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## Preparation and Properties of Inorganic Perovskite Quantum Dots

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# Preparation and Properties of Inorganic Perovskite Quantum Dots

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**Abstract.** All inorganic perovskite quantum dots have excellent luminous properties such as high quantum efficiency, broad luminescence spectrum and narrow emission peak, which have potential applications in the field of photovoltaic and light emitting devices. All inorganic perovskite CsPbBr<sub>1.5</sub>I<sub>1.5</sub> quantum dots were prepared by an ion exchange method based on the traditional hot injection method. The luminescence and structure properties were tested, and we found that this method can get different light emitting position by adjusting the content of Br or I, and the structure of inorganic perovskite would not be changed.

## 1. Introduction

As early as the 1950s, researchers have prepared inorganic lead halide materials and studied their physical and chemistry properties have been studied. The luminous property of this material wasn't discovered until 1997 [1]. For a long time, the research progress of this kind of inorganic lead halide materials was very slow. In recent years, a series of novel metal organic halide materials CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub> (X = Cl, Br, I) were successfully prepared and applied in solar cells, which got a high energy conversion rate and up to 23.2%. Since Protesescu reported all-inorganic cesium lead halide perovskite quantum dots (QDs) (CsPbX<sub>3</sub>, X=Cl, Br, I) in 2015, this materials could potentially provide comparable optoelectronic properties as a promising class of materials for solar cells, photodetector, light-emitting diode (LED) with enhanced thermal and moisture stabilities compared to organic lead halide species and are not as sensitive as organic metal halides to the moisture and oxygen in the air.

In 2016, Zeng Haibo group prepared quantum dots of CsPbX<sub>3</sub> (X=Cl, Br) by saturation recrystallization process at room temperature [2]. Cesium halide and lead halide were firstly dissolved in DMF, oleic acid and oleamine were added as ligands, and appropriate amount was taken and dropped into toluene at room temperature. Because the solubility of CsPbX<sub>3</sub> in DMF is much higher than that in toluene, it is equivalent to transfer the ion solution containing Cs<sup>+</sup>, Pb<sup>2+</sup>, and X<sup>-</sup> neutral to its insoluble toluene solution. Since Cs<sup>+</sup> and Pb<sup>2+</sup> in toluene are over saturated, CsPbX<sub>3</sub> crystals can be precipitated out. This method takes advantage of the fact that CsPbX<sub>3</sub> QDs are ionic crystals. This method can be completed in a few seconds, without heating and inert shielding gas and hot injection operations, making the preparation of inorganic perovskite QDs more time-saving and labor-saving.



The ion exchange method also is an effective and feasible method for QDs synthesis. The core of this method is to replace one element of the crystal with another element, so as to change the chemical composition, so as to change the physical properties of the crystal. Herein, we synthesized the  $\text{CsPbBr}_{1.5}\text{I}_{1.5}$  QDs through hot injection method and an ion exchange process. The prepared QDs were tested by PL, TEM, and XRD.

## 2. Experimental Section

### 2.1. Experimental drugs and instruments

Cesium acetate, AR, 99.0%; Lead bromide, AR, 99.0%; Lead iodide, AR, 99.0%; Octadecene, AR, 99.0%; Oleic acid, AR, 90.0%; Oley amine, AR, 90.0%; Methylbenzene, AR; n-hexane, AR; All above chemical reagents purchased from Aladdin. UV-visible absorption spectrum, TU1810PC, Beijing general instrument co. LTD; Transmission electron microscopy, JEM-2100F, JEOL; X-ray diffraction equipment, SmartLab 2000, Rigaku.

### 2.2. QDs synthesis by hot injection [3]

Cesium oleate (Cs-OA) was first synthesized by follow processes: 2 mmol cesium acetate ( $\text{CsOOCCH}_3$ ), 2 ml oleic acid (OA) and 8 mL ODE were added into a 50 mL three-neck flask respectively, and a magneton was added in this flask, then connected the reaction device.

First, the three-necked flask was heated to 120°C and vacuum-pumped for 1h to remove water and air from the reaction flask. After that, the vacuum pump was shut down and heated to 150°C under Ar air protection, until cesium acetate was completely dissolved. The solution presented a transparent light yellow color, indicating that Cs-OA was generated. Cs-OA will be precipitated at room temperature, and the solution will be turbid. It should be placed in the oven at 50°C for preservation.

$\text{CsPbBr}_3/\text{CsPbI}_3$  QDs were synthesized by follow processes: 0.16 mmol  $\text{PbBr}_2/\text{PbI}_2$  0.5 mL oleic acid (OA), 0.5 mL oil amine (OAm), 5 mL octadecene (ODE) were added into a 50 mL three-necked flask, then added the magneton and connected the reaction device. The flask was heated to 120°C, then kept a vacuum using vacuum pump for 1 h after lead halide dissolved. At last, closed the vacuum pump and piped Ar gas in system. The flask was continued heating to 170°C, then 0.4 mL of as prepared Cs-OA solution was injected into this flask quickly. When  $\text{PbBr}_2$  was used in the reaction flask, with the injection of Cs-OA solution, the solution color changed from transparent yellow to yellowish green turbidity immediately. When  $\text{PbI}_2$  was used in the reaction flask, with the injection of Cs-OA solution, the solution color changed from orange to black and red turbidity. After reaction for 5 s~10 s, the reaction is abruptly cooled to room temperature by ice water.

### 2.3. Post-processing of $\text{CsPbBr}_3/\text{CsPbI}_3$ QDs

The synthesized perovskite  $\text{CsPbBr}_3/\text{CsPbI}_3$  QDs were placed two centrifuge tubes separately, each centrifuge tube contained about 3 mL solution, and symmetrically put into the centrifuge. The original solution was centrifuged directly at a speed of 12000 r/min to obtain the QDs precipitated. The precipitate was dissolved in 0.5mL toluene and centrifuged for 1 min at a speed of 1000 r/min to discard the lower layer of the precipitate. The upper quantum dot solution was mixed with 2 times the volume of methyl acetate. Centrifuge at 10000 r/min for 6 min. The solid  $\text{CsPbBr}_3/\text{CsPbI}_3$  QDs was obtained after the precipitate was placed in a vacuum freeze dryer for 24 h.

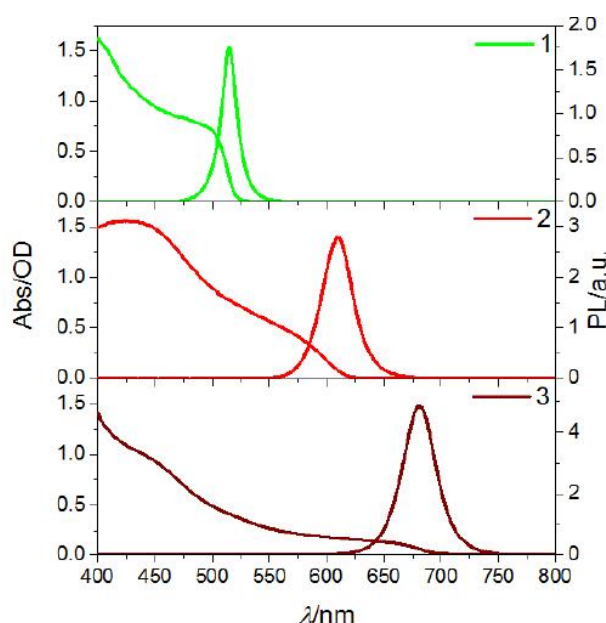
### 2.4. Prepared of $\text{CsPbBr}_{1.5}\text{I}_{1.5}$ QDs by ion exchange

The prepared solid  $\text{CsPbBr}_3$  and  $\text{CsPbI}_3$  QDs were removed from the freeze-dryer and prepared into a solution with a same concentration. To prepare  $\text{CsPbBr}_{1.5}\text{I}_{1.5}$  QDs, equal volume ratio was necessary by a simple mixing process at room temperature.

### 3. Results and discussion

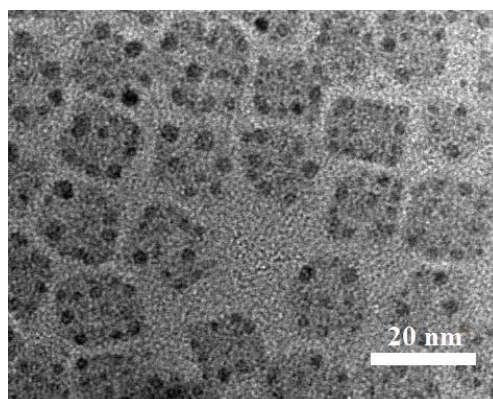
#### 3.1. Absorption and emission diagrams of inorganic perovskite QDs

UV-vis absorption and photoluminescence spectra (PL) of CsPbBr<sub>3</sub>, CsPbBr<sub>1.5</sub>I<sub>1.5</sub> and CsPbI<sub>3</sub> perovskite QDs irradiated by a 325 nm laser are showed in Figure 1. As can be seen from Figure 1, the luminous peak of this PL spectrum is in the visible light region, and the CsPbBr<sub>3</sub> perovskite QDs obtained a luminous peak at 515 nm under the laser excitation at 325 nm. In addition, CsPbBr<sub>3</sub> perovskite QDs have a narrow emission spectrum, and the half-peak width measured from the figure is 15 nm. And this luminescence peak comes from the radiation recombination of excitons in CsPbBr<sub>3</sub> perovskite QDs. QDs have a quantum limited effect, and their emission spectra can be controlled by changing the size of QDs. By changing the size and chemical composition of QDs, the emission spectra can cover the entire visible region. In Figure 1, with the decrease of Br content and the increase of I content in CsPbBr<sub>3</sub> perovskite QDs, the luminescence peak turns red shift to 605 nm and 690 nm.



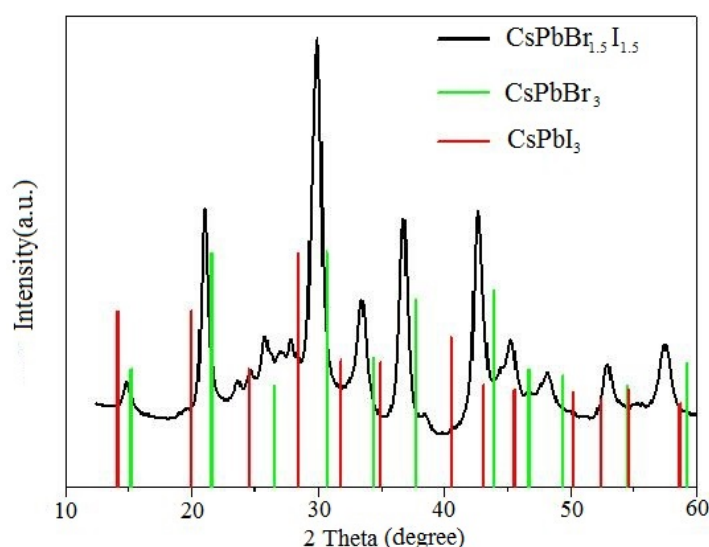
**Figure 1.** UV-vis absorption and photoluminescence spectra of inorganic perovskite QDs.

#### 3.2. Morphological and structural analysis



**Figure 2.** The TEM image of CsPbBr<sub>1.5</sub>I<sub>1.5</sub> perovskite QDs.

The TEM image of  $\text{CsPbBr}_{1.5}\text{I}_{1.5}$  perovskite QDs is showed in Figure 2. The particle size distribution (14~18 nm) of the square block crystal reflects the structural properties of the cubic lattice, and also indicates that the anion exchange reaction will not change the morphology of the inorganic perovskite QDs. It is well-known that cubic phase nanocrystalline will be obtained by hot injection at a temperature range from 160°C to 200°C. Interestingly, the subsequent anion-exchange manipulations of the halide ions do not seem to affect the cationic sub lattice and the cubic perovskite crystal structure is maintained despite the low temperature of the anion-exchange reaction. The TEM samples was prepared as follow steps.  $\text{CsPbBr}_{1.5}\text{I}_{1.5}$  perovskite QDs were dissolved in n-hexane and diluted to an appropriate concentration. Capillarity blood vessels were used to absorb the appropriate amount of samples and drip them onto the carbon film copper network, which was then naturally dried under air flow.



**Figure 3.** XRD patterns of inorganic perovskite QDs

The comparison was made with the standard card of XRD diffraction peak, as shown in Figure 3. Combining PDF#54-0752 ( $\text{CsPbBr}_3$ ) and ICSD#161481 ( $\text{CsPbI}_3$ ), which provides further proof that the  $\text{CsPbBr}_{1.5}\text{I}_{1.5}$  QDs synthesized by ion exchange method is cubic crystal system. Diffraction peaks lie between  $\text{CsPbI}_3$  and  $\text{CsPbBr}_3$ , indicating that this method can produce a single  $\text{CsPbBr}_{1.5}\text{I}_{1.5}$  QDs, rather than a mixture of  $\text{CsPbI}_3$  and  $\text{CsPbBr}_3$  QDs. The diffraction peak positions of  $\text{CsPbBr}_3$ ,  $\text{CsPbBr}_{1.5}\text{I}_{1.5}$  and  $\text{CsPbI}_3$  QDs can be explained by the change of atomic radius. Since the atomic radius  $D_{\text{Cl}} < D_{\text{Br}} < D_{\text{I}}$ ,  $\text{CsPbBr}_{1.5}\text{I}_{1.5}$  QDs can be regarded as the isomorphous substitution of  $\text{CsPbBr}_3$  QDs, and the I ion with a large radius replaces the Br ion with a small radius, making the lattice constant larger and the XRD peak shift to the left as a whole. The characterization of TEM and XRD further demonstrated that inorganic perovskite QDs belongs to ionic crystals, and the QDs formed by ion exchange reaction maintains the morphology and phase of the parent.

#### 4. Conclusion

This paper describes the synthesis of inorganic perovskite QDs, and introduces the synthesis by hot injection method and ion exchange method. The basic characterization methods of the materials were introduced, and the inorganic perovskite QDs was verified to be an ionic crystal through the characterization and analysis of  $\text{CsPbBr}_{1.5}\text{I}_{1.5}$  perovskite QDs by TEM and XRD.

### Acknowledgments

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