CsCu$_2$I$_3$ Nanocrystals: Growth and Structural Evolution for Tunable Light Emission

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1. INTRODUCTION

Metal halide perovskites of ABX$_3$ (A$^+$ is CH$_3$NH$_3$$^+$, HC-(NH$_2$)$_2$$^+$, Cs$^+$ or their combinations, B$^{2+}$ is Pb$^{2+}$ or Sn$^{2+}$, and X$^-$ is halide anion such as Cl$^-$, Br$^-$, I$^-$, or their mixture) have attracted numerous research interest in recent years for their promising application in next-generation displays.1-4 Although CsPbX$_3$ (X = Cl$^-$, Br$^-$, I$^-$) has shown excellent optoelectronic properties, such as wide color gamut, high photoluminescence quantum yield (PLQY >90%), and narrow full width at half-maxima (FWHM, 12–25 nm), which enable them to be used in solid-state lighting, visible-light communications, and phototherapy,5-7 the presence of the toxic lead could cause serious environmental problems and human injury. Finding synthesizing lead-free perovskite-like substances is essential. At present, researchers have found that Sb(III),9 Bi(III),10 Mn(II),11 Zn(II),12 and Mg(II)13 could mostly substitute or be doped, leading to lead-free perovskite-like compounds. But these lead-free perovskite compounds usually contain high concentration defects, resulting in them being quite unstable under ambient conditions and showing unsatisfactory performance compared to lead-included ones.

Different from these lead-free perovskites, copper halide perovskite-like compounds contain fewer defects and exhibit a large Stokes shift.14-16 For example, Cs$_3$PbBr$_5$ has been found to give a Stokes shift as large as 220 nm and a photoluminescence quantum yield (PLQY) value of up to 45%.17 Up to now, two kinds of stoichiometric ternary copper halide compounds, low-dimensional Cs$_3$Cu$_2$X$_3$ and Cs$_3$Cu$_2$X$_5$ (X = Cl, Br, I, or mixtures thereof), have been demonstrated to show broadband fluorescence emission with a full width at half-maximum larger than 80 nm.18,19 Among them, CsCu$_2$I$_3$ and Cs$_3$Cu$_2$I$_5$ NCs showing yellow and blue emission, respectively, could be mixed to achieve white light emission that could be suitable for application in LEDs.20 The quality of CsCu$_2$I$_3$ NCs has a great impact on the color feature of white light. Furthermore, as previously reported, CsCu$_2$I$_3$ nanomaterials could be synthesized by several routes, including colloidal synthesis, antisolvent method, and so on.21-23 Solution process is essential for the synthesis of CsCu$_2$I$_3$ NCs. Therefore, nucleation and growth of CsCu$_2$I$_3$ NCs are highly dependent on organic solvents involved in the reaction and also the reaction temperature. Increasing the temperature can dissociate copper ions from three kinds of complex (liner, triangular, and tetrahedral) and promote the process of crystal growth. However, the growth and structural evolution of CsCu$_2$I$_3$ NCs...
in the solution reaction process and the impact on its photoluminescence emission are still not clear.

Here, we investigated the growth and structural evolution of CsCu$_2$I$_3$ NCs in the hot-injection reaction system with the increasing reaction temperature. We found that the reaction conditions at high temperature and low concentration of oleic acid (OA) and oleylamine (OAm) were favorable to obtain phase-pure CsCu$_2$I$_3$ nanorods. Moreover, accompanying the growth of nanorods and structural evolution from Cu$_3$Cs$_2$I$_5$ to CsCu$_2$I$_3$, the color of photoluminescence (PL) emission of NCs changed from blue to nearly white and to yellow. This work puts forward a clear course of the structural evolution of copper-containing perovskite-like NCs, which could be helpful for investigating the intriguing properties and potential applications of lead-free materials.

2. RESULTS AND DISCUSSION

The morphologies and elemental distribution of the as-obtained NCs by controlling the reaction temperatures in the range of 130–180 °C were monitored by field-emission scanning electron microscopy (FE-SEM) (Figure 1), transmission electron microscopy (TEM) (Figure 2), and energy-dispersive spectroscopy (EDS) mapping (Figure 3). The corresponding size distributions are presented in the inset of

![Figure 1. SEM images of (a) CCI-130, (b) CCI-140, (c) CCI-150, (d) CCI-160, (e) CCI-170, and (f) CCI-180 samples.](Image)

![Figure 2. TEM images of (a) CCI-140, (b) CCI-150, and (c) CCI-160 samples.](Image)

![Figure 3. Chemical composition revealed by EDS for CCI-130 and CCI-170. (a) and (f) Their SEM images. (b)–(d) and (g)–(i) Their elemental mapping images. (e) and (j) Their EDS spectra.](Image)
The results of EDS are presented in Figure 3 and Table 1. The distribution of Cs, Cu, and I elements are nearly homogeneous regardless of nanoparticles or nanorods. The semiquantitative data revealed that all NCs had a close atomic ratio lattice parameters of the CsCu₂I₃ phase

| samples   | atomic ratio | lattice parameters of the CsCu₂I₃ phase |
|-----------|--------------|----------------------------------------|
| CCI-130   | 1.0 2.2 3.0  | a (Å) 10.552(1) b (Å) 13.191(1) c (Å) 6.0917(7) V (Å³) 847.9(1) |
| CCI-140   | 1.0 2.0 2.6  | a (Å) 10.564(2) b (Å) 13.197(2) c (Å) 6.097(1) V (Å³) 850.0(2) |
| CCI-150   | 1.0 2.3 3.0  | a (Å) 10.574(1) b (Å) 13.214(1) c (Å) 6.110(1) V (Å³) 853.7(2) |
| CCI-160   | 1.0 2.2 2.9  | a (Å) 10.543(2) b (Å) 13.181(2) c (Å) 6.114(1) V (Å³) 849.7(2) |
| CCI-170   | 1.0 2.0 2.9  | a (Å) 10.547(2) b (Å) 13.188(2) c (Å) 6.109(1) V (Å³) 849.7(2) |
| CCI-180   | 1.0 2.4 3.0  | a (Å) 10.541(1) b (Å) 13.211(1) c (Å) 6.1099(5) V (Å³) 850.8(1) |

Figure 4. Photoluminescence performance. (a) Optical images of fresh CCI-T’s colloidal solutions excited by UV light. (b) PL spectra of the CCI-T NCs monitored at 302 nm. (c) Histogram of the relative intensity of the β peak at 570 nm with the reaction temperature.

Table 1. Elemental Analysis from the EDS Data and the Lattice Parameters Determined by Reitica Program for CCI-T (T = 130−180) NCs. The morphologies of the particles in the samples of CCI-130 and CCI-140 look like a loaded composite (Figures 1a and 2a), but their nanorods and nanoparticles have the same elemental distribution. The results of EDS are presented in Figure 3 and Table 1. The distribution of Cs, Cu, and I elements are nearly homogeneous regardless of nanoparticles or nanorods. The semiquantitative data revealed that all NCs had a close composition to that of CsCu₂I₃.
value. Therefore, CCI-T NCs could provide a kind of possibility to fabricate energy-saving intrinsic white-light LED as a next-generation lighting source.

Many factors could affect the light emission of perovskite semiconductor NCs. Taking homologous compounds of perovskite nanocrystals CsPbX3 (X = Cl, Br, I) as examples, the emission varied with the anions, just like mixed-halide perovskites like CsPb(Cl/Br)3 and CsPb(Br/I)3 can be readily produced by the combination of blue, green, and red emission.27−30 Doping and substitution of lead sites also affect the position of the emission peak.25,31,32 Obviously, emission changes of our as-synthesized NCs in Figure 5a could not be attributed to the anion exchange and doping effect. On the other hand, the emission of two-dimensional halide double perovskite (BA)4AgBiBr8 (BA = CH3(CH2)3NH3+) NCs can be changed by the structure from the monoclinic space group C2/m to the monoclinic space group P21/c.33 Liu’s group found that the single emission would change to double emission when the surface motif reconstruction presented in Au NCs.34 For cesium tin halide perovskite NCs, the oxidation of tin ions resulted in an emission shift from 970 nm for CsSnI3 to 620 nm for Cs2SnI6.35,36 To understand the origin of double emission peaks observed for our as-synthesized CCI-T NCs, the valence state of ions and the phase structure must be examined.

In our CCI-T NCs, copper ions could most likely to change their valence state if the reaction atmosphere was not well controlled. To examine the valence state of copper, the XPS spectra of CsCu2I3 NCs were recorded (Figure 5). The Cu 2p spectrum of CCI-130 exhibits (Figure 5a) two strong photoelectron peaks at 932.19 and 951.82 eV, which are assigned to the spin−orbit signals of Cu 2p 3/2 and 2p 1/2, respectively.37 The shake-up satellites of 2p 3/2 and 2p 1/2 are hardly seen, demonstrating the copper ion in monovalence. This conclusion is also verified by the Cu LMM spectrum in Figure 5b. The Cu LMM of CCI-130 locates at 916.0 eV, closer to 916.8 eV for that of Cu2O.38 As for CCI-140, the Cu 2p 3/2 and 2p 1/2 peaks shift to 932.78 and 952.48 eV, respectively, but their binding energies are still much closer to that of Cu2O. Also, the Cu LMM line at 915.60 eV (Figure 5b) indicates a Cu+ oxidation state in sample CCI-140. Even when the reaction temperature increased to 180 °C, the photoelectron lines of Cu 2p 3/2 and 2p 1/2 no longer show an obvious shift. Therefore, copper ions in all CCI-T NCs are monovalent. The survey spectra of all of the crystals are presented in Figure S4, showing strong signals of Cs, Cu, and I elements. No other metal signal was detected except those of Cs and Cu. The observations from the XPS spectra suggest that the change in light emission with the reaction temperature in Figure 4b is not caused by the oxidation state of copper ions and cation doping.

The XRD patterns of CCI-T NCs are shown in Figure 6. At first glance, all patterns seem to match the standard data of JCPDF No. 45-0076, indicating that the as-obtained NCs could be predominantly crystallized in an orthorhombic structure with the space group Cmcm. The strong peaks, such as (110), (020), (220), (130), (221), (040), etc., are marked. By a careful examination, we found that there was extremely weak diffraction around 15°, as denoted in the inset of Figure 6. This weak diffraction could be attributed to the (020) peak of Cs3Cu2I5 (space group of Pnma). Therefore, the samples prepared at low temperature could contain traces of Cs3Cu2I5 NCs, i.e., the samples are a mixture of CsCu2I3 and Cs3Cu2I5. From the patterns, we could see that the relative intensity of the diffraction peaks changed distinctly, which may be related to the external stress and the orientation of nanocrystals. In our XRD measurement, the colloid NCs was dropped onto the silicon holder and dried at room temperature to obtain a filmlike sample for the XRD test. This process could produce a coarse texture and stress in the filmlike sample, which generated the potential of the preferred orientation.39,40 On the other hand, the existence of nanorods...
in CCI-T NCs also affects the intensities of diffraction peaks. Comparatively, the position of intense peaks belonging to the CCI-T NCs did not shift much, which confirmed that its lattice parameters were nearly the same with an increase in the reaction temperatures. Considering that the content of CsCu$_2$I$_3$ is very small (its diffraction peaks are hardly distinguishable except for CCT-150), the XRD patterns of CCI-T were refined by one phase of CsCu$_2$I$_3$ (space group Cmcm) using Rietica program in the LeBail model. The refined patterns are exhibited in Figures S5−S10, and the obtained lattice parameters of CsCu$_2$I$_3$ NCs are listed in Table 1.

To confirm the existence of the Cs$_3$Cu$_2$I$_5$ component in the as-synthesized CCT-130, we carefully examined the initially dispersed colloid mixture and the clear solution obtained after resting for a few minutes for the as-synthesized CCI-130 (Figure S11). The PL emission intensity of the clear solution is higher than that of the initially dispersed colloid. More importantly, the weak tailing peak disappeared, as shown in the inset of Figure S11b. The TEM image of Figure S11c shows that the NCs in the clear solution have a nearly spherical morphology, without any nanorods. The average diameter of the spherical NCs was 54.0 nm. This observation might suggest that most of the tiny particles in CCI-T NCs could crystallize in Cs$_3$Cu$_2$I$_5$, which gives an intense emission at 440 nm.

The formation of Cs$_3$Cu$_2$I$_5$ is related to the coordination of copper ions with OAm. At low temperatures, the high dosage of OAm might promote the formation of Cs$_2$Cu$_3$I$_5$. To confirm this conjecture, we did three controlling syntheses by adjusting the dosage of OA and OAm at 0.3, 0.7, and 0.8 mL. The XRD patterns of the as-prepared three products are illustrated in Figure S12. When the dosage of OA and OAm is below 0.8 mL, the main phase of the as-prepared products is CsCu$_2$I$_3$. At the dosage of 0.8 mL, the pattern of the as-prepared product (Figure S12) matches well with Cs$_3$Cu$_2$I$_5$. Moreover, the colloid solution of this product showed a symmetrical PL emission with a peak at 440 nm (Figure S13), demonstrating that only Cs$_3$Cu$_2$I$_5$ NCs are involved in this as-prepared product.

Based on the above discussion, the crystal growth route of perovskite-like CsCu$_2$I$_3$ NCs can be proposed, as illustrated in Figure 7. Copper ion coordinates with OAm, which promotes the dissolution of CuI in ODE. Copper exhibits rich coordination chemistry with complexes. Copper ion has a spherically symmetric configuration of 3d$^{10}$. When CuI dissolves in the mixed solution of OA, OAm, and ODE, copper ions coordinate with complexes of OA and OAM in three geometries of linear, trigonal planar, and tetrahedral (as shown in Figure 7), in which the copper ions with the two-coordinate linear have the lowest barrier potential and can steadily react with Cs oleate to form small NCs. Compara-
tively, the reaction barrier potentials of the other two geometries are high, and it is difficult for the copper ions in trigonal planar and tetrahedral geometries to combine with Cs oleate to form NCs at low temperature. According to organic chemistry, the barrier potential can be overcome by increasing the reaction temperature. Therefore, the molar ratio of Cu/Cs in the formed nanocrystals is dependent on the concentration of the complexant and reaction temperature. A high reaction temperature is favorable to the formation of CsCu2I3 NCs.

On the other hand, in the reaction system involving OA, OAm, and ODE molecules, the surface of the formed tiny NCs is not naked but packed with a dense ordered layer of oleates and oleylamine molecules. The carboxylates presumably chelate with surface metal atoms, similar to the conventional colloidal quantum dot systems,43 while ammonium interacts with halide atoms by [I=N···]. These hydrogen-bonding interactions, as suggested by the related crystal structures in hybrid perovskites.42 This kind of hydrogen-bonding interaction is not as strong as the carboxylate coordinate bond. Increasing the reaction temperature can weaken the adhesion of OA and OAm molecules on the surface of NCs, reducing the surface coverage of these ligand molecules. The dynamic solvation and ligand exchange on and off the surface of growing crystals with temperature could help us obtain CsCu2I3 NCs with different morphologies.43,44

CCI-T NCs exhibit an obvious preparation temperature-dependent emission spectra (Figure 4b), which is highly related to the content of CsCu2I3 and Cs2CuI4 rather than quantum-confinement effect,45 Stokes shift,46 or defect.47 Figure 8 displays the exciton lifetime data, in which CCI-130 and CCI-140 were collected at 445 nm only due to the low content of CsCu2I3. The lifetimes of CCI-130 and CCI-140 are nearly the same, about 1.7 μs detected at 445 nm, close to the previous report for Cs2CuI4.49 Since CCI-T (T = 150, 160) NCs exhibit two strong emission peaks corresponding to Cs2CuI4 (α emission) and CsCu2I3 (β emission), respectively. we collected both PL lifetimes at 445 and 575 nm. The PL lifetimes of CCI-150 and CCI-160 at 445 nm were 1.99 and 1.94 μs, a little bit longer than that of CCI-130 and CCI-140. When detected at 575 nm, their PL lifetime became 3.09 and 1.39 μs, respectively. Similarly, CCI-170 and CCI-180 were tested only at 575 nm, for the content of Cs2CuI4 was too low to test. The lifetimes of CCI-170 and CCI-180 were 1.44 and 1.55 μs, respectively. From Figures 4b and 8a, it can be concluded that the emission of Cs2CuI4 NCs is weaker, but its lifetime is close to that of CsCu2I3. This feature determines that CCI-180 NCs have the lowest statistical PLQYs.

3. CONCLUSIONS

In summary, the growth and structural evolution of CsCu2I3 NCs with increasing reaction temperature in the hot-injection reaction system was investigated in this work. In the conditions of low temperature and high dosage of OA and OAm, the Cs2CuI4 nanoparticles were generated more preferentially than CsCu2I3 NCs. With an increase in the temperature, Cs2CuI4 NCs were more likely to be formed and the pure CsCu2I3 phase was stably synthesized at 180 °C. The structural evolution from copper-less NCs to copper-rich ones was explained by the change in the copper coordination with OAm, i.e., increasing the reaction temperature can dissociate copper ions from complex and promote the process of crystal growth. Photoluminescence measurements show that with the growth of CsCu2I3 NCs and structural evolution from Cu2CsI3 to CsCu2I3, the color of light emission gradually warmed up from blue to nearly white and to yellow, while the photoluminescence quantum yield decreased from 36.00 to 9.86%. This work puts forward a clear process of the crystal growth and structural evolution of CsCu2I3, providing valuable help to further study the properties and potential applications of copper-containing perovskite-like halides in white LEDs.

4. EXPERIMENTAL SECTION

4.1. Materials and Chemicals. Cesium carbonate (Cs2CO3, 99.9%), oleic acid (AR), 1-octadecene (ODE, 90%), and oleylamine (Aladdin, 80–90%) were purchased from Aladdin, copper iodide (CuI, 99.5%) was from Sinopharm Chemical Reagent Corp (P. R. China), and toluene (AR) was from Beijing Chemical Works. All materials and chemicals were used as received without further purification.

4.2. Synthesis of Cs Oleate. Cs2CO3 (0.814 g), oleic acid (2.5 mL), and ODE (40 mL) were added into a 100 mL three-neck flask, dried at 120 °C for 1 h, and then heated under nitrogen to 150 °C until all Cs2CO3 reacted with oleic acid. It should be noted that Cs oleate precipitated out of ODE at room temperature has to be preheated to 100 °C before another injection.

4.3. Synthesis of CsCu2I3 Nanocrystals. ODE (5 mL) and CuI (0.188 mmol) were added into a 25 mL three-neck flask and dried under vacuum at 120 °C for 0.5 h. When oleic acid (0.5 mL) and oleylamine (0.5 mL) were injected at 120 °C under N2 atmosphere, the CuI salt dissolved immediately and formed a transparent solution. Then, the reaction temperature was raised to X °C (X = 130, 140, 150, 160, 170, and 180) and the previously synthesized Cs oleate solution (0.4 mL) was swiftly injected into the solution. After a ten-minute reaction, the solution containing the nanocrystals was quickly cooled to room temperature using an ice bath. The crude NCs were first separated through high-speed centrifugation at 10 000 rpm for 5 min. After centrifugation, the supernatant was discarded and the precipitates were redispersed in toluene. The toluene solution was centrifuged once more at 10 000 rpm for 10 min. The supernatant was discarded again and the precipitates were dispersed in toluene (5 mL) to form long-term steady colloidal solutions. According to the preparation temperature, the samples are named CCI-T (CCI means cesium copper iodide NCs, and T = 130, 140, 150, 160, 170, and 180).

To investigate the formation of CsCu2I3 NCs, the added dosage of oleic acid and oleylamine was also adjusted from 0.3 to 0.8 mL, while the reaction temperature was kept at 130 °C.

4.4. Characterization of CsCu2I3 Crystals. Field-emission scanning electron microscopy (FE-SEM) (Hitachi SU8020) and high-resolution transmission electron microscopy (HRTEM) (Tecnai G2 S-Twin F20) were used to observe the morphologies of CsCu2I3 NCs. Energy-dispersive spectroscopy (EDS) (Oxford X-Max80) was employed to acquire the elemental analysis and mapping images for components in CsCu2I3 NCs. Powder X-ray diffraction (XRD) (Rigaku miniflex600) with Cu Kα radiation (λ = 1.5418 Å) was used for recording the structural information of CsCu2I3 NCs. The step scanning is in a 2θ range of 10–70° with intervals of 0.02°. X-ray photoelectron spectroscopy (XPS) (ESCA-LAB MKII) with a monochromatic Al Kα (hv = 1486.6 eV) radiation source was performed to determine the...
oxidation states for CsCu$_2$I$_3$ NCs. The charging shifts were calibrated by a primary C is value at 284.6 eV.

4.5. Photochemistry Measurements of CsCu$_2$I$_3$ NCs. All of the photoluminescence spectra were measured for the fresh colloidal solutions. A FL920 fluorescence spectrometer was used to acquire the photoluminescence (PL) spectra. Time-resolved PL decay was measured using time-correlated single-photo counting by Edinburgh FL920 with a 290 nm laser. Time-resolved PL decay curves were fitted to single exponential and biexponential decay functions (see eqs 1 and 2) decay curves of

$$A(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_0$$

$$A(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_0 + A_2 \exp\left(-\frac{t}{\tau_2}\right)$$

The average lifetimes were calculated using

$$\tau_{avg} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$

To explore the kinetic luminescence process, the radiative rate of perovskite NCs and their nonradiative decay rates were calculated by adopting photoluminescence quantum yields (PLQYs) and the mean lifetimes ($\tau_{avg}$) of the samples. PLQY can be obtained using the formula $Q_Y = N_{fl}/N_{pa}$, where $N_{fl}$ is the number of photons emitted during photoluminescence from the sample and $N_{pa}$ is the number of photons absorbed by the sample. Both the radiative recombination and the nonradiative recombination are in an excited state.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c05024.

Comparison of the TEM images of CCI-150 NCs; diameter distribution of CCI-170 and CCI-180; refined XRD patterns of the CCI NCs prepared at different reaction temperatures; CIE color coordinates of CCI-150 and -160; XPS survey spectra; XRD patterns and PL spectra of the CCI NCs prepared with different dosages of OA and OAm; and PL and TEM comparisons of the initially dispersed CCI-130 mixture and clear solution after resting for a few minutes (PDF)

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work is financially supported by the National Natural Science Foundation of China (NSFC) (Grants 21771075, 21671077, and 21871106).

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