Photoluminescence and Self-Assembly of Cesium Lead Halide Perovskite Nanocrystals: Effects of Chain Length of Organic Amines and Reaction Temperature

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Abstract

All-inorganic halide perovskites have become one of the most prospective materials for lightening and display technology due to their color-tunable and narrow-band emission. Herein, we have systematically studied the effects of organic amines with different hydrocarbon chain length on the optical properties and morphology as well as the crystal structure of colloidal CsPbBr₃ nanocrystals (NCs), which were synthesized in the presence of oleic acid (OA) and organic amines by using a simple hot-injection approach. The hydrocarbon chain length has shown an independent correlation to the morphology and crystal structure of the as-obtained CsPbBr₃ NCs at 160 °C, but their optical properties can be affected to some extent. The photoluminescence quantum yields (PLQYs) of the CsPbBr₃ NCs synthesized in the presence of organic amines with long carbon chain length are generally in the range of 55-80% for different reaction time, but the PLQYs of less than 20% are obtained for the products synthesized in the presence of octylamine (OTAm) with short carbon chain length. The effects of the reaction temperature on the optical properties, size and crystal structure of the CsPbBr₃ NCs synthesized in the presence of cetylamine (CTAm) are studied. Interestingly, some nanoplates also appear in these CsPbBr₃ NCs obtained at relatively low temperatures (120 and 140 °C), which have a strong tendency to self-assemble into face-to-face nanostructures. Such a similar self-assembly behavior is also observed in the product synthesized in the presence of oleylamine (OLAm), but only flat nanoplates are observed in the products in the presence of OTAm at 120 °C. The results indicate that the lower reaction temperature and hydrocarbon chain length of the organic ligands play a significant role in the self-assembly of CsPbBr₃ NCs. This work opens up an alternative approach to controllable-synthesis of perovskite NCs through varying the carbon chain length of organic surfactants, and enlightens the fabrication of different nanostructures via self-assembly methods for further optoelectronic applications.

Keywords: CsPbBr₃; Photoluminescence; Self-assembly; Perovskite nanocrystals; Synthesis

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1. Introduction

Colloidal semiconductor NCs (known as semiconductor quantum dots) have been studied extensively due to their narrow emission bandwidth and size-dependent optical properties, which have exhibit potential applications in next-generation lighting and display technologies [1-4]. However, the further commercialization suffers from the complicated synthesis process and intrinsic cadmium ions. Very recently, lead halide perovskite NCs, such as all-inorganic lead halide and organic-inorganic lead halide perovskites, have attracted much attention due to their excellent optical and electronic properties including narrow bandwidth, high photoluminescence quantum yields (PLQYs) and simple controllable morphology [5-16]. As a result, these superiorities enable halide perovskite NCs to be an important candidate in quantum-dot light photodetectors [17-24]. To meet the demand of the development of optoelectronic devices, it is necessary to exploit novel synthetic protocols for preparing lead halide perovskite NCs with high PLQYs and controllable geometries and size. To date, many groups have developed a variety of colloidal methods to prepare organometal halide perovskite NCs ($\text{CH}_3\text{NH}_3\text{PbX}_3$, $\text{X}=\text{Cl}, \text{Br}, \text{I}$) and cesium lead halide perovskite NCs (CsPbX_3 , $\text{X}=\text{Cl}, \text{Br}, \text{I}$), in which the morphology, size and emission wavelength can be tailored through precisely manipulating the reaction parameters, such as reaction temperature, types of organic ligands, precursor ratios and so on [5-16]. In 2014, Pérez-Prieto et al. firstly reported the synthesis of luminescent $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NCs with a diameter of 6 nm through a simple and reliable nontemplate method, and their PLQY was only 20% [5]. Following by fine-tuning the precursor ratios and organic ligands, the PLQY of $\text{CH}_3\text{NH}_3\text{PbBr}_3$ could be enhanced to be 83% [6]. In 2015, Zhong's group developed a ligand-assisted reprecipitation strategy to produce brightly luminescent and color-tunable colloidal organolead perovskite NCs, and the absolute PLQY could reach up to 70% [7]. Rogach et al. adopted such an approach to control over the size of the $\text{CH}_3\text{NH}_3\text{PbBr}_3$ NCs by varying the temperature, and the absolute PLQY reached 93% [8]. Much progress has been made in the synthesis of highly luminescent organometal halide perovskite NCs, however, the stability limits their further optoelectronic application [16]. Therefore, all-inorganic perovskite NCs emerged at the moment, which may be expected to show improved stability. As a matter of fact, the synthesis, crystallography and photoconductivity of CsPbX_3 perovskites were reported more than half a century ago [25, 26], however, the pioneering work on the synthesis of colloidal CsPbX_3 NCs was reported in 2015 by Kovalenko's group, in which monodispersed colloidal CsPbX_3 nanocubes were synthesized through a simple hot-injection and fast-cooling approach and the emission spectra could cover the entire visible spectra region by varying the size and halide composition [10,27]. Inspired by this work, different-shaped CsPbX_3 NCs including nanowires, nanoplates, nanorods and nanodots have been exploited through precise modulation the reaction temperature, organic surfactants and halide ratios in a very short time, and the maximum PLQY is up to 90% without any surface passivation [11-16]. After all, the synthesis of colloidal CsPbX_3 NCs is just beginning, thus there is no end to exploit a facile synthesis of brightly and different-shaped colloidal CsPbX_3 NCs and to understand their unique optical behavior.

It is well known that organic surfactants are often used in the shape-controlled synthesis of colloidal inorganic NCs, which can effectively affect the growth kinetics and direct the growth of the colloidal inorganic NCs [27-32]. Previous studies demonstrated that the shape of the colloidal CsPbX_3 NCs could be manipulated just by choosing different organic acid and amine ligands via a simple reprecipitation process [11]. More recently, Liu et al. studied comprehensively the roles of

organic amines and acids in the ligand-mediated synthesis of colloidal CsPbBr₃ NCs, and they found that the ammonium ions could effectively control the growth of anisotropic nanoplatelets and the carboxylate ligands played an important role in the size-tunability of isotropic nanocubes [17]. In these reports, however, the self-assembly behavior of CsPbBr₃ nanoplates was rarely discussed. In 2015, Alivisatos et al. demonstrated that the CsPbBr₃ nanoplates could self-assemble into highly ordered hierarchies, which may be as an ideal platform for fundamental optoelectronic studies [16]. Therefore, it is interesting to study the effects of organic ligands and reaction temperature on the luminescence and self-assembly of colloidal perovskite CsPbX₃ NCs. In this paper, we have demonstrated the effects of organic amines with different hydrocarbon chain lengths on the optical properties, morphologies and crystal structures of colloidal CsPbBr₃ NCs at different reaction temperatures, which were synthesized in the presence of oleic acid (OA) and different organic amines through a simple colloidal chemistry approach. The as-obtained CsPbBr₃ NCs are nanocubes with a cubic phase for different organic amines at 160 °C, and PLQYs of the products synthesized in the presence of CTAm and OLAm are generally in 55-80% while the PLQY of the products synthesized in the presence of OTAm is less than 20%. The effects of reaction temperature on the optical properties, morphology and crystal structure of the CsPbBr₃ NCs synthesized in the presence of cetylamine (CTAm) were studied. Apart from nanocubes are present in the CsPbBr₃ NCs, some nanoplates are also observed. More interestingly, these nanoplates can self-assemble into face-to-face stacked nanostructures. In contrast to the perovskite NCs synthesized in the presence of CTAm at 120 °C and 140 °C, no face-to-face oriented assemblies appear in the product at 160 °C. Moreover, a similar self-assembly behavior is observed in the products synthesized in the presence of oleylamine (OLAm), but only flat nanoplates are observed in the product in the presence of octylamine (OTAm). As a result, it can be concluded that the long hydrocarbon chain of organic amines and lower reaction temperature may be responsible for the self-assembly behavior of the CsPbBr₃ NCs.

2. Experimental

2.1 Materials

Cs₂CO₃ (99%, Aladdin), octadecene (ODE, 90%, Alfa Aesar), oleic acid (OA, 90%, Aladdin), octylamine (OTAm, 99%, Acros Organic), cetylamine (CTAm, 90%, Alfa Aesar), oleylamine (OLAm, 80-90%, Aladdin), lead(II) chloride (PbCl₂, 99%, Alfa Aesar), lead(II) bromide (PbBr₂, 98%, Alfa Aesar), lead(II) iodide (PbI₂, 98.5%, Alfa Aesar). Other solvents such as acetone and toluene are reagent grade and purchased from Beijing Chemical Reagent Company. All chemicals were used as received without any further purification.

2.2 Synthesis of Cesium Oleate (Cs-oleate) precursors

The synthesis of Cs-oleate precursors were prepared following a previous synthetic method [10]. Typically, Cs₂CO₃ (0.204 g) was loaded into a 25 mL of four-necked flask, and then 10 mL of ODE and 0.625 ml of OA were added. The mixture was degassed under N₂ at room temperature for 20 min, and then dried at 110 °C for 1 h. Afterwards, the reaction temperature was increased to 150 °C until Cs₂CO₃ was dissolved completely in the mixture under the protection of N₂ flow. It should be noted that the Cs-oleate could be precipitated out of ODE at room temperature, and the Cs-oleate precursors should be re-heated to 100 °C before next step.

2.3 Synthesis of CsPbBr₃ NCs

In a typical synthesis of CsPbBr₃ NCs, PbBr₂ (0.138 g) and ODE (10 mL) were loaded into a

25 mL four-necked flask, and the mixture was then degassed under N₂ flow for 20 min, following by drying at 110 °C for 1 h. Afterwards, 1 mL of OA and 1 mL of organic amines including OTAm, CTAm and OLAm were injected into the reaction mixture. It should be noted that the CTAm is solid at room temperature, which should be heated to become fluid before injection. After complete solubilization of PbBr₂ salt, the temperature was set at 160 °C, and then 0.8 mL of Cs-oleate precursor solution was injected into the reaction mixture quickly, and the color of the reactants immediately changed to green. The aliquots were extracted at different reaction time and then cooled by the ice-water bath. To study the effects of the reaction temperature on the PL properties and morphology of the CsPbBr₃ NCs, the reaction temperature was changed to 120 and 140 °C while other reaction conditions remained unchanged.

The acetone was added into the crude solution to promote precipitation, and then the solution was centrifuged at 8000 rpm for 5 min. The as-obtained CsPbBr₃ NCs were collected and then re-dispersed into toluene to form stable colloidal solution for further characterization and measurement.

2.4 Characterization

Transmission electron microscopy (TEM) images were recorded on a JEM-1400 transmission electron microscope with an accelerating voltage of 100 kV, and high-resolution TEM (HRTEM) images were collected on a JEM-2010 with an acceleration voltage of 200 kV. The Energy dispersive X-ray spectrum (EDS) were studied by using JEM-2010 transmission electron microscope equipped with an energy-dispersive X-ray analyzer. X-ray diffraction (XRD) patterns were conducted on a Bruker D8 Advance diffractometer with a Cu K α radiation source (λ = 1.5406 Å). Fourier transform infrared (FTIR) spectra were collected by a Varian Excalibur 3100 spectrometer. The UV-vis absorption spectra were collected by an HR2000CG-UV-NIR spectrometer from Ocean Optics. The PL spectra were recorded on a FLUORAT-02-PANORAMA spectrophotometer.

The relative PLQY was measured by using Rhodamine B as a standard reference (QY=97%, in ethanol), which can be calculated as follows:

$$QY_S = QY_R \times \frac{I_S}{I_R} \times \frac{A_R}{A_S} \times \frac{n_S^2}{n_R^2}$$

where the subscript R means Rhodamine B and S means the as-obtained products, all the data were measured under the excitation wavelength of 375 nm. QY is the quantum yield, I is the measured integrated area of PL intensity, n is refractive index (n = 1.497 for toluene; n = 1.362 for ethanol), and A is the absorbance at the excitation wavelength, which is typically lower than 0.10. All of the measurements were performed at room temperature.

3. Results and discussions

In most of previous studies, the CsPbBr₃ NCs were often synthesized by injection of Cs-oleate precursors into a mixture containing PbBr₂ and the organic surfactants including OA and OLAm as well as the un-coordinating solvent ODE [10-15]. Organic ligands play a crucial role in the synthesis of all-inorganic perovskite NCs, which are in close association with the morphology, size and optical properties of the products. However, the respective effects of OA and OLAm on the surface of perovskite NCs are still unclear. To study the role of OA and OLAm in the synthesis of CsPbBr₃ NCs, some control experiments were carried out by using individual OA or OLAm as

a capping ligand. Unexpectedly, the products synthesized in the presence of only OA as a capping ligand at 160 °C were agglomerated and the PL performance was very poor. In contrast, cubic CsPbBr₃ NCs were obtained when only OLAm was used as a capping ligand, and the particle size was increased from 7.9±0.8 nm to 9.4±1.0 nm with the reaction time prolonging from 5 s to 10 min (Fig. S1 of Supplementary data). Accordingly, the temporal absorption and PL peak shifted to longer wavelength and the bandwidth of the PL spectra became narrower with an increase of the reaction time (Fig. S2). If the single capping ligands (OLAm) were changed to CTAm and OTAm, the cubic CsPbBr₃ NCs were also obtained, but there was some aggregation in the TEM images of the products synthesized in the presence of organic amines with relatively short chain length (Fig. S3A and B), and the PL spectra were characteristic by the narrow emission line width of 20-25 nm (Fig. S3C and D). Therefore, it can be concluded that the organic amines plays an important role in the formation of CsPbBr₃ NCs.

Fig.1 (A) Absorption and (B) PL spectra of CsPbBr₃ NCs synthesized in the presence of OA and organic amines with different hydrocarbon chain length for 5 s and 10 min; (C) the corresponding digital photos of different products obtained at 10 min, from top to bottom: OLAm, CTAm and OTAm; (D) The time-resolved PL decay and fitting curves of the peak emission with an excitation wavelength of 375 nm for different products obtained at 10 min; (E) The relative PLQY comparison of CsPbBr₃ NCs synthesized using different organic amines.

To further study systematically the effects of organic amines with different hydrocarbon chain length on the morphology, structure and optical properties of CsPbBr₃ NCs, parallel reactions are carried out under similar conditions, in which the OA and organic amines with different chain length are used as capping ligands. Fig. 1A and B depict the absorption and PL spectra of CsPbBr₃ NCs synthesized in the presence of OLAm, CTAm and OTAm for the reaction time of 5 s and 10 min, respectively, in which the reaction temperature is 160 °C. For the CsPbBr₃ NCs synthesized in the presence of different organic amines, there is little red-shift of absorption and PL peaks with the reaction time increasing from 5 s to 10 min. This indicates that extending the reaction time has little effects on the absorption and PL maximum of the CsPbBr₃ NCs synthesized in the presence of organic amines with relatively long hydrocarbon chain. All the PL spectra of the CsPbBr₃ NCs synthesized in the presence of different amines are characteristic by

the narrow emission line widths of 19-24 nm and small Stokes shifts of 10-15 nm between absorption edge and the PL peak, which can be attributed to the direct exciton recombination process [11]. Fig. 1C gives the digital photos of the CsPbBr₃ NCs solution in toluene before and after UV illumination, and green color can be observed. It should be noted that the brightness of the products synthesized in the presence of OLAm and CTAm is stronger than the product synthesized in the presence of OTAm under UV illumination. Time-resolved PL decay measurements were carried out to get the information of the excited states, and representative time-resolved PL decay spectra of the CsPbBr₃ NCs synthesized in the presence of different organic amines for 10 min are presented in Fig. 1D, which were measured in toluene. The time-resolved PL decays were fitted into triexponential decay functions, which give a short-live PL time (τ_1), an intermediate PL lifetime (τ_2) and a long lifetime (τ_3), and the fitting parameters are given in Table. S1. The average PL decay lifetimes are calculated to be 28.1, 15.1 and 15.6 ns for the products synthesized in the presence of OTAm, CTAm and OLAm, respectively. The short-live PL time mainly originates from radiative lifetimes, which is decreased slightly as the PL peak shifts to longer wavelength for the products synthesized in the presence of different amines, suggesting that the PL decay mainly takes place through the exciton radiative recombination in the product synthesized in the presence of CTAm [8,11]. The relatively long lifetime should be attributed to the nonradiative recombination lifetimes, which have a greater contribution to the products synthesized in the presence of OTAm due to poor surface passivation or structural distortion [34]. Just as the change of absorption and PL emission peaks, little change is observed in the time-resolved PL decay spectra of the products obtained at 5 s and 10 min, which were synthesized in the presence of OLAm (Fig. S4). To further compare the PL performance of the CsPbBr₃ synthesized in the presence of different organic amines, the relative PLQYs of all the products are depicted in Fig. 1E, and the relative PLQYs of the CsPbBr₃ NCs synthesized in the presence of OTAm are less than 20%, and the PLQYs of the other products are in the region of 55-76%, which suggests that the carbon chain length variation of organic amines has a strong correlation to the optical properties of NCs. The important information about the optical properties for the corresponding CsPbBr₃ NCs is summarized in Table.1. To expel the quenching of the PLQY of the products using acetone washing technique, herein, we compare the PLQY of the CsPbBr₃ NCs obtained at 10 min synthesized in the presence of OLAm by using four types of solvents to precipitate the products. As shown in Fig. S5, the PLQY is measured to in the range of 69-80%, and PL quenching by the acetone is not apparent, and thus the acetone is used to precipitate the CsPbBr₃ NCs to keep the reaction parameters similar for all the products in this work.

Table.1 Summary of the important parameters including optical properties, shape and average size for the CsPbBr₃ NCs synthesized in the presence of OA and organic amines with different hydrocarbon chain length for 5 s and 10 min

Amine	Time	PL peak (nm)	FWHM (nm)	Shape	Size (nm)	PLQY (%)
OTAm	5 s	514	19	Nanoplates and	9.1±2.4	17
	10 min	516	19	nanocubes	10.6±2.4	12
CTAm	5 s	510	23	Nanocubes	8.1±1.5	55
	10 min	512	24		8.4±1.3	76
OLAm	5 s	513	20	Nanocubes	10.1±1.2	60
	10 min	514	21		10.2±1.7	74

The growth of CsPbBr₃ NCs synthesized using CTAm and OA as surfactants was studied by using the temporal absorption and PL spectra, which were collected by withdrawal of some samples from the reaction mixture at different time (5 s, 1 min, 10 min and 20 min). A little red-shift of the broad absorption peak beyond 500 nm is observed with an increase of the reaction time (Fig. S6A). In contrast, the corresponding PL spectra remain nearly unchanged (Fig. S6B). Moreover, the relative PLQYs of the products increase from 55% (5 s) to 76% (10 min) and then decrease to 70% (20 min) (Fig. S6C). The corresponding TEM images and size distribution histograms of CsPbBr₃ NCs collected at different reaction time are given in Fig. S7, and most of the products are nanocubes, and the average size increases from 8.1 nm to 8.4 nm and then decreases to 6.7 nm for the products obtained at 20 min, and the size reduction may arise from de-focusing due to the depletion of the monomer concentration over longer growth duration [35].

Fig.2 TEM images of CsPbBr₃ NCs synthesized in the presence of organic amines with different chain length: (A, B) OTAm; (C, D) CTAm; (E, F) OLAm. The top and bottom panels represent the product obtained at 5 s and 10 min, respectively.

Fig. 2 shows the TEM images of the CsPbBr₃ NCs synthesized in the presence of different organic amines and OA at 160 °C, and the top and bottom panels display the typical TEM results of the products collected at 5 s and 10 min, respectively. For the product synthesized in the presence of OTAm, the nanocubes and some nanoplates are present at early stage (Fig. 2A), and the inset shows the TEM images of some ultrathin nanoplates. As the reaction time is extended to 10 min, most of the products are nanocubes, but some ultrathin nanoplates are also present in the products (Fig. 2B). The formation of ultrathin nanoplates in the presence of OTAm with shorter chain is in good agreement with the previous report [17]. The corresponding average size of nanocubes increases from 9.1 ± 2.4 nm to 10.6 ± 2.4 nm with the reaction time extending from 5 s to 10 min by counting 100 particles (Fig. S8A, B and Table 1), which contributes to the red-shift of absorption and PL peaks due to the quantum size effects (Fig. 1A) [10]. When OTAm with shorter hydrocarbon chain was replaced by CTAm and OLAm with longer hydrocarbon chain, uniform CsPbBr₃ nanocubes were obtained at different reaction time (Fig. 2C-F). Based on the size distribution histograms shown in Fig. S8C-F, the average size of the product in the presence of

CTAm is the least of all, which is consistent with the blue-shift of the PL maximum as compared to other products synthesized in the presence of OLAm and OTAm. The difference may arise from the intrinsic solid state of CTAm at room temperature, which has a stronger bonding interaction with the surface of NCs. The FTIR studies provide the evidence of the bonding interaction of different organic amines with the surface of NCs, which are shown in Fig. S9, in which all the products are washed by toluene/acetone. As shown in Fig. S9A, two sharp bands in the region of 2950-2850 cm^{-1} are observed, which arise from asymmetric methyl stretching and methylene stretching modes, respectively [36,37]. To detect the surface ligands on the nanocrystal surface, a magnified FTIR spectra in the region of 1200-1600 cm^{-1} is given in Fig. S9B. Different from two other products synthesized in the presence of OLAm and OTAm, an obvious peak at 1535 cm^{-1} and a weak but non-negligible peak at 1580 cm^{-1} are observed in the product synthesized using CTAm, which can be attributed to carboxylate asymmetric stretching vibration and the N-H bending mode from amines [17]. This indicates that the both carboxylates and ammoniums binding to the nanocrystal surface of the products synthesized using CTAm are difficult to be removed due to the nature of solid state of CTAm at room temperature.

Fig.3 (A) HRTEM image of CsPbBr₃ NCs synthesized by using CTAm obtained at 10 min, and the inset shows the SAED pattern; (B) the corresponding EDS pattern.

A typical HRTEM image of cubic CsPbBr₃ NCs synthesized in the presence of CTAm at 160 °C is presented in Fig. 3A, and clear lattice fringes can be observed throughout each single nanoparticle. The interplanar distances of two typical particles are measured to be 0.41nm and 0.59nm, which correspond to (110) and (100) facets of cubic CsPbBr₃ structure. The selected area electron diffraction (SAED) pattern inserted in Fig. 1A confirms that the as-obtained CsPbBr₃ NCs are cubic structure with a good crystallinity. Based on the formula of CsPbBr₃ structure, the ideal atomic ratio of Pb to Br should be 1:3 for bulk materials. Herein, energy dispersive X-ray spectroscopy (EDS) measurement was employed to confirm the atomic ratio of Pb to Br of the as-obtained CsPbBr₃ NCs, which is present in Fig. 3B. The EDS result reveals the presence of Cs, Pb and Br elements, and the atomic ratio of Pb to Br is 1:3.4, which indicates the product has a Br-rich surface with CTAm and OA capping [7,9].

Fig. 4A shows the XRD patterns of the CsPbBr₃ NCs synthesized in the presence of OLAm, CTAm and OTAm. All the products have four main peaks at $2\theta = 21.4, 30.4, 37.5, 43.7^\circ$, which correspond to (110), (200), (211) and (220) diffractions of cubic CsPbBr₃ (JCPDS No.75-0412). There are no other phases detected in the XRD patterns. The schematic illustration of the crystal structure of cubic CsPbBr₃ is given in Fig. 4B. The XRD results indicate that the organic amines with different chain length have no effects on the crystal structure of CsPbBr₃ NCs.

Fig.4 (A) XRD patterns of CsPbBr₃ NCs synthesized in the presence of three different amines, and the bottom vertical lines represent the standard diffraction lines of cubic CsPbBr₃ (JCPDS No.75-0412); (B) Schematic illustration of crystal structure of cubic CsPbBr₃.

Fig.5 (A) Absorption and PL spectra of CsPbBr₃ NCs synthesized in the presence of CTAm for different reaction temperatures, and the inset shows the digital photo of PDMS film containing CsPbBr₃ irradiated under the UV light; (B) The plots of PL peaks, full width at half maximum (FWHM) and relative PLQY as a function of reaction temperature.

Based on the previous reports, reaction temperature played a significant role in the nucleation and growth of inorganic NCs, and thus their size and morphology could be tailored effectively [37-42]. Previous report demonstrated that the size of CH₃NH₃PbBr₃ NCs was increased from 1.8 nm to 3.6 nm with the reaction temperature elevating from 0 to 60 °C [8]. Besides, the shape and thickness of the CsPbBr₃ nanoplates could be controlled by varying the reaction temperature, which was reported by Alivisatos et al. [16]. In this work, in consideration of the intrinsic nature of solid CTAm, some control synthesis of CsPbBr₃ NCs was conducted in the presence of CTAm by varying the reaction temperatures. Fig. 5A depicts the absorption and PL variation with the reaction temperature increasing from 120 °C to 160 °C. As shown in Fig. 5A, the PL spectrum of the products obtained at 120 °C exhibits a weak shoulder peak at 458 nm and a strong peak at 486 nm, and the shoulder peak disappears gradually with an increase of the reaction temperature. Fig. 5B gives the variation trend of the PL peak, full width at half maximum (FWHM) and PLQY of the CsPbBr₃ NCs as a function of reaction temperature. As the reaction temperature is increased from 120 to 160 °C, a red-shift of PL peak from 486 nm to 512 nm is observed, and the FWHM is reduced from 31 to 24 nm with the PLQY increasing from 58% to 76%, and the corresponding important information is summarized in Table.2. The aforementioned results indicate that the reaction temperature has an important effect on the optical properties of CsPbBr₃ NCs.

Table.2 Summary of the important parameters of the CsPbBr₃ NCs synthesized in the presence of CTAm for different reaction temperatures

Temperature (°C)	PL peak (nm)	FWHM (nm)	Shape	Size (nm)	PLQY (%)
120	486	31	Nanocubes	7.7±1.4	58
140	504	26	Nanocubes	7.8±1.5	63
160	512	24	Nanocubes	8.4±1.3	76

To further clarify what brings about the optical change of CsPbBr₃ NCs with the variation of reaction temperature, the TEM images and XRD patterns of the CsPbBr₃ NCs synthesized under different reaction temperature are presented in Fig. 6. The products obtained under different reaction temperatures exhibit a cubic shape (Fig. 6A-C), and the average size increases from 7.7±1.1 to 8.4±1.3 nm with the reaction temperature elevating from 120 to 160 °C (Fig. S10). The variation of size supports the red-shift of PL emission peak with an increase of reaction temperature due to the quantum-size effects [9]. As shown in Fig. 6D, the diffraction peak of (200) plane is dominant over the XRD pattern of the product obtained at 120 °C, and the intensity of other diffraction peaks is relatively weak. In contrast, four main diffraction peaks assigning to (110), (200), (211) and (220) are clearly observed in the XRD patterns of the products synthesized at 140 and 160 °C. The TEM and XRD results indicate that lower temperature is not beneficial for the rapid nucleation and growth of CsPbBr₃ NCs in the presence of CTAm, which results in relatively poor crystallinity. On the contrary, cubic CsPbBr₃ NCs with better crystallinity can be obtained at higher temperature, which can facilitate the nucleation and growth of the NCs and quicken the movement of the surfactant CTAm.

Fig.6 TEM images of CsPbBr₃ NCs synthesized in the presence of CTAm for different reaction temperatures: (A) 120 °C; (B) 140 °C and (C) 160 °C; (D) the corresponding XRD patterns together with the bottom lines of cubic CsPbBr₃.

Interestingly, apart from the monodispersed CsPbBr₃ nanocubes, the nanoplates also appear in the TEM images of the products synthesized at 120 °C and 140 °C, which are self-assembled into face-to-face lamellar structures. Fig. 7 shows the TEM results of the self-assembly behavior of

CsPbBr₃ nanoplates obtained at 120 and 140 °C. At 140 °C, very thin nanoplates are observed in the product obtained at 5 s, which grow along with lamellar structures with the length is beyond 100 nm (Fig. 7A). As a matter of fact, the nanoplates are made up of some small CsPbBr₃ nanoparticles connected via the organic surfactants. As the reaction time is prolonged to 5 min and 10 min, low-symmetry CsPbBr₃ nanoplates are self-assembled into highly-ordered face-to-face geometry with large area up to several micrometers (Fig. 7B and C). If the reaction time temperature is reduced to 120 °C, bigger NCs can be obtained with a high-aspect ratio, which can also self-assemble into highly-ordered nanostructures (Fig. 7D). However, no self-assembly behavior is observed in the products obtained at 160 °C, which suggests that the high reaction temperature is not beneficial to the self-assembly behavior of CsPbBr₃ NCs due to high molecular motion, which may break the self-assembly behavior. Such a similar result is also observed in Bekenstein's work [16]. This result suggests that the reaction temperature contributes to the self-assembly behavior of the CsPbBr₃ NCs.

Fig.7 TEM images of the self-Assembly of the CsPbBr₃ NCs synthesized in the presence of CTAm at different reaction temperatures for different reaction time :(A) 140 °C, 5 s; (B) 140 °C, 5 min; (C) 140 °C, 10 min; (D) 120 °C, 10 min; The insets show the corresponding monodispersed NCs.

Fig. 8 (A) Absorption and PL spectra of CsPbBr₃ nanocrystals synthesized by using OTAm and OLAm at 120 °C, and the corresponding TEM images: (B) OTAm; (C) OLAm; The inset shows the corresponding monodispersed NCs.

In general, the formation of self-assembly behavior of inorganic NCs is mainly resulted from the cohesive interaction through interdigitation or interpenetration of alkyl chain of organic ligands with long hydrocarbon length. In addition, the synergistic effects of the steric repulsions, the van der Waals attraction, directional dipolar interactions and the surface charge state may also contribute to the self-assembly behavior of inorganic NCs [43-47]. Herein, to further study the

influence factors of the self-assembly behavior of CsPbBr₃ nanoplates, the optical properties and morphology of CsPbBr₃ NCs synthesized in the presence of OTAm and OLAm at 120 °C are given in Fig. 8. As shown in Fig. 8A, the CsPbBr₃ NCs synthesized in the presence of OLAm exhibits a narrow PL band at 516 nm with a FWHM of 18 nm, and the first exciton absorption peak at 478 nm. In contrast, the PL peak of the product synthesized in the presence of OTAm is located at 509 nm, and the emission band width is up to 28 nm. As compared to the change trend of the PL peak of the products obtained at 160 °C, the PL peak of the CsPbBr₃ NCs synthesized in the presence of OTAm at 120 °C shifts to short wavelength. The difference in the change of the PL peak can be explained by the TEM results of the CsPbBr₃ NCs obtained at 120 °C. According to the insets of the Fig. 8B and C, the product synthesized in the presence of OTAm exhibits a quasi-cubic shape, but the product synthesized in the presence of OLAm has a cubic shape, and the average of the latter sample is bigger than that of the former one, which contributes to the blue-shift of the PL peak due to the quantum-size effect. More surprisingly, some bigger cubic nanoplates can be detected in the products obtained at 120 °C in the presence of OTAm (Fig. 8B), which are consisted of the small-sized particles connected through the organic ligands, which demonstrates that the organic mesostructures act as the growth directing soft templates based on previous work [16]. Most of the nanoplates are flat on the substrate, and no self-assembly behavior is observed in Fig. 8B, and this arrangement may reduce the exposed surface energy due to the ultrathin plate. In contrast, the products obtained in the presence of OLAm can self-assemble into face-to-face nanostructures, which is similar to the results observed in the products synthesized in the presence of CTAm at 120 and 140 °C. The aforementioned results indicate that the carbon chain length of the organic ligands plays a critical role in the self-assembly behavior of CsPbBr₃ NCs. When the organic ligand with short carbon chain length is capped on the surface of NCs, the cohesive interaction between adjacent NCs through the interdigitation or interpenetration of alkyl chain is weaker than that of the NCs capped by longer alkyl chains. Thus the NCs are inclined to be flat on the substrate to reduce the surface energy. On the contrary, the NCs capped by the longer alkyl chain (CTAm and OLAm) can stand vertical to the substrate through the interdigitation or interpenetration of the alkyl chain, thus the whole surface energy is reduced greatly.

4. Conclusions

In summary, bright colloidal CsPbBr₃ NCs have been synthesized in the presence of OA and organic amines with varying hydrocarbon chain length. The time-resolved PL decay lifetime can be tuned from 15.1 to 28.1 ns by varying the chain length of the organic amines. The PLQYs of 70-80% can be obtained in the CsPbBr₃ NCs with relatively long carbon chain for a longer reaction time. The hydrocarbon chain length has little effect on the morphology and crystal structure of the CsPbBr₃ NCs. When the CTAm is used in the synthesis of CsPbBr₃ NCs, the red-shift of the PL peak is detected with an increase of the reaction temperature from 120 to 160 °C, and the emission band width is decreased from 31 to 24 nm with the PLQYs increasing from 58 to 76%. The red-shift of the PL peak can be explained by the increase of the average size due to the quantum-size effects. More interestingly, the nanoplates can be obtained at 120 and 140 °C, which have a strong tendency to self-assemble into face-to-face arrangements. The comparison of the geometries of the nanostructures obtained in the presence of OTAm and OLAm at 120 °C suggests that the carbon chain length of the organic ligands plays a critical role in the

self-assembly behavior of the CsPbBr₃ NCs. These observations may shed light on the roles of organic surfactants with different carbon chain length in the synthesis of perovskite NCs, which paves the way for self-assembly of perovskite NCs for further optoelectronic applications.

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TOC Figure