Moisture-assisted Near-UV Emission Enhancement of Lead-free $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ Double Perovskite Nanocrystals

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ABSTRACT: Lead-based halide perovskite nanocrystals (NCs) are recognized as emerging emissive materials with superior photoluminescence (PL) properties. However, the toxicity of lead and the swift chemical decomposition under atmospheric moisture severely hinder their commercialization process. Herein, we report the first colloidal synthesis of lead-free $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ layered double perovskite NCs via a facile moisture-assisted hot-injection method stemming from relatively nontoxic precursors. While moisture is typically detrimental to NC synthesis, we demonstrate that the presence of water molecules in $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ synthesis enhances the PL quantum yield (mainly in the near-UV range), induces a morphological transformation from 3D nanocubes to 2D nanoplatelets, and converts the dark transitions to radiative transitions for the observed self-trapped excitons relaxation. This work paves the way for further studies on the moisture-assisted synthesis of novel lead-free halide perovskite NCs for a wide range of applications.

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Benefiting from their reduced toxicity, compositional tunability, and superior structural stability,^{1–4} lead-free double perovskites have attracted increasing attention in recent years both in the form of bulk films^{5–8} and colloidal nanocrystals (NCs),^{9–12} as substitutive materials of lead-based halide perovskites for potential commercial applications, i.e. light-emitting diodes (LEDs),¹³ solar cells,¹⁴ and photodetectors.¹⁵ Compared to the well-investigated cubic double perovskites with structure $\text{Cs}_2\text{M(I)M(III)X}_6$ (M(I): Ag^+ , Cu^+ , etc.; M(III): Bi^{3+} , Sb^{3+} , In^{3+} , etc.; X: Cl^- , Br^- , I^-),^{16–20} the recent discovery of vacancy-ordered layered double perovskites with formula $\text{Cs}_4\text{M(II)M(III)}_2\text{X}_{12}$ (M(II): Cu^{2+} , Mn^{2+} , etc.), has been demonstrated several attractive figures of merits including large compositional space, direct bandgap nature, and outstanding structural stability.^{21–24} The layered double perovskite structure comprises one layer of $[\text{M(II)X}_6]^{4-}$ octahedra inserted in between two layers of $[\text{M(III)X}_6]^{3-}$ octahedra. As a representative, $\text{Cs}_4\text{CuSb}_2\text{Cl}_{12}$ has been successfully synthesized both in the form of single-crystalline powder²² and NCs,^{23,25} exhibiting a narrow direct bandgap (1.0–1.8 eV) and impressive stability, which however still suffers from the high toxicity of Sb element and the absence of emission at room temperature. To overcome these drawbacks, $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$, with toxic Sb^{3+} substituted by relatively non-toxic In^{3+} , could be a promising candidate to fulfill the requirement of compositional engineering and optical tunability particularly in the UV range. Yet, to date, the synthesis of $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ layered double perovskites has not yet been reported for neither bulk film nor NCs.

Herein, we report the first-ever colloidal synthesis of lead-free $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ layered double perovskite NCs using a modified hot-injection method.^{20,25} The synthetic details are described in the Supporting Information (SI). While a standard hot-injection reaction in moisture-free environment resulted in $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ with a very low photoluminescence quantum yield (PLQY) of 0.12%, we found that the handling of synthesis precursors in the presence of moisture

(RH~40%) enhances PLQY by more than one order of magnitude up to 1.56 %. Water-assisted *in-situ* synthesis has been recognized as an effective strategy to tune the optical properties and stability for both lead-based^{26,27} and lead-free halide perovskite NCs^{28,29} via the controlling of NCs size, shape, and crystallinity. Nevertheless, there is still a lack of deep understanding of how water influences NCs growth regime and corresponding PL property, especially for lead-free double perovskite NCs. The introduction of moisture in the precursor (namely “wet” precursor conditions) of Cs₄CuIn₂Cl₁₂ NCs (w-Cs₄CuIn₂Cl₁₂) induces the morphological transformation from 3D nanocubes (NCus) to 2D nanoplatelets (NPLs), driven by the ionized H₃O⁺ and OH⁻ from the water content as additional capping ligands. The ultrafast transient absorption studies suggest a strengthened self-trapped exciton (STE) effect for w-Cs₄CuIn₂Cl₁₂ NCs compared to the NCs synthesized in “dry” conditions (d-Cs₄CuIn₂Cl₁₂ NCs), resulting in the conversion of dark transitions into radiative transitions, which directly contributes to the PLQY.

The absorption and PL spectra of as-synthesized d-Cs₄CuIn₂Cl₁₂ and w-Cs₄CuIn₂Cl₁₂ NC suspensions are presented in **Figures 1a** and **b**, with direct bandgap energies of 3.82 eV and 3.56 eV, respectively, as determined by Tauc analysis (Figure 1a, inset). The absorption spectrum of d-Cs₄CuIn₂Cl₁₂ NCs peaks at 269 nm, and their weak emission maximum is at 374 nm. Upon the involvement of moisture in the reaction, the absorption spectrum of w-Cs₄CuIn₂Cl₁₂ NCs exhibits a slight red-shift but with a long absorption tail in the visible range, which contributes to the visualization of a violet color in suspension compared to the whitish color observed for d-Cs₄CuIn₂Cl₁₂ NCs (Figure 1b, inset). The corresponding PL spectrum of w-Cs₄CuIn₂Cl₁₂ NCs

Figure 1. (a) Absorption spectra and (b) photoluminescence (PL, excitation at 300 nm) spectra of Cs₄CuIn₂Cl₁₂ NC suspensions synthesized with (w-Cs₄CuIn₂Cl₁₂) and without (w/o) (d-Cs₄CuIn₂Cl₁₂) moisture, combining with a PL excitation (PLE, emission at 381 nm) spectrum (dotted line) of w-Cs₄CuIn₂Cl₁₂ NCs. Insets: Tauc plots in (a) and a photograph of the NC toluene suspensions in (b). (c) X-ray diffraction (XRD) patterns of d-Cs₄CuIn₂Cl₁₂ and w-Cs₄CuIn₂Cl₁₂ NCs, comparing with the simulated XRD pattern for bulk Cs₄CuIn₂Cl₁₂ in a pure phase. (d) Crystal structure of a Cs₄CuIn₂Cl₁₂ unit cell.

experiences a significant amplitude enhancement mainly in the near-UV range (320–400 nm) by showing an absolute PLQY of 1.56 %, which is more than one order of magnitude higher than that (0.12 %) of d-Cs₄CuIn₂Cl₁₂ NCs. A relatively broad (FWHM = 73 nm) and slightly asymmetric PL spectral shape, with a long emission tail towards 500 nm, is detected in the case of w-Cs₄CuIn₂Cl₁₂ NCs. The enhanced PL intensity of w-Cs₄CuIn₂Cl₁₂ NCs could be attributed to the STEs originating from the water-induced Jahn-Teller distortion of the [M(II)Cl₆] (i.e. [CuCl₆]) octahedra in the excited state, as it has also been observed for other types of lead-free perovskites, such as

Cs₂AgInCl₆³⁰ and Rb₂InCl₅.²⁸ In addition, the PL excitation (PLE) spectrum (Figure 1b) of w-Cs₄CuIn₂Cl₁₂ NCs, monitored at the emission peak (381 nm), presents a different profile from their corresponding absorption spectrum, further suggesting that the emission may stem from different defect states and/or surface-related states, such as STEs, due to the coordination of water molecules.²⁸ The optical properties of as-synthesized Cs₄CuIn₂Cl₁₂ NCs are summarized in **Table 1**.

Table 1. Optical properties of as-synthesized Cs₄CuIn₂Cl₁₂ NCs.

NCs	^{a)} λ_{abs} (nm)	^{b)} λ_{PL} (nm)	^{c)} FWHM (nm)	PLQY (%)	^{d)} E_g (eV)
d-Cs ₄ CuIn ₂ Cl ₁₂	269	374	95	0.12	3.82
w-Cs ₄ CuIn ₂ Cl ₁₂	273	381	73	1.56	3.56

^{a)}First exciton peak; ^{b)}Emission peak; ^{c)}Full width at half maximum; ^{d)}Bandgap.

The X-ray diffraction (XRD) patterns of Cs₄CuIn₂Cl₁₂ NCs formed in the presence or absence of moisture in the reaction show a negligible deviation from the simulated pattern of bulk Cs₄CuIn₂Cl₁₂ in a pure phase without considering any impurities (Figure 1c left), determining a monoclinic crystal structure with a space group of C2 / *m*. The set of characteristic peaks positioned at 23.6°, 24.5°, and 34.0° were assigned to (311), (020), and (222) planes, corresponding to the Cs₄CuIn₂Cl₁₂ layered double perovskite crystal phase with distorted [CuCl₆] octahedra, which has also been observed for Cs₄CuSb₂Cl₁₂ NCs.²⁵ Based on our simulation results (**Table S1**), the lattice parameters were calculated as $a = 13.18 \text{ \AA}$, $b = 7.29 \text{ \AA}$, $c = 13.16 \text{ \AA}$, $\beta = 111.8^\circ$ with a unit cell volume of 1174.6 Å³ (see the crystal structure of one Cs₄CuIn₂Cl₁₂ unit cell in Figure 1d). It is noteworthy that the XRD pattern of w-Cs₄CuIn₂Cl₁₂ NCs shows a slightly upward shift in the peak positions compared to that of the reference d-Cs₄CuIn₂Cl₁₂ NCs, e.g. from 23.66° to 23.81° at (311) (Figure 1c right), indicating that the water molecules indeed trigger the shrinkage of the unit cell during the NC growth. The stabilities of the NCs were further studied by measuring XRD

patterns as a function of storage time. In specific, we studied the intensity evolution of the characteristic peak at (311) plane for two NCs samples (**Figure S1**). Up to 4 weeks storage, w- $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ NCs retains 95% of the initial intensity, while a more than 50% drop in intensity occurs for d- $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ NCs, indicating that the moisture-assisted NCs possess good structural stability under ambient conditions (RH~40%). Energy-dispersive X-ray spectroscopy (EDS) analysis elucidated the actual elemental ratios of Cs:Cu:In:Cl as 4.0:0.7:1.9:12.0 and 4.0:0.8:1.9:11.9 for the d- $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ and w- $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ NCs, respectively, both matching well the nominal stoichiometric ratio of $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$. The EDS layered images of w- $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ NCs film (**Figure S2**) for different compositional elements show the homogeneous elemental distribution on the surface of the NC film. Our inductively coupled plasma mass spectroscopy (ICP-MS) analysis (**Table S2** and **S3**) further confirmed the metal cation ratios of Cs:Cu:In matching the desired stoichiometric ratio (4:1:2) for both NCs samples.

Figure 2. (a) Transmission electron microscopy (TEM) image and (b) size distribution histogram of d- $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ NCs. (c) High-resolution TEM (HRTEM) image of a single d- $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ NCu. (d) Selected area electron diffraction (SAED) pattern for the TEM image (a). (e) TEM image of w- $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ NCs (the yellow frames highlight the NPLs). (f) Size distribution histogram of w- $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ NCs. (g) HRTEM image of a single w- $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ NPL. (h) SAED pattern for the TEM image of NPLs in (e). (i) TEM image of large lateral size of w- $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ NPLs in a view of stacking (guided by arrows).

Transmission electron microscopy (TEM) measurements demonstrate that the d-Cs₄CuIn₂Cl₁₂ NCs have a cube-like shape (**Figure 2a**) with an average diameter of 17.1 ± 1.6 nm (Figure 2b). High-resolution TEM (HRTEM) image (Figure 2c) highlights that d-Cs₄CuIn₂Cl₁₂ NCs possess a well-defined crystalline structure with a lattice *d*-spacing of 0.376 nm, which is assigned to the (311) crystal plane, highly consistent with the crystalline direction determined from the selected area electron diffraction (SAED) pattern (Figure 2d). These, together with the previous XRD data (Figure 1c), further verified a monoclinic crystal structure. Interestingly, the NCs synthesized with the moisture in the precursor consist of a mixture of NCus and NPLs (Figure 2e). The nanocubes (w-Cs₄CuIn₂Cl₁₂) show an average diameter (17.8 ± 1.9 nm) like that of d-Cs₄CuIn₂Cl₁₂ NCus, while a large average lateral size of 27.1 ± 3.6 nm is separately presented for the w-Cs₄CuIn₂Cl₁₂ NPLs in Figure 2f. From the HRTEM image of NPLs (Figure 2g), the measured lattice *d*-spacing of 0.372 nm, also corresponding to (311) crystal facets (Figure 2h), was slightly lower than that (0.376 nm) of d-Cs₄CuIn₂Cl₁₂ NCus, which is consistent with the shift in the peak positions of XRD data towards larger Bragg angles (Figure 1c). Some ultra-large lateral size (up to ~50 nm) of NPLs and stacking of NPLs with an estimated thickness of ~2 nm for one NPL were observed (Figure 2i), further confirming the formation of 2D NPLs induced by water molecules. It is known that H₂O molecules can be partly ionized into H₃O⁺ and OH⁻ with the assistance of OA⁻ and OAm⁺,³¹ which could act as additional capping ligands to activate the NC surface. We, thus, propose an NC growth scheme (**Scheme 1**) for better understanding the water-induced morphological transformation from 3D NCus to 2D NPLs for Cs₄CuIn₂Cl₁₂ NCs. Upon the injection of TMS-Cl into the metal carboxylate precursors, there is a dynamic equilibrium between the attachment and detachment of capping ligands (i.e. OA and OAm) to influence the monomer attachment on the surface of the initially formed cluster.³² With a standard concentration of ligands

(no moisture involved), there are many detachments of ligands from the cluster surface, and then with free ions (e.g. Cs^+ and Cl^-) more monomer attachments occur to further form nanocubes. When the water molecules are involved in the precursor, the ionized H_3O^+ and OH^- act as additional capping ligands, thus binding to the cluster surface and effectively blocking potential sites for monomer attachment, resulting in very few ligand detachments. Consequently, the NCs grow in 2D direction to form nanoplatelets. This moisture-assisted shape change has been previously observed for CsPbBr_3 NCs.²⁶

Scheme 1. Possible formation process of $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ NCs synthesized with and without moisture in the precursor.

To thoroughly investigate the photophysical properties of $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ NCs, ultrafast transient absorption (TA) measurements were conducted for as-synthesized $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ NCs. **Figure 3a** and **b** show the TA spectra of d- $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ and w- $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ NCs, respectively, excited at 320 nm. A broad positive photo-induced absorption (PIA) was observed in the probe range of 410–650 nm for both samples, providing direct evidence of STEs.²⁸ The ultrafast PIA signal growth (<1 ps) indicates a transition from free excitons to STEs trapping.³³ The TA spectra of w- $\text{Cs}_4\text{CuIn}_2\text{Cl}_{12}$ NCs display a clear red-shift, particularly after 2 ps, compared to those of d-

Cs₄CuIn₂Cl₁₂ NCs, revealing an enhanced STE effect upon the involvement of water molecules during the NC growth. Figure 3c compares the TA decays for d-Cs₄CuIn₂Cl₁₂ and w-Cs₄CuIn₂Cl₁₂ NCs, monitored at 440 nm and 460 nm, respectively, which can be fitted well with a tri-exponential function (see the fitting results in **Table S4**). We assign two fast processes comprising an ultrafast

Figure 3. Ultrafast TA spectra of (a) d-Cs₄CuIn₂Cl₁₂ and (b) w-Cs₄CuIn₂Cl₁₂ NCs in suspension, excited at 320 nm with an excitation power of 50 μ W. The arrows highlight a spectra evolution. (c) TA decays of d-Cs₄CuIn₂Cl₁₂ and w-Cs₄CuIn₂Cl₁₂ NCs, monitored at 440 nm and 460 nm, respectively. Solid lines present the fitting results with a tri-exponential function: $\Delta O.D. = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + A_3 \exp\left(-\frac{t}{\tau_3}\right)$, $\Delta O.D.$ is the change of optical density. Inset shows the magnified decays in late timescale. (d) Configuration coordinate diagram for the STE mechanism of Cs₄CuIn₂Cl₁₂ NCs with (rad_w) and without (dark_d) moisture in the reaction.

component (lifetime of <2 ps) and a middle-fast component (lifetime of 700–800 ps) to nonradiative transitions, and a slow component (lifetime of >3 ns) to the radiative recombination

of STEs.³⁴ Nevertheless, in d-Cs₄CuIn₂Cl₁₂ NCs, the slow radiative component shows a negative signal (Figure 3c, inset), indicating that the STEs are dominated by the nonradiative (dark) transition. This suggests that the water molecules indeed produce a Jahn-Teller distortion in [CuCl₆] octahedra that involves the contraction of the 4 horizontal Cu-Cl bonds for w-Cs₄CuIn₂Cl₁₂ NCs, resulting in the longer STEs lifetime and radiative transition rather than the dark transition in d-Cs₄CuIn₂Cl₁₂ NCs showing weak UV emission (see the STE mechanism of Cs₄CuIn₂Cl₁₂ NCs in Figure 3d).

In summary, for the first time, we have successfully synthesized lead-free Cs₄CuIn₂Cl₁₂ layered double perovskite NCs. The critical role of moisture (RH: ~40%) during the growth of the NCs has been investigated. It not only led to significantly enhanced PLQYs in the near-UV range, higher structural stability, and morphological transformation from 3D nanocubes to 2D nanoplatelets, but also induced a conversion of dark transitions to radiative transitions for STEs in the excited state. Our study provides an effective approach to tune the PL emission in layered double perovskites by tailoring the octahedral distortion in presence of water molecules. The results presented here will trigger further understanding of PL and photophysical properties for lead-free double perovskites.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge at...

Experimental details, simulated structural properties, structural stability, EDS layered images, elemental analysis, ICP-MS data, fitting results of transient absorption decays.

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Notes

The authors declare no competing financial interest.

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