Phase transition and energy transfer of lead-free Cs$_2$SnCl$_6$ perovskite nanocrystals by controlling the precursors and doping manganese ions

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ABSTRACT
Perovskite quantum dots (QDs), such as all-inorganic CsPbX$_3$ ($X$ = Cl, Br, or I), are novel fluorescent semiconductor nanocrystals (NCs) that have attracted tremendous attention due to their excellent optical properties and great applications (e.g. display backlights, light-emitting diodes, and photodetectors). The instability and toxicity of lead-based perovskite QDs, however, are intrinsic defects that obstruct their application and commercialization. Poison is released from the lead of the unstable CsPbX$_3$ NCs, which are generally ascribed to the labile surface, ionic character, and metastable structure. In this work, lead-free Cs$_2$SnCl$_6$ perovskite NCs are successfully synthesized via hot injection. Particularly, by controlling the different precursor ratios, phase transition (CsCl to Cs$_2$SnCl$_6$) was clearly observed from X-ray diffraction (XRD) measurements. The Cs$_2$SnCl$_6$ NCs exhibited a highly efficient deep-blue emission at 425 nm, with a 55 nm Stokes shift and an 84 nm full width at half maximum (FWHM). After doping Mn ions, the preferred formation of CsSnCl$_3$:Mn$^{2+}$ with double-wavelength emission was demonstrated based on the XRD and photoluminescence spectra. The study showed that doping synthesis should be widely used in lead-free perovskite NCs as an important strategy for next-generation solid-state lighting.

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1. Introduction
Perovskite quantum dots (QDs) were named such due to the calcium titanium oxide (CaTiO$_3$) mineral, which was found by L.A. Perovski (a Russian mineralogist), because the two materials possess the same perovskite structure [1]. Lead halide perovskites (LHPs) instead crystallize in the form of a colloidal APbX$_3$-type perovskite lattice, such as hybrid organic–inorganic [CH$_3$NH$_3$PbX$_3$ or CH(NH$_2$)$_2$PbX$_3$] LHPs and all-inorganic CsPbX$_3$ LHPs (where $X$ = Cl, Br, or I), have been intensively investigated of late [2–5]. The cesium lead halide (CsPbX$_3$) perovskite QDs have become promising materials for light-emitting diodes (LEDs), solar cells, and laser due to their superior optical properties, including high photoluminescence quantum yield (PLQY; up to 90%), narrow full width at half-maximum (FWHM; down to 50 nm), small exciton binding energy, and tunable full visible spectrum (380–780 nm), achieved by controlling the halide ion composition and through size modification [5–15].

Unfortunately, the relatively low stability and serious toxicity of the Pb$^{2+}$ ions of lead-based colloidal perovskite nanocrystals (NCs) are major challenges for their practical application [16,17]. Many strategies have been developed to resolve and ameliorate these issues. First, surface ligand modification methods, such as the use of tightly bound ligands [poly(maleic anhydride-alt-1-octadecene); PMA], ligand replacement (alkyl phosphinic acid), and crosslinking intermolecular C = C bonding, can enhance the stability of CsPbX$_3$ NCs through various synthetic processes [18–20]. Second, the core–shell structure has contributed to the stabilization and application of CsPbX$_3$ NCs by encapsulating the SiO$_2$ or polystyrene matrix [21,22]. As a result, the core–shell nanoparticles (NPs) display excellent stability against long-term storage in air and dispersion in the aqueous solution. Third, during the chemical reaction, benzoyl or zinc halides can be efficiently used as halide sources to synthesize the stable CsPbX$_3$ NCs due to metal carboxylate formation and surface passivation [23,24].
The structural and optical characterizations indicate that the alternative halide-based CsPbX₃ NCs are highly stable, without distinct changes in the X-ray diffraction (XRD) results, photoluminescence (PL), particle size, and morphology under ambient air conditions. Fourth, an effective manganese substitution strategy can also significantly stabilize the crystal lattices of CsPbX₃:Mn²⁺ perovskite QDs for improving their optical performance and thermal stability. The lattice contraction and the increase in formation energy are major reasons for the formation of stable CsPbX₃:Mn²⁺ QDs [25].

Metal halide perovskite NCs predominantly rely on the adoption of lead halides (PbX₂, X = Cl, Br, I) as the divalent metal precursors, but there are rising concerns about the hazards that lead poses to the environment and human health, and also about its being an obstruction in the application of Pb-based perovskite NCs. As such, much effort has been devoted to the exploration of Pb substitutes with nontoxic elements that have an analogous electronic band structure, such as Sn, Ge, Bi, and Sb [26–29]. For instance, the structural and optical properties of A₃SnX₉, A₃Bi₂X₉, and A₃Sb₂X₉ (A = Cs or Rb; X = Cl, Br, I) lead-free perovskite QDs have been reported [30–36], but these lead-free perovskite QDs generally show low PLQY and poor stability, which give rise to their intrinsic shortcomings, including vulnerability to oxidation, undesirable ionic conductivity, large band gap, and many surface defects.

In this work, blue-emission Cs₂SnCl₆ NCs were successfully synthesized through a modified precursor-assisted hot-injection method. The specific phase transition from CsCl to Cs₂SnCl₆ was proven based on the XRD results. The Mn-doped mechanism of Cs₂SnCl₆ has not been reported to date. Especially, bright Mn²⁺ red emission was discovered in the preferred blue-emission CsSnCl₃ host when Mn ions were gradually doped into the Cs₂SnCl₆ matrix. The spectrum is ascribed to the energy transfer from the CsSnCl₃ host to the Mn²⁺ activators with d–d orbital transition. These Sn-based perovskite NCs exhibited high air stability due to the strategy. Hence, highly efficient lead-free perovskite NCs will be the target of the next indispensable work.

2. Experiment
2.1. Chemicals

Cesium carbonate (Cs₂CO₃, Alfa Aesar, 99%), oleic acid (OA, Sigma-Aldrich, 90%), oleylamine (OAm, Sigma-Aldrich, 70%), octadecene (ODE, Sigma-Aldrich, 90%), tin(II) chloride dehydrate (SnCl₂, Alfa Aesar, 99%), tin(IV) chloride (SnCl₄, Acros, 99.999%), manganese chloride tetrahydrate (MnCl₂·4H₂O, Sigma-Aldrich, ≥ 98%), and hexane (C₆H₁₄, Acros organics, 96%) were purchased from commercial sources and used without further purification.

2.2. Preparation of cesium oleate

A 0.4M Cs-oleate solution was prepared in a 50 mL three-neck flask by mixing cesium carbonate (0.8140 g) with ODE (10 mL) and OA (2.5 mL). The mixture was degassed under vacuum at 120°C for 1 h, and was subsequently heated to 150°C under N₂ flux until the solution appeared clear.

2.3. Synthesis of undoped and Mn-doped Cs₂SnCl₆ NCs

In a representative synthesis, SnCl₂ (0.08–0.36 mmol), 7 mL ODE, 0.5 mL OA, and 0.5 mL OAm were loaded onto a 25 mL three-neck flask. The reaction vessel was heated to 230°C under N₂ flow for 3 h, at 100°C. The reaction vessel was heated to 230°C under N₂ flow, and then 0.4 mL Cs-oleate was swiftly injected into the flask. The reaction was quenched after 10 min by cooling through an ice water bath. The product solution was centrifuged at 4000 rpm for 10 min, and the supernatant was subsequently discarded. Then the precipitated NCs were redispersed in hexane. Furthermore, Cs₂Sn₁₋ₓMnₓCl₆ (x = 2, 4, and 6%) samples were prepared following the same steps, except that the desired amount of MnCl₂•4H₂O was added to the starting reaction mixture.

2.4. Characterization methods

XRD analysis was performed on a Bruker D2 Phase X-ray diffractometer equipped with monochromatic Cu Kα radiation (λ = 1.54056 Å) operating at 30 kV and 10 mA in transmission mode. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) images were collected by a JEM2100F electron microscope with a 200 kV accelerating voltage. These samples were prepared by dropping dilute suspensions of NCs onto the carbon-coated copper grids. The UV-visible absorption spectra were collected using a JASCO V-730 spectrophotometer in absorption mode. The PL spectra of the samples were recorded with a FluoroMax-4 HORIBA spectrophotometer equipped with an Xe lamp and a photomultiplier tube. The X-ray photoelectron spectroscopy (XPS) spectra were measured on a VG scientific ESCALAB 250 spectrometer equipped with twin aluminum-magnesium anodes, using monochromatic Al Kα X-ray radiation (hv = 1486.6 eV). The samples were gently spread over
3. Results and discussion

The synthesis of lead-free perovskite NCs was performed using a modified precursor-assisted hot-injection method. The XRD patterns of the as-prepared samples with different Cs:Sn precursor ratios indicate that cubic perovskite structures were formed in the pure CsCl phase, the co-existing CsCl and Cs$_2$SnCl$_6$ phases, and the pure Cs$_2$SnCl$_6$ phase, as shown in Figure 1. Interestingly, distinct phase transition (CsCl → Cs$_2$SnCl$_6$) was observed in the formation procedure of pure Cs$_2$SnCl$_6$ NCs, which can be indexed to the planes of cubic space group Fm-3m (ICSD #9023). The initial product CsCl with space group Pm-3m (ICSD #53847) consisted of a stoichiometric (Cs:Sn = 1:0.5) molar ratio and was gradually transformed into the primary product Cs$_2$SnCl$_6$ (Cs:Sn = 1:1.5–2.25) when the molar ratio of tin increased.

The synthesized perovskite NCs with different Cs:Sn molar ratios, and standard patterns for CsCl (ICSD #53847) and Cs$_2$SnCl$_6$ (ICSD #9023).

The sliding glass and were put inside a vacuum chamber for XPS measurements.
Figure 2(a and b) show the transmission electron microscopy (TEM) images of the pure Cs$_2$SnCl$_6$ NCs with a Cs:Sn = 1:1.75 precursor ratio. The spherical-like NCs have well-defined diameters with < 100 nm lengths, larger than the typical CsPbX$_3$ perovskite QDs (size: 4–15 nm) obtained from the common OA/OAm ligand solution. The crystallinity was clearly verified by high-resolution TEM (HRTEM) with a 3.76 Å interplanar distance (Figure 2(c)), which consists of the face-centered cubic phase. In Figure 2(d), the selected-area electron diffraction (SAED) pattern of the Cs$_2$SnCl$_6$ NCs reveals the presence of (-20-2), (02-2), and (220) planes of the cubic phase, further verifying the formation of a perovskite structure.

To understand the photophysical properties of Cs$_2$SnCl$_6$ NCs, the UV-visible absorption and PL spectra were measured under ambient atmosphere, and are shown in Figure 3(a). The pristine Cs$_2$SnCl$_6$ NPs show a precipitous optical absorption edge at 316 nm (3.92 eV), consistent with the previous studies for excitonic absorption at 3.9–3.93 eV (317–315 nm) [37,38]. The PL excitation (PLE) spectrum with a prominent peak at 370 nm (3.35 eV, red line) is very similar to the Cs$_2$SnCl$_6$:Bi compound, which was previously reported for excitation at 365 nm [38]. For the PL spectrum at 370 nm excitation, there is a strong luminescent center at 425 nm (2.92 eV, blue line) with a 55 nm Stokes shift and a wide FWHM (84 nm), attributed to the energy from the electron–hole pair recombination. The elemental analysis using high-resolution X-ray photoelectron spectra (XPS) analysis revealed a zoom-in scan highlighting the Sn element of Cs$_2$SnCl$_6$ (Figure 3(b)). The two peaks are from the spin–orbit splitting corresponding to electrons from the 3d$_{3/2}$ and 3d$_{5/2}$ states located at 488.2 and 496.5 eV, respectively. The XPS data show only tetravalent tin (Sn$^{4+}$) in the Cs$_2$SnCl$_6$ sample. This means that the higher oxidation state of tin (Sn$^{4+}$) is more stable against oxygen and moisture compared to the lower oxidation state of tin (Sn$^{2+}$).

For the nanomaterials, the appropriate dopants of the host lattices were extensively explored as an effective approach to modulating the optical and electronic performance of diverse NCs and to stabilizing specific
crystallographic phases [39–42]. To stabilize Cs$_2$SnCl$_6$ NCs, a desired amount of MnCl$_2$·4H$_2$O was added in the synthesis of Cs$_{2-x}$Sn$_x$Cl$_6$ (x = 0, 2, 4, and 6%) while maintaining all the other synthetic parameters. The preferred monoclinic-phase CsSnCl$_3$ (ICSD #14199) with a space group of P2$_1$/n, however, gradually formed when the Mn doping concentration increased, as shown in Figure 4. Based on the results, it can be said that the derivative of perovskite NCs may be created by doping adequate dopants.

Irregular and aggregative NPs of the 6%Mn-doped Cs$_2$SnCl$_6$ compound are clearly observed in Figure 5(a and b). The changed morphology may be ascribed to the coexistence of the two Cs$_2$SnCl$_6$ and CsSnCl$_3$ phases. Figure 5(c) shows that the interplanar spacing was 3.36 Å, which is smaller than that of the pure Cs$_2$SnCl$_6$ NCs (3.76 Å, Figure 2(c)), suggesting phase transition from the initial Cs$_2$SnCl$_6$ NCs to the final CsSnCl$_3$ NCs with different Mn doping concentrations. Furthermore, there were many extra dots (red circle) in the SAED pattern of the Cs$_2$SnCl$_6$ NCs, as shown in Figure 5(d). Based on these results, it can be speculated that phase transformation occurs in the Mn doping reaction of lead-free perovskite NCs.

Except for the XRD results, the PL spectra can also be used as evidence of the phase transition. The excitation spectra show a small red shift and are slightly broader when the Mn concentration increases (Figure 6(a and b)). Upon 6%Mn doping, there is a strong excitation center at 333 nm under 628 nm emission, which suggests that a high doping concentration benefits the phase transition from Cs$_2$SnCl$_6$ to CsSnCl$_3$ NCs. When a dopant is inside a NC, fast energy transfer from the NC exciton to the dopant is expected. The monitoring of the excitation spectra as well as PL revealed that the peak positions of the excitonic and dopant emissions provide clear signatures for the phase transition through the successful incorporation of a dopant. As shown in Figure 6(c), a bright Mn$^{2+}$ red emission was detected due to the d-d orbital transition emission ($^{4}T_1 \rightarrow ^{6}A_1$), and energy transfer from the excitons to the Mn$^{2+}$ activators was proven. These results prove the existence of Mn$^{2+}$ in

Figure 5. (a,b) TEM images, (c) HRTEM image, and (d) SAED pattern of the 6%Mn-doped Cs$_2$SnCl$_6$ NCs. Scale bar: (a) 2 μm; (b) 0.2 μm; and (c) 5 nm.
Figure 6. Typical normalized excitation (black line) and emission (blue and red lines) spectra of the as-synthesized Cs$_2$Sn$_{1-x}$Mn$_x$Cl$_6$: (a) 2%Mn; (b) 4%Mn; and (c) 6%Mn. Insets: Photographs of the Mn-doped NC solutions under UV illumination ($\lambda_{ex} = 365$ nm).

Figure 7. Schematic illustration of the Cs$_2$SnCl$_6$ NC formation and Mn$^{2+}$ ion doping mechanisms.

Figure 8. Emission spectra of (a) Cs$_2$SnCl$_6$ NCs and (b) CsSnCl$_3$:6%Mn$^{2+}$ NCs recorded after different preservation times in air. Photographs of (c) Cs$_2$SnCl$_6$ NCs and (d) CsSnCl$_3$:6%Mn$^{2+}$ NCs under irradiation with a UV lamp (365 nm excitation).
the CsSnCl₃ matrix. Moreover, the stable CsSnCl₃:Mn²⁺ solution can maintain its red luminescence for over two weeks.

Figure 7 illustrates the proposed reaction mechanism for the Cs₂SnCl₆ NC formation and the incorporation of Mn²⁺ in the CsSnCl₃ NCs. Utilizing a non-stoichiometric modified precursor-assisted hot-injection method, the pure Cs₂SnCl₆ NCs can be easily synthesized without adding metal ions. Unexpectedly, phase transition from Cs₂SnCl₆ to CsSnCl₃ was introduced by doping MnCl₂•4H₂O. The analogous precursor (SnCl₂) and the charge of Mn (MnCl₂) are possible reasons for the existence of bright-red-emission CsSnCl₃:Mn²⁺ NCs.

Stability is an important issue for the practical application of perovskite nanomaterials. Moisture and heat are serious problems that impede the development of the new class of materials in products for the lighting and solar cell market. The stability levels of Cs₂SnCl₆ and CsSnCl₃:6%Mn²⁺ NCs were compared. As shown in Figure 8(a and b), the variation of the PL spectra demonstrated that Mn-doped Sn-based perovskite NCs are quite stable after storing for 4 days in air. On the contrary, a drastic change was found in the emission spectra of the Cs₂SnCl₆ NCs. In Figure 8(c and d), the corresponding luminescent photographs of the Cs₂SnCl₆ and CsSnCl₃:6%Mn²⁺ NCs also indicate that doping synthesis is an important approach to improving the stability of lead-free perovskite nanomaterials.

4. Conclusion

In conclusion, blue-emission Cs₂SnCl₆ nanocrystals (NCs) were successfully synthesized using a modified precursor-assisted hot-injection approach. By doping Mn ions, phase transition of the CsSnCl₃ NCs appeared involuntarily in the process of Cs₂SnCl₆ NC formation. The CsSnCl₃:Mn²⁺ NCs showed bright-red luminescence, and the compound displayed extraordinary stability towards oxygen in the ambient atmosphere. The strategy provides a general method of creating the derivative of free-lead perovskite NCs and stabilizing the compound’s performance. These tin-based NCs will also create possibilities for application in the next-generation solid-state lighting and displays.

Disclosure statement

No potential conflict of interest was reported by the authors.

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