}{B_1 + B_2}$$

$$\tau_{avu} = \frac{B_1 \tau_1^2 + B_2 \tau_2^2}{B_1 \tau_1 + B_2 \tau_2}$$

Figure 2(c), shows a monotonous decline in lifetimes. On increasing the amount of Mn²⁺ ion doping concentration, the average lifetime shows a decreasing trend as compare to un-doped CsPbCl₃ PQDs. When Mn²⁺ is 0.3 g the average time decay is 18.1 ns. Detailed PL time decay are shown in table 1.

As discussed earlier that Al³⁺ is much suitable to incorporate in CsPbCl₃ PQDs because of its ionic radius which is smaller than the tolerance factor of CsPbCl₃. We propose and investigate an alternative blue-emissive transition material by adding Al³⁺ ions with Mn²⁺ ion in CsPbCl₃ PQDs. The Mn²⁺ ion doping amounts were 0.05 g, 0.1 g, 0.2, and 0.3 respectively, while Al³⁺ ion doping concentration is fixed i.e 0.1 g. After incorporating Al³⁺ and Mn²⁺ ions in CsPbCl₃ PQDs, an alluring emission features. As shown in (figure 3(a)). PL emission spectra of co-doped PQDs, are presented. We can see similar double emission peaks of every sample, a blue

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**Table 1.** Detailed PL time decay of Mn-doped CsPbCl₃ PQDs.

| Un-Doped | 0.3 Mn Doped | 0.2 Mn Doped | 0.1 Mn Doped | 0.05 Mn Doped |
|----------|-------------|-------------|-------------|--------------|
| τ₁ = 12.5 ns | τ₁ = 9.0 ns | τ₁ = 9.68 ns | τ₁ = 10.79 ns | τ₁ = 11.6 ns |
| τ₂ = 65.5 ns | τ₂ = 40 ns | τ₂ = 50.9 ns | τ₂ = 48.62 ns | τ₂ = 50.01 ns |
| τ₂ = 43.9 | τ₂ = 39.2 | τ₂ = 45.90 | τ₂ = 50.9 | τ₂ = 54.0 |
| τ_{avg} = 35 ns | τ_{avg} = 18.1 ns | τ_{avg} = 27.8 ns | τ_{avg} = 29.5 ns | τ_{avg} = 32.2 ns |

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**Figure 2.** Optical characterization of Mn-doped CsPbCl₃ PQDs. (a) PL spectra with different Mn²⁺ doping concentration. (b) UV–vis Abs of Mn²⁺ doped CsPbCl₃. (c) Time resolved photoluminescence decays of Mn²⁺ PQDs monitored at 375 nm.
emission peak and an orange emission which later on will convert to near white emission by increasing doping concentration. The blue emission peaks starts from 420 to 428 nm. The co-doped PQDs exhibits an intense orange emission between 570 and 600 nm because of exciton transition of perovskite host and associated with Mn incorporation. The co-doped PQDs exhibits an intense emission peak and an orange emission which later on will convert to near white emission by increasing doping concentration. The blue emission peaks starts from 420 to 428 nm. The co-doped PQDs exhibits an intense orange emission between 570 and 600 nm because of exciton transition of perovskite host and associated with Mn incorporation.

To know comprehensive structural details of all as-prepared samples, XRD was performed. As shown in figure 3(b), all prepared samples un-doped, Mn doped and co-doped PQDs show well-defined peaks, verifying that they were highly crystallized in nature. All diffraction patterns were according to the standard XRD pattern of cubic CsPbCl₃ PDF #18-0366. After doping, no extra peaks or major variations were found. This suggests that incorporation of Mn₂⁺ ions didn’t affect the PQDs resulting cubic structure. However, we’ve seen a slight change in the main XRD peak position, which is due to the change in the PQDs unit cell. The crystalline lattice constants for the un-doped and Mn doped PQDs (100), (110), and (200) diffraction patterns are shown in table 3. As shown in (figure 4(b)) changes are not seen and according to the standard PDF # 18-0366 CsPbCl₃ PQDs. The (100) diffraction plane shows a slight shift certainly to the larger diffraction angle, and the lattice constants of the (110) and (200) diffraction planes decreased with the Mn²⁺ ion doping concentrations are shown in table 4. This suggests that the cubic and crystalline structure of the co-doped PQDs was further contracted by the incorporation of guest ions.

### Table 2. Detailed PL Time Decay of Co-doped CsPbCl₃ PQDs.

| Mn Doped Concentration (%) | τ₁ (ns) | τ₂ (ns) | τ₃ (ns) | τ₄ (ns) |
|---------------------------|---------|---------|---------|---------|
| Un-Doped                  | 12.5    | 65.5    | 36      | 45.3    |
| 0.05 Mn Doped             | 12      | 32.5    | 43.9    | 49.2    |
| 0.1 Mn Doped              | 9       | 18      | 48      | 62      |
| 0.2 Mn Doped              | 4       | 18      | 53.31   | 4.3     |
| 0.3 Mn Doped              | 4 ns    | 25      | 53.31   | 4.3     |

Table 2 shows the PL lifetime of Co-doped CsPbCl₃ PQDs monitored at 375 nm.
The transmission electron microscopy (TEM) photographs of all 3 states are shown in (figures 5(a)–(c)). The average particle size of Un-doped CsPbCl₃ is 0.42 nm which shows slight contraction after Mn²⁺ doping. Whereas after Co-doing Al³⁺ and Mn²⁺ the average particle size is around 0.40 nm which is due to incorporation of smaller ionic radius of Al³⁺. Figures 5(d)–(f) show high resolution transmission electron microscopy (HRTEM) images of un-doped, Mn-doped and Co-doped CsPbCl₃ PQDs.
microscopy (HRTEM) images. TEM findings also consistent with our XRD results. Such observations also indicate that these cations are successfully doped into CsPbCl$_3$.

Energy dispersive x-ray spectroscopy (EDS) mapping was done to check the incorporation and distribution of all possible elements present in PQDs. The EDS mapping images are shown in (figure 6). To obtain statistically valid results, EDS mapping was performed on specific area having large number of PQDs. The EDS results prove that Mn$^{2+}$ and Al$^{3+}$ are doped in the CsPbCl$_3$ PQDs in intermediate concentrations. Moreover, no signs were observed for phase segregation or surface preference, which concludes that the distribution of the guest ions are uniform and consistent. It could be seen Cs$^+$, Pb$^+$, Cl$^-$, Al$^{3+}$, and Mn$^{2+}$ all possible components have simple elemental profiles around the co-doped monodisperse CsPbCl$_3$ PQDs. EDS mapping proves that the presence of Al and Mn elements in the CsPbCl$_3$ PQDs, which is also valid proof of successful doping. We may contemplate that Al and Mn ions are co-doped into CsPbCl$_3$ PQDs and Mn$^{2+}$ substitutes Cs$^+$ ions partially, and most Al$^{3+}$ ions remain on the surface of the PQDs. Furthermore XPS survey and EDS graphs also show a valid evidence of successful incorporation in CsPbCl$_3$ PQDs. (see supporting information S1, S2 (available online at stacks.iop.org/NANOX/1/030033/mmedia))

### 3.3. Device fabrication and stability

We further fabricate WLED device to validate as-prepared PQDs are good for commercial LEDs and tested with tunable color temperatures from 19000 K to 4250 K. For the device fabrication, We adopted previous reported method used by our group zhang et al [37]. As-prepared PQDs were blended with PMMA chloroform solution and were spin coated at 1500 rpm on flexible PET substrate. In addition to coat larger area, we can use doctor blade technique finally, the PET films were cut into a suitable size as $3' \times 4\ mm^2$, and packaged in a tube shell and with the help glue paste these shell on UV LEDs for exciton. These LEDs were further tested to measure color coordinates. The (CIE) color coordinates of un-doped Mn doped and co-doped CsPbCl$_3$ PQDs are (0.22, 0.14) (0.50, 0.40) (0.35, 0.28) respectively under an excitation of 365 nm. The concentration of doping for near white light emission is 0.1 g of Al$^{3+}$ and 0.3 g Mn$^{2+}$ respectively. Figure 7(a) shows CIE coordinates of all three states. Inset is the photographic representation of all 3 states PQDs under 365 nm UV light, PET film and working WLED. Furthermore, the stability of as-prepared PQDs were constantly monitored by measuring their PL intensity, which has been frequently used in previous work [39]. As shown in (figures 7(b), (c)). PL emission of Mn$^{2+}$ doped and co-doped CsPbCl$_3$ samples reveal that prepared PQDs are stable and have strong emission. We noted that Mn$^{2+}$ doped peaks centred at 415, 600 nm and after 36 h, it’s around 400, 580 nm, whereas, Al$^{3+}$ co-doped PQDs were at 428, 590 nm and remains stable after 36 h with a slight change. From these findings, we may conclude that co-doped CsPbCl$_3$ PQDs are more stable as compare to Mn doped. (See supporting information S3 for different concentration of co-doped PQDs under UV light and WLED working device)

### 4. Conclusions

In summary we have successfully incorporated Mn$^{2+}$ & Al$^{3+}$ ion in CsPbCl$_3$ PQDs for the first time by hot injection technique. Structural morphology was characterized by XRD TEM and EDS mapping, while optical properties were measured through PL spectra and Absorbance spectra. Results show that doping of these elements did not change its cubic structure. Furthermore we noticed reduced average particle size of CsPbCl$_3$ PQDs and PL time decay was greatly reduced after incorporation of Al$^{3+}$. Stable near white light emission was
successfully achieved with this incorporation. WLEDs were also fabricated and tested. The CIE chromaticity coordinates for near white light were at \((0.35, 0.29)\) and the color temperature of 5261 K was obtained. Results suggest that prepared Co-doped PQDs are stable and an ideal candidate for future optoelectronic applications.

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Conflicts of interest

There are no conflicts to declare.

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Figure 7. The optical performance of WLED. (a) CIE chromaticity of un-doped Mn-doped and co-doped PQDs. Inset is the photographic representation of all states PQDs, PET film and working WLED. (b) PL spectra as a function of time for Mn-doped PQDs. (c) PL spectra as a function of time for co-doped PQDs.
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