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Size-controlled synthesis of highly luminescent organometal halide perovskite quantum dots

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ABSTRACT

Size-tunable organometal halide perovskite $CH_3NH_3PbBr_3$ quantum dots (QDs) were successfully synthesized by a simple surfactant-assisted reprecipitation technique, in which the size-tunability was realized by varying the molar ratios of methylammonium bromide (CH_3NH_3Br) to $PbBr_2$ while the total amount of octylamine (OTAm) and CH_3NH_3Br remained unchanged. The diameters of $CH_3NH_3PbBr_3$ QDs could be effectively tuned from 1.6 to 3.9 nm, and these QDs exhibited an obviously size-dependent optical properties, whose photoluminescence (PL) covered the spectral region from 440 to 530 nm and the emission width was 20–32 nm. The maximum absolute PL quantum yield (PLQY) was measured to be as high as approximately 80% at room temperature. A plausible formation mechanism was proposed and the quantum confinement effect was discussed based on effective mass approximation. Moreover, this synthetic approach could also be extended to prepare different halide perovskite QDs including $CH_3NH_3PbCl_xBr_{3-x}$ and $CH_3NH_3PbBr_{3-x}I_x$ ($x = 1–3$), which realized the color-tunability over the entire visible spectral region of 390–750 nm. The size- and compositional-tunable emission colors of organometal perovskite QDs endows them wide potential applications in next-generation optoelectronic devices.

1. Introduction

In the past few decades, colloidal semiconductor QDs were extensively studied due to their size- and surface-dependent optical properties as well as their wide potential applications in optoelectronics and biological labels [1–6]. However, the complicated synthetic technique and high-cost raw materials limited their further commercialization. Very recently, organometal halide perovskites ($CH_3NH_3PbX_3$, X = Cl, Br and I) have drawn extensive attention due to their breakthrough in solar energy conversion, and nearly 20% power conversion efficiency has already been reported [7–14]. Moreover, the inherent superiorities including band-gap tunability, low solution-processing temperature and narrow band emission make halide perovskites alternative candidates for application in low-cost and large-area light-emitting diodes and photodetectors [15–20].

It is well known that the unique feature of the colloidal semiconductor QDs endows them with imponderable optical advantages compared to their bulk counterparts due to the quantum-confinement effects, which play an important role in the interfacial charge transfer, photo-physics and carrier multiplications of the semiconductor QDs [21–24]. As a newly emerging candidate of QDs family, what can the optical and electrical properties of the perovskites become if their size is reduced to be comparable or smaller than the exciton Bohr diameter? Therefore, it is interesting and necessary to study the optical properties of perovskite QDs. To date, some work has been reported on the quantum-confinement effects of organic-inorganic $CH_3NH_3PbX_3$ (X = Cl, Br and I) and all inorganic perovskite cesium lead halides ($CsPbX_3$, X = Cl, Br and I) QDs [25–30]. For example, Kovalenko and co-workers reported the synthesis of all inorganic $CsPbX_3$ (X = Cl, Br and I) QDs with composition- and size-dependent emission color, which exhibited obvious quantum-size effects [25]. Very recently, Alivisatos' group [26] and Prato's group [27] realized the quantum confinement effects of $CsPbBr_3$ by controlling the self-assembly of $CsPbBr_3$ nanoplates and tuning the amount of HBr in the reaction, respectively. Moreover, the synthesis of organic-inorganic $CH_3NH_3PbX_3$ QDs was

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also reported recently. Zhong and co-workers developed a ligand-assisted reprecipitation strategy to prepare highly luminescent colloidal $CH_3NH_3PbX_3$ (X = Cl, Br and I) QDs, and all of these perovskite QDs exhibit a slight quantum confinement effect [15]. Rogach's group prepared highly luminescent $CH_3NH_3PbBr_3$ QDs by changing the reprecipitation temperature, but the controlling mechanism is not clear [28]. More recently, Urban's group [29] and Ma's group [30] both studied the quantum size effects in colloidal organometal halide perovskite nanoplatelets with different thickness, but the highest PLQY in their study is not over 50% due to the quantum confinement just in one dimension. Therefore, it remains challengeable to prepare highly luminescent and color-tunable organometal $CH_3NH_3PbX_3$ QDs and to study both their quantum confinement effects and formation mechanism, which is conducive to specifically engineer $CH_3NH_3PbX_3$ QDs with desired optical properties.

In this paper, a simple surfactant-assisted reprecipitation technique was adopted to realize the size-tunability of $CH_3NH_3PbBr_3$ QDs, in which the ratio of CH_3NH_3Br to $PbBr_2$ was varied while the amount of OTAm and CH_3NH_3Br remained unchanged. The size of these $CH_3NH_3PbBr_3$ QDs could be effectively tailored from 1.6 to 3.9 nm, and the PL emission was size-dependent and covered the spectral region of 440–530 nm. The experimental data could fit well to the calculation results based on the effective mass approximations. The excellent optical properties including narrow emission linewidth of 20–32 nm and high absolute PLQY (*ca.*80%) made $CH_3NH_3PbBr_3$ QDs comparable with the classical semiconductor QDs such as CdSe and CdTe QDs. Besides, through compositional modulations by different halogen elements in the perovskite QDs, the PL emission spectra could be readily regulated over the entire visible spectral region of 390–750 nm. The size- and composition-tunable optical properties made halide perovskite QDs become a contender in the next-generation optoelectronic applications.

2. Experiment section

2.1. Materials

Lead(II) chloride ($PbCl_2$, 99%), lead(II) bromide ($PbBr_2$, 98%), lead(II) iodide (PbI_2, 98.5%), methylamine (CH_3NH_2, 40 wt% in methanol) and hydriodic acid (HI, 57 wt% in water) are purchased from Alfa Aesar. 1-octylamine (OTAm, 99%) is purchased from Acros Organic. Oleic acid (OA, 90%) is purchased from Aladdin Reagent Company. Other reagents and solvents including hydrochloric acid (HCl, 37%), hydrobromic acid (HBr, 47%) and common ethanol, toluene, diethyl ether and *N*,*N*-dimethylformamide (DMF) are commercially available analytical-grade products and purchased from Beijing Chemical Reagent Company. All chemicals were used in our experiments as received without any further purification.

2.2. Synthesis of methylammonium halid (CH_3NH_3X, X = Cl, Br, I)

The CH_3NH_3X (X = Cl, Br, I) was synthesized through the reaction of CH_3NH_2 with the corresponding acid based on previous work [31]. A typical synthesis of CH_3NH_3Br is listed as follows: 45 mL of CH_3NH_2 and 20 mL of HBr were added into 100 mL of round-bottom flask, and then the reaction was stirred for 2 h at 0 °C. Afterwards, the precipitates were obtained by rotary evaporation at 50 °C for 1 h. The precipitates were washed three times by diethyl ether, and then dried in vacuum at 75 °C overnight. Similarly, the synthesis of CH_3NH_3Cl and CH_3NH_3I was performed according to the above procedures except HCl or HI was used to replace HBr.

2.3. Synthesis of $CH_3NH_3PbX_3$ (X = Cl, Br, I) QDs

For a typical synthesis of $CH_3NH_3PbBr_3$ QDs, 0.19 mmol of CH_3NH_3Br, 0.2 mmol of $PbBr_2$, 0.01 mmol of OTAm and 0.5 mL of OA were dissolved in 5 mL of DMF under magnetic stirring at room temperature to form a precursor solution. Then 0.5 mL of the precursor solution was injected into 10 mL of toluene under vigorous magnetic stirring. Once the precursor solution was mixed with the toluene, the color of the mixture became green immediately. Afterwards, the $CH_3NH_3PbBr_3$ QDs were obtained by centrifugation at 13000 rpm for 20 min. To obtain different-sized $CH_3NH_3PbBr_3$ QDs, some control experiments were performed based on the above procedure except the variation of the molar ratios of CH_3NH_3Br to $PbBr_2$ while the total amount of CH_3NH_3Br and OTAm was kept at 0.2 mmol.

The synthesis of $CH_3NH_3PbCl_3$ and $CH_3NH_3PbI_3$ QDs was carried out by using the similar synthetic procedure of $CH_3NH_3PbBr_3$ QDs except the precursors were changed to $PbCl_2$, PbI_2 as well as CH_3NH_3Cl and CH_3NH_3I. Moreover, $CH_3NH_3PbCl_{3-x}Br_x$ and $CH_3NH_3PbBr_xI_{3-x}$ QDs (x = 0–3) were synthesized by varying the types and amount of PbX_2 and CH_3NH_3X (X = Cl, Br and I) based on the above synthetic procedure.

2.4. Characterization

Transmission electron microscopy (TEM) images of the samples were recorded on a JEM-1400 transmission electron microscope operating at an accelerating voltage of 100 kV. High-resolution TEM (HRTEM) images were recorded on a JEM-2010 at an acceleration voltage of 200 kV. X-ray diffraction (XRD) patterns of all the samples were obtained by using a Bruker D8 Advance diffractometer

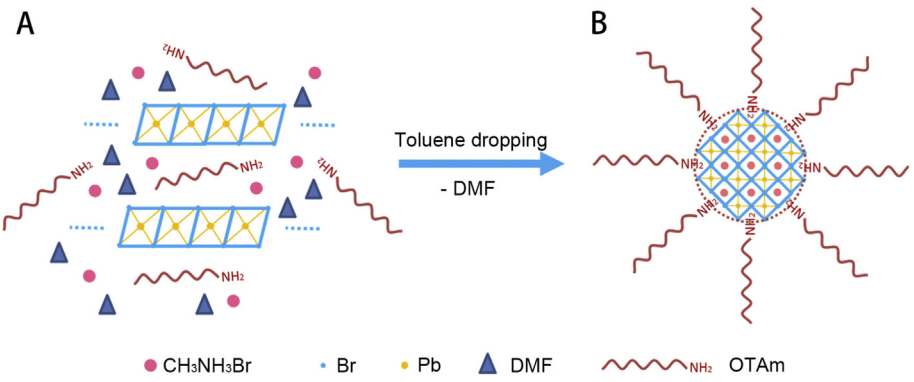

Fig. 1. Schematic illustration for the formation of the $CH_3NH_3PbBr_3$ QDs: (A) Free-standing layered precursor solution; (B) Structure of $CH_3NH_3PbBr_3$ QDs.