

Synthesis parameter optimization for uniform and stable perovskite quantum dots

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Abstract. Colloidal lead halide perovskites nanocrystals, also known as quantum dots, have been intensively studied as promising optoelectronic materials and have attracted widespread attention due to their unique optical versatility, high photoluminescence quantum yield and convenient synthesis. Among them, the potential of all-inorganic halide caesium lead perovskite (CsPbX₃, X = Cl, Br, I) is particularly prominent. In this work, by adjusting the experimental parameters, including precursor preservation condition, reaction temperature and the isolation/purification process, CsPbBr₃ quantum dots with uniform size, neat arrangement, narrow full width at half maxima and excellent luminescent properties have been successfully prepared, which lays a good foundation for its potential application in practical optoelectronic devices.

1 Introduction

CsPbBr₃ quantum dots (QDs) have broad application prospects in the fields of lighting and display due to their narrow emission line width (12-42 nm), high quantum yield (50-90 %) and short radiation lifetime (1-29 ns), and have attracted widespread attention in scientific field [1-4].

Since Møller [5] reported CsPbX₃ (X = Cl, Br or I) perovskite in 1958, the research on lead halide perovskite nanocrystals has made rapid progress in the past few decades. Protesescu [6] et al. prepared high luminescent perovskite-based colloidal QDs and demonstrated a new way to prepare halide perovskites. They used cheaper materials and simple methods to synthesize monodisperse colloidal nanocubes of all-inorganic caesium halide lead perovskite with cubic shape and cubic perovskite crystal structure, which opened a new door for the preparation of lead halide perovskite nanocrystals.

However, the performance of CsPbBr₃ QDs needs to be improved for practical applications. Therefore, meticulous preparation of QDs with multiple controllable parameters has become a top priority [7-10]. Herein, we successfully synthesized uniform and stable CsPbBr₃ QDs by thermal injection method. More importantly, by optimizing experimental parameters, including precursor preservation condition, reaction temperature and the isolation/purification process, the size distribution, colour purity, and storage stability of CsPbBr₃ QDs have been significantly improved, which lays a foundation for its future application [11-13].

2 Materials and Methods

2.1 Materials

Lead (II) bromide (PbBr₂, 99.99%), oleic acid (OA, 90%), oleylamine (OAm, 90%) and 1-octadecene (ODE, 90%) were bought from Alfa Aesar. Caesium carbonate (Cs₂CO₃, 99.99%), methyl acetate (MAC, GR, 99%), ethyl acetate (EAC, GR, 99.5%), toluene (TL, GR, 99%), tert-butanol (TBA, GR, 99%) and n-hexane (Hex, GC, 99.0%) were bought from Aladdin. All chemicals were used without purification unless otherwise noted.

2.2 Synthetic methods

2.2.1 Preparation of Cs-Oleate Solution

Cs₂CO₃ (407 mg), 20 mL of ODE and 1.25 mL of OA were added to a 50 mL three-necked flask and maintained under vacuum at 120 °C for 60 min. The mixture was stirred under N₂ to 150 °C until all Cs₂CO₃ was dissolved. The solution was put aside for later use with the heating temperature being kept by various methods.

2.2.2 Synthesis of CsPbBr₃ QDs

PbBr₂ (414 mg) and 30 mL of ODE were placed in a 100 mL three-necked flask and maintained under vacuum at 120 °C for 60 min. Then the reaction system was switched to nitrogen protection, 3 mL of OA and 3 mL of OAm were injected into the solution. Then the temperature was raised

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to 150 °C, 160 °C and 180 °C, respectively, and the Cs-oleate was swiftly injected. After 5 s, the reaction solution was put in an ice water bath and cooled to room temperature.

3 Results and Discussion

3.1 The influence of precursor preservation condition on the morphology of CsPbBr₃ QDs

As mentioned in the synthetic method, the synthesis of CsPbBr₃ QDs consisted of two steps, namely the precursor solution preparation followed by nucleation of the nanocrystals. The precursor solution played an important role in the whole experimental process, and its quality directly affected the results of the experiment.

In the preparation of precursor solution, CsCO₃ was dissolved in organic solvent under high temperature. The obtained precursor solution was preserved in a vacuum oven at 120 °C, such method has been normally adopted in literature. However, after a period of time, the dissolved CsCO₃ partially precipitated and caused the precursor solution to become turbid (Fig.1a). Therefore, we modified the precursor preservation condition by keeping it in an oil bath with inert atmosphere. As shown in Fig.1b, a clear and transparent precursor solution can be obtained.

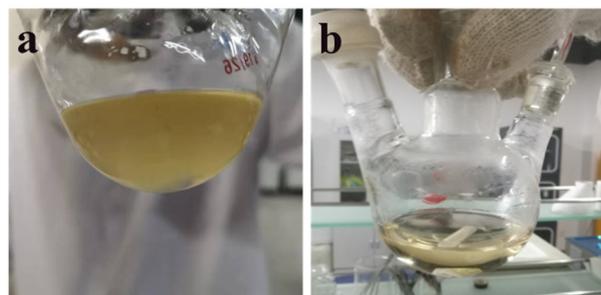


Fig. 1. Precursor solution after being preserved in (a) vacuum oven and (b) oil bath.

The different precursor preservation conditions had great influence on the resultant morphologies of obtained CsPbBr₃ QDs. TEM tests were carried out on the QDs prepared by the two thermal preservation methods. As shown in Fig.2 (a-c), QDs prepared by the precursor preserved in the vacuum oven was large in size and varied greatly in dimension. In comparison, as shown in Fig.2 (d-f), the QDs prepared by the precursor preserved in the oil bath are very uniform in size and neatly arranged. The average size of these QDs was about 8 nm as measured from TEM images.

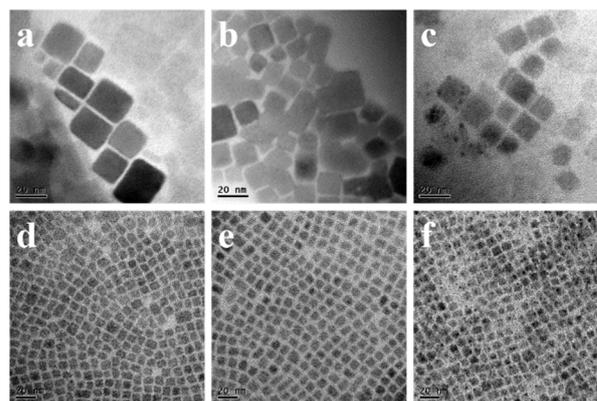


Fig. 2. TEM images of CsPbBr₃ QDs prepared by using the precursor preserved in (a-c) vacuum oven. And (d-f) oil bath.

XRD measurement was carried out on the prepared QDs shown in Fig. 2(d-f) to examine their crystal structure in comparison with the standard PDF card. It can be obtained from Fig.3 that the prepared QDs had a cubic crystal structure, and all diffraction peaks corresponded perfectly to the standard card (PDF#54-0752) of CsPbBr₃ QDs.

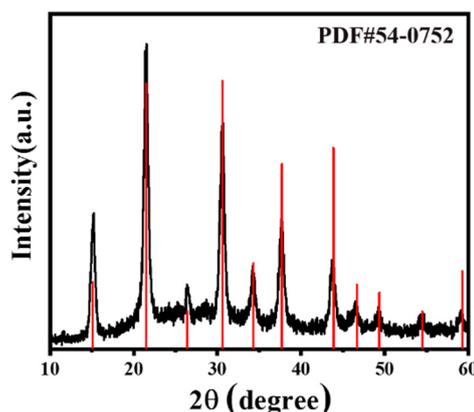


Fig. 3. XRD pattern of the prepared CsPbBr₃ QDs.

3.2 The influence of reaction temperature on the size of CsPbBr₃ QDs

The reaction temperature had a very crucial effect on the size of CsPbBr₃ QDs, The average size of QDs have been successfully adjusted by adjusting the reaction temperature.

Fig.4 (a-c) shows the TEM images of CsPbBr₃ QDs prepared at different temperatures of 150 °C, 160 °C and 180 °C. The average particle sizes of QDs prepared at 150 °C, 160 °C and 180 °C were measured to be 7.35 nm, 7.44 nm and 8.15 nm respectively, with the size distributions shown in Fig. 4(d-f), indicating that in a certain range, the higher the preparation temperature, the larger the average particle size.

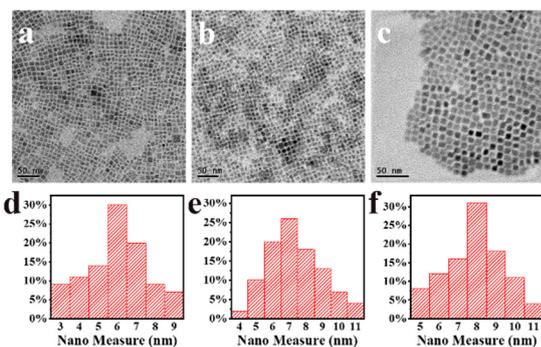


Fig. 4. TEM images of CsPbBr₃ QDs prepared at (a) 150 °C, (b) 160 °C and (c) 180 °C. Particle size distributions of CsPbBr₃ QDs prepared at (d) 150 °C, (e) 160 °C and (f) 180 °C.

3.3 The influence of isolation/purification on optical properties of CsPbBr₃ QDs

Isolation/purification of prepared QDs is a very important step that determines the dispersity and optical properties of QDs. During the isolation/purification of QDs, the excessive reagent as well as surface ligand were removed. Thus, the choice of solvents and washing times is the key to the long-term storage of QDs. Improper reagents will directly cause the agglomeration of QDs, and even destroy its structure, resulting in photoluminescence (PL) quenching [14]. So it is necessary to select appropriate reagents from a large number of attempts.

We divided the optimization of isolation/purification into three steps, namely choice of washing reagent, composition of washing reagent, and washing times. Four reagents were selected to purify QDs, namely TL, mixed solution of MAC and Hex, mixed solution of EAC and Hex, and mixed solution of TBA and Hex. PL test was carried out on the samples obtained by these four methods (Fig.5).

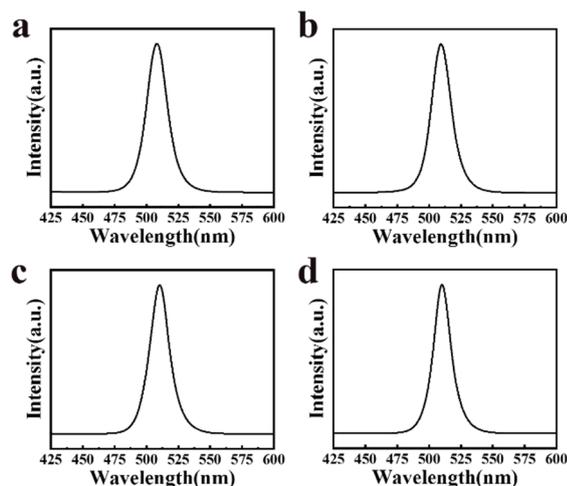


Fig. 5. PL patterns of CsPbBr₃ QDs washed by (a) TL, (b) mixed solution of MAC and Hex, (c) mixed solution of EAC and Hex and (d) mixed solution of TBA and Hex.

The full width at half maxima (FWHM) of the four samples were measured and listed in Table 1. It can be seen that the FWHM of the QDs washed with TL was the largest, up to 23.5 nm. The FWHM of the QDs washed by

MAC/Hex and EAC/Hex were smaller, being 21.5 nm and 20 nm, respectively. And the FWHM of the QDs washed by mixed solution of TBA and TL was the smallest, being only 16 nm. However, TBA would lead to easy agglomeration of QDs, thus reducing the optical performance and storage stability of QDs.

Table 1. PL analysis of QDs washed by different reagents.

Washing method	TL	MAC and Hex	EAC and Hex	TBA and Hex
Emission peak (nm)	508	509.5	510.5	510
FWHM (nm)	23.5	21.5	20	16

In the previous attempt, the FWHM of the QDs washed by MAC/Hex and EAC/Hex were small, so we further adjusted the proportions of different reagents in the mixed solution. The PL spectra of QDs washed by the optimum reagent ratio of 3:1 are shown in Fig.6.

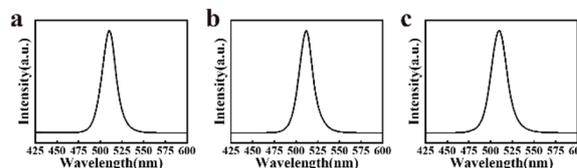


Fig. 6. PL patterns of CsPbBr₃ QDs washed by (a) MAC: Hex=3:1, (b) EAC: Hex=3:1 and (c) Hex.

It can be seen from Table 2 that the FWHM of the QDs washed with EAC: Hex=3:1 is smallest, being 19 nm, while those of the QDs washed with MAC: Hex=3:1 and Hex were larger, both of which being 21 nm.

Table 2. PL analysis of QDs washed by different reagents.

Washing method	MAC: Hex=3:1	EAC: Hex=3:1	Hex
Emission peak (nm)	510	511.5	510
FWHM (nm)	21	19	21

Finally, the influence of washing times on QDs was also analysed. By fixing the washing reagent of EAC: Hex=3:1, QDs were washed by different times and then analysed by PL test (Fig.7).

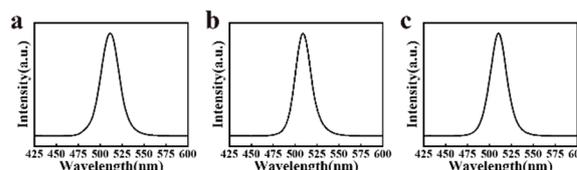


Fig. 7. PL patterns of CsPbBr₃ QDs washed with EAC: Hex=3:1 for (a) once, (b) twice and (c) three times.

As shown in Table 3, the FWHM of the QDs obtained after twice washing was 18.5 nm, which is significantly smaller than those of QDs washed once and three times. The smaller the FWHM, the higher the luminous purity of

QDs. Therefore, the optimized washing parameters of QDs was determined to be washed twice with EAC: Hex=3:1.

Table 3. Effect of washing times with EAC: Hex=3:1 on QDs.

Washing times	1	2	3
Emission peak (nm)	511.5	509	510
FWHM (nm)	20	18.5	19.5

CsPbBr₃ QDs can be greatly affected by the polarity of organic solvents. Solvent with strong polarity would have a significant negative impact on the optical property and structure integrity of QDs. Therefore, Hex with less polarity was used as the solvent of CsPbBr₃ QDs.

It can be seen from Fig.8, after adjusting the experimental parameters, the synthesized CsPbBr₃ QDs was a clear and transparent light green solution, which emits green fluorescence under the irradiation of ultraviolet (UV) lamp (365nm).

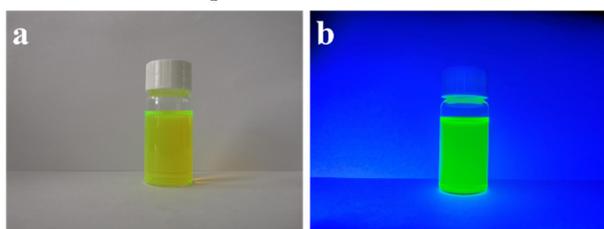


Fig. 8. Photographs of the CsPbBr₃ QDs solution under (a) natural light and (b) UV light (365 nm)

3.4 Research on storage stability of CsPbBr₃ QDs

CsPbBr₃ QDs are very fragile and may lose their structure integrity and optical properties by a variety of external stimuli, including light, heat, and oxygen, which is a major limiting factor for its practical application [15, 16].

The prepared CsPbBr₃ QDs were stored in a fridge frozen chamber, and taken out for PL and UV tests every other week. It can be seen from Fig.9 that after nearly a month of storage, the PL and UV curves of QDs were basically unchanged, being highly coincident with the beginning curve, showing good storage stability of CsPbBr₃ QDs prepared by optimized method.

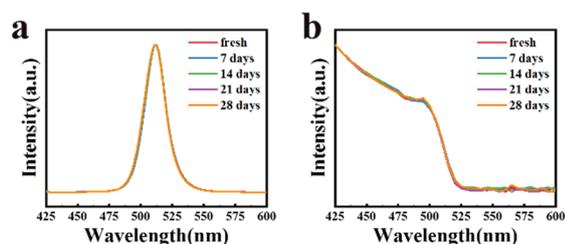


Fig. 9. (a) PL and (b) UV spectra of CsPbBr₃ QDs after various storage periods up to 28 days.

4 Conclusion

In conclusion, we demonstrate a systematic analysis on the synthesis parameters of CsPbBr₃ QDs by adjusting precursor preservation condition, reaction temperature and isolation/purification process. Compared with the previously reported CsPbBr₃ QDs, the QDs synthesized in this work show a high degree of monodispersity and narrow FWHM. More importantly, satisfactory storage stability has been demonstrated, which is of great significance for the potential practical application of perovskite QDs.

Acknowledgments

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