



Facile synthesis and characterization of CsPbBr₃ and CsPb₂Br₅ powders

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Abstract. All-inorganic caesium lead-halide perovskite CsPbBr₃ and CsPb₂Br₅ powders have emerged as attractive optoelectronic materials owing to their stabilities and highly efficient photoluminescence (PL). Herein we report a facile chemical route to prepare highly luminescent monoclinic CsPbBr₃ and tetragonal CsPb₂Br₅ powders at room temperature. The CsPbBr₃ powders exhibit regular crystal shape and demonstrate polyhedral geometry with an average particle size of 10 μm. The CsPb₂Br₅ powders show platelet morphologies and the lateral sizes of the particles are from 5 up to 200 μm. Both CsPbBr₃ and CsPb₂Br₅ powders present a narrow emission line-width and PL emission of 528 and 527 nm, respectively. A direct band gap of 2.35 eV and an indirect band gap of 3.01 eV are calculated for CsPbBr₃ and CsPb₂Br₅ powders, respectively. In addition, the monoclinic CsPbBr₃ can be transformed to tetragonal CsPb₂Br₅ in the presence of water. The large-scale synthesis of CsPbBr₃ and CsPb₂Br₅ will be advantageous in future applications of optoelectronic devices.

Keywords. CsPbBr₃; CsPb₂Br₅; powders; synthesis; characterization.

1. Introduction

Due to excellent charge transport properties [1] and broad chemical tenability [2], hybrid organic–inorganic lead halide-based perovskites have been broadly studied for potential applications in photovoltaic cells [3,4], light-emitting diodes (LEDs), lasers and photodetectors [5–10]. However, hybrid organic–inorganic perovskites are very sensitive to the environment, especially to water or moisture, which hinders large-scale practical and commercial applications [11,12]. Recently, the all-inorganic perovskites have been proposed as an alternative candidate for optoelectronics because of their higher chemical stability and unique electronic properties as compared with their hybrid organic–inorganic counterparts [13–15]. The general composition of all-inorganic perovskite is CsPbX₃ (X=Cl, Br and I), which has triggered a surge of investigations.

CsPbBr₃ and CsPb₂Br₅ are a kind of all-inorganic perovskites. Both of them have emerged as attractive semi-conducting materials owing to their unique optoelectronic properties. Kulbak *et al* [16] prepared solar cells using CsPbBr₃ as a light absorber material. The solar cells showed performances comparable to those from the organic material, especially in generating high open circuit voltages. Pan *et al* [17] reported that CsPbBr₃ quantum dots (QDs) can produce high photoluminescence (PL) quantum yield with unprecedented operational stability in ambient conditions and high pump fluences. Song *et al* [18] for the first time reported QD LEDs based on all-inorganic perovskite CsPbBr₃, showing a

promising luminescence intensity of 946 cd m⁻². Zhang *et al* [19] prepared LEDs using all-inorganic CsPbBr₃–CsPb₂Br₅ composite as the emitting layer, displaying a maximum luminance of 3853 cd m⁻², with current density of 8.98 cd A⁻¹ and external quantum efficiency of 2.21%. Tang *et al* [20] reported that CsPb₂Br₅ microplates exhibited large optical gain and lasing emission under both one- and two-photon excitation, as well as enhanced stability.

Arising from the high performance, the synthesis and properties of CsPbBr₃ and CsPb₂Br₅ attract much attention. Traditionally, caesium lead-halide perovskites nanopowders have been prepared by the reaction of PbBr₂ with metal–organic complex in organic solvent (for example, octadecene and oleylamine) at relatively high temperature [20–22]. However, the metal–organic complex decomposition is a complex, expensive and limited-scale synthesis method. The growing interest in caesium lead-halide perovskites motivates us to develop simple and cheap alternative methods for large-scale synthesis of CsPbBr₃ and CsPb₂Br₅ powders.

In this article, we report a facile precipitation route for synthesis of CsPbBr₃ and CsPb₂Br₅ powders in aqueous solution. The process is quite simple, so that the production rate is expected to be much higher than those of other methods. Detailed crystal structural characterization reveals that CsPbBr₃ and CsPb₂Br₅ powders crystallize in a monoclinic and tetragonal phase, respectively. Optical measurements show that both CsPbBr₃ and CsPb₂Br₅ display strong PL. These powders have potential applications in optoelectronics.

2. Experimental

2.1 Preparation of CsPbBr₃ and CsPb₂Br₅ powders

Lead(II) acetate trihydrate (Pb(CH₃COO)₂ · 3H₂O) (Macklin Chemical, China, purity: 99.5%), hydrobromic acid (HBr) (Macklin Chemical, China, 40% w/w) and caesium bromide (CsBr) (Macklin Chemical, China, purity: 99.5%) were selected as the starting materials.

First, lead(II) acetate trihydrate was fully dissolved in hydrobromic acid at room temperature to obtain solution I. Caesium bromide was fully dissolved in a blend solution of hydrobromic acid and deionized water at room temperature to obtain solution II. Later, solution II was added slowly into solution I with successive stirring. The mole ratio of Cs⁺/Pb²⁺ in mixed solution was adjusted to 1/1, 2/1 and 1/2. The obtained products were washed by diethyl ether three times, and were dried in vacuum for 12 h.

2.2 Characterization

The X-ray diffraction (XRD) measurements of the powders were performed with an X-ray diffractometer (Bruker D8 Davinci, Germany) with Cu K_α radiation (40 kV, 60 mA) in the range of 2θ = 10–50°. The scan was performed at a scan rate of 5° min⁻¹ with the step size of 0.02°. The morphologies of the powders were examined by field emission scanning electron microscopy (SEM, Hitachi S-4800, Tokyo, Japan). The PL spectra were measured using a 473 nm solid-state laser for excitation, detected using a grating spectrometer. UV–Vis absorption spectra were collected using a Hitachi U2001 spectrophotometer in the reflectance mode.

3. Results and discussion

The phases of powders obtained with various mole ratios of Cs⁺/Pb²⁺ in the solution are studied. Figure 1 shows the XRD pattern of sample obtained with Cs⁺/Pb²⁺ mole ratio of 1/1. It is found that the diffraction peaks of monoclinic CsPbBr₃ (PDF#18-0364) and tetragonal CsPb₂Br₅ (PDF#25-0211) coexist in the sample. As the Cs⁺/Pb²⁺ mole ratio of rises to 2/1, the diffraction peaks of tetragonal CsPb₂Br₅ disappear completely, and only diffraction peaks of monoclinic CsPbBr₃ can be observed, as shown in figure 2. The as-obtained monoclinic CsPbBr₃ powders show an orange colour. When the Cs⁺/Pb²⁺ mole ratio decreases to 1/2, the XRD pattern (figure 3) contains the sharp diffraction peaks of tetragonal CsPb₂Br₅, indicating that well-crystallized tetragonal CsPb₂Br₅ powder is prepared. The as-obtained tetragonal CsPb₂Br₅ powder shows a white colour.

Based on the results of the XRD analysis, it can be seen that the Cs⁺/Pb²⁺ mole ratio has an effect on the phase of final product in this synthesis process. Generally speaking, the reaction that occurs for the formation of CsPbBr₃ by CsBr

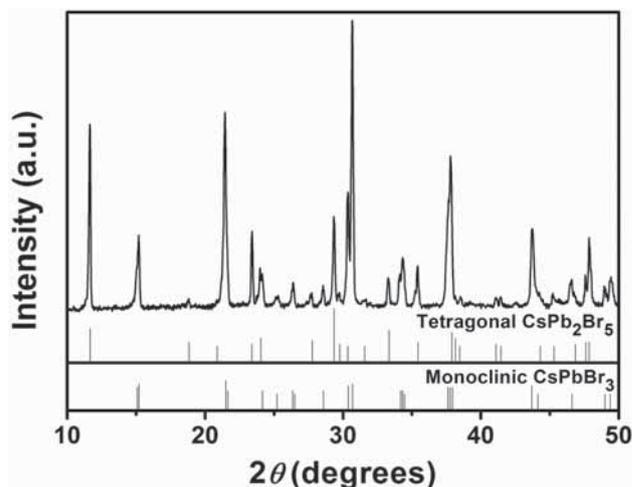


Figure 1. XRD pattern of powders obtained at a Cs⁺/Pb²⁺ mole ratio of 1/1.

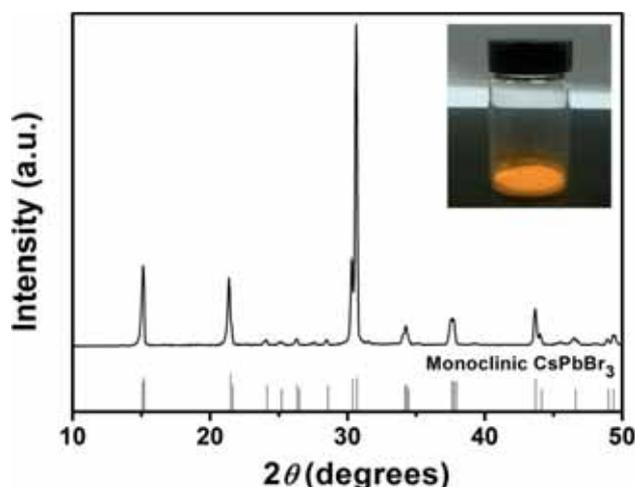
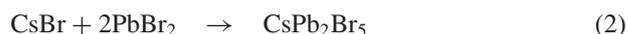


Figure 2. XRD pattern of powders obtained at a Cs⁺/Pb²⁺ mole ratio of 2/1. Inset is photographs of as-obtained CsPbBr₃ powders.

and PbBr₂ is



According to this reaction, as the Cs⁺/Pb²⁺ mole ratio is 1/1, the product should be pure CsPbBr₃. However, the real product is a mixture of monoclinic CsPbBr₃ and tetragonal CsPb₂Br₅ (figure 1). Pure CsPbBr₃ powder can be prepared when the Cs⁺/Pb²⁺ mole ratio is 2/1 (figure 2). Intriguingly, when the Cs/Pb mole ratio is 1/2, pure CsPb₂Br₅ can be obtained, in accordance with the reaction



Here, it is believed that at the conditions of this synthesis, different Cs⁺/Pb²⁺ mole ratios lead to modification of the solution environment, resulting in a change in the

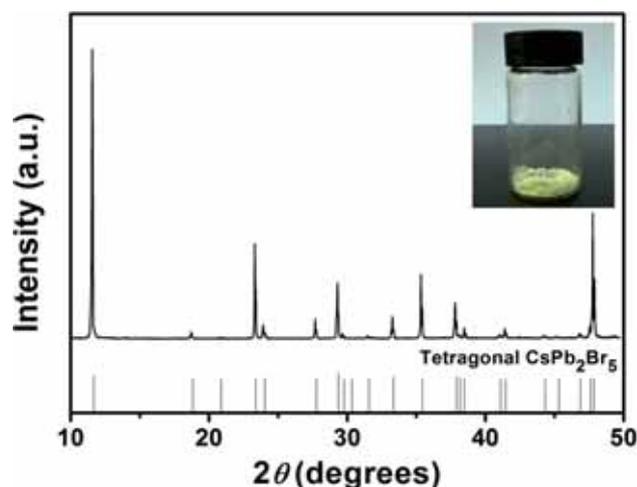


Figure 3. XRD pattern of powders obtained at a $\text{Cs}^+/\text{Pb}^{2+}$ mole ratio of 1/2. Inset is photographs of as-obtained CsPb_2Br_5 powders.

thermodynamically favoured phase of the caesium lead halide. Therefore, in this work, the $\text{Cs}^+/\text{Pb}^{2+}$ mole ratio influences the phase of final product.

It is reported that caesium lead bromide belongs to the family of trihalides compounds, in which several successive phase transitions occur between room temperature and melting temperatures. CsPbBr_3 crystallizes in monoclinic polymorph at room temperature and with rising temperature it transforms to tetragonal phase. Above 130°C , CsPbBr_3 crystallizes in cubic polymorph with the perovskite structure [23,24]. The existing methods for CsPbBr_3 nanopowders are normally at the high synthesis temperature of 150 or 170°C , producing a cubic perovskite phase [25,26]. In this work, the CsPbBr_3 crystallizes in the monoclinic phase, which can be attributed to the room temperature synthesis.

The morphologies of the CsPbBr_3 and CsPb_2Br_5 powders synthesized are shown in figure 4. Both of the CsPbBr_3 and CsPb_2Br_5 powders are well separated. The CsPbBr_3 powders have regular crystal shape and demonstrate polyhedral geometry. The average particle size of CsPbBr_3 powders are $10\ \mu\text{m}$ (figure 4a). The CsPb_2Br_5 powders show platelet morphologies and the lateral sizes of the particles are from 5 up to $200\ \mu\text{m}$ (figure 4b).

It is well known that the crystal growth behaviour is determined by the intrinsic symmetry of its crystal structure. Therefore, the different morphologies of CsPbBr_3 and CsPb_2Br_5 powders in this synthesis process result from their different intrinsic symmetries of the crystal structures. The monoclinic phase of CsPbBr_3 presents a perovskite structure, in which the $\{\text{PbBr}_6\}^{4-}$ octahedron extends to three dimensions via sharing the vertex and Cs^+ ions localize in the octahedral voids, as shown in figure 5a. Figure 5b shows the crystal structure of the tetragonal CsPb_2Br_5 . It is found that one layer of Cs^+ ion is sandwiched between two layers of $[\text{Pb}_2\text{Br}_5]^-$. The features of the tetragonal CsPb_2Br_5

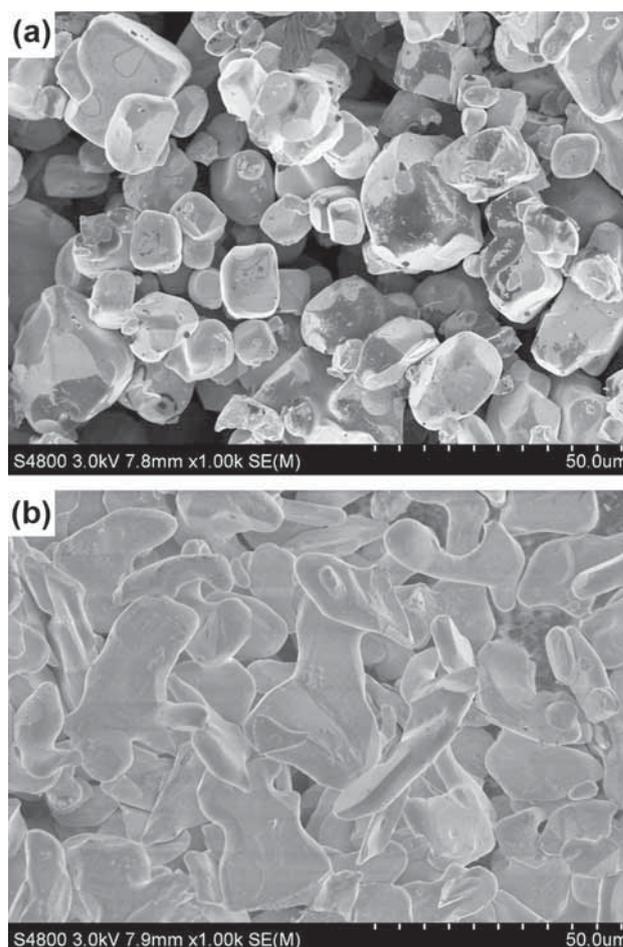
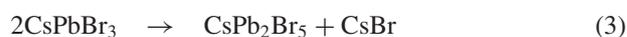


Figure 4. SEM micrographs of (a) CsPbBr_3 and (b) CsPb_2Br_5 powders.

crystal structure are similar to that of layered double hydroxides, whose platelet morphology has been easily obtained by the facile precipitation method [27].

In order to study the chemical stability of CsPbBr_3 in water, distilled water is added to the CsPbBr_3 powders. Figure 6 shows the colour changes of CsPbBr_3 powders soaked in water. It can be seen that the initial orange colour changes to white colour completely in $90\ \text{s}$, illustrating that CsPbBr_3 is very sensitive to water and CsPbBr_3 transforms to a new phase in the presence of water. To further investigate the phase transformation of CsPbBr_3 in water, the crystal structures of obtained white product and material obtained by drying the clear supernatant (figure 6) are analysed. As shown in figures 7 and 8, the white product is characterized as tetragonal CsPb_2Br_5 (PDF#25-0211), and the matter obtained by drying the clear supernatant is confirmed as cubic CsBr (PDF# 73-0391). According to the results of XRD analysis (figures 7 and 8), it is proposed that CsPbBr_3 decomposes to CsPb_2Br_5 and CsBr in the presence of water, which occurs as follows:



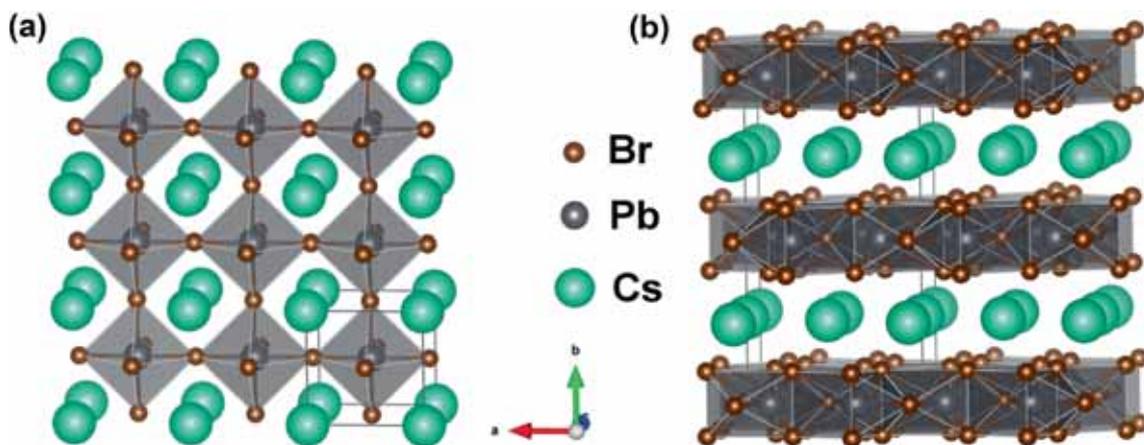


Figure 5. Perovskite crystal structure of (a) CsPbBr_3 and (b) perovskite-related crystal structure of CsPb_2Br_5 .

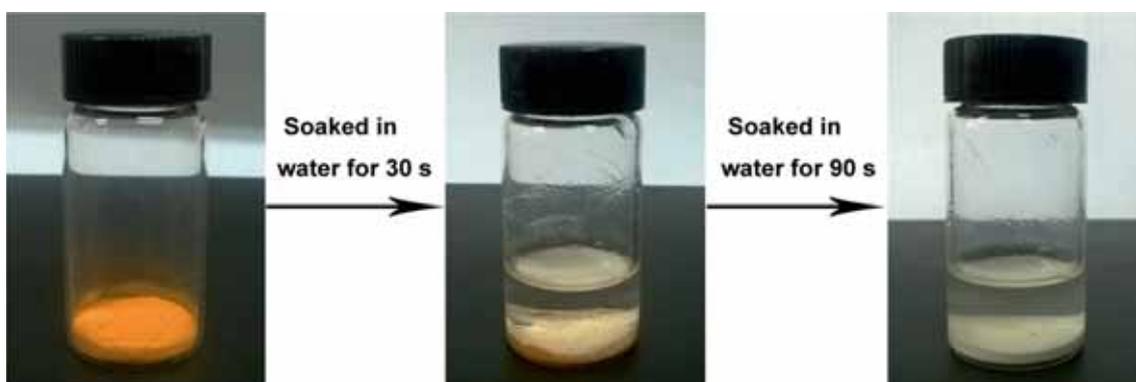


Figure 6. Photograph of the colour changes of CsPbBr_3 powders soaked in water.

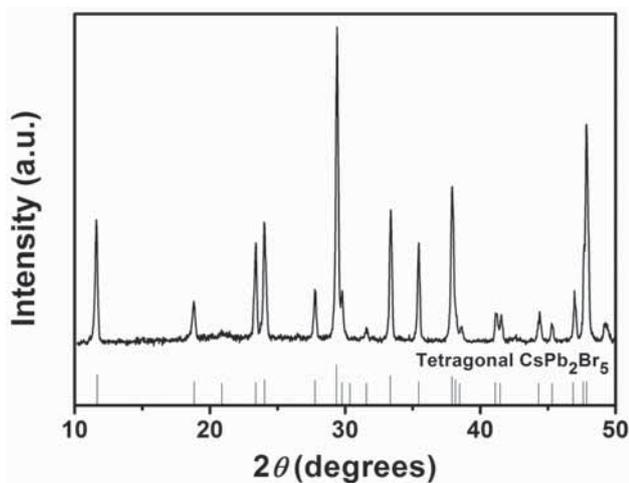


Figure 7. XRD pattern of the white product shown in figure 6.

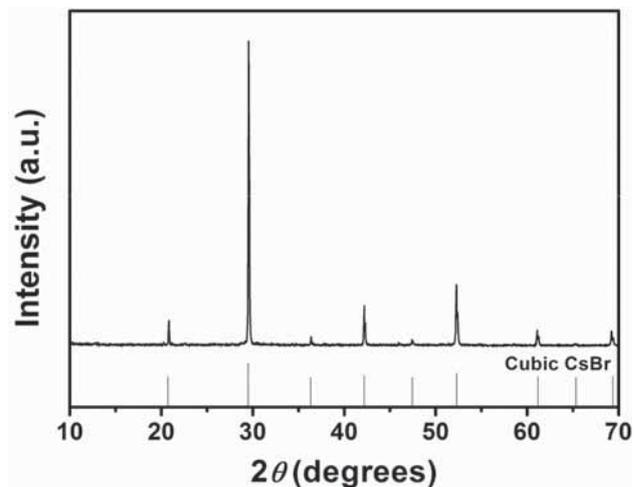


Figure 8. XRD pattern of material obtained by drying the clear supernatant shown in figure 6.

In this reaction process, water can be acted as a catalyser, as reported in the decomposition of organic–inorganic hybrid perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ [11,28].

The optical properties of the CsPbBr_3 and CsPb_2Br_5 powders are studied by measuring the UV–Vis absorption and PL spectra. Figure 9a shows the UV–Vis adsorption and PL

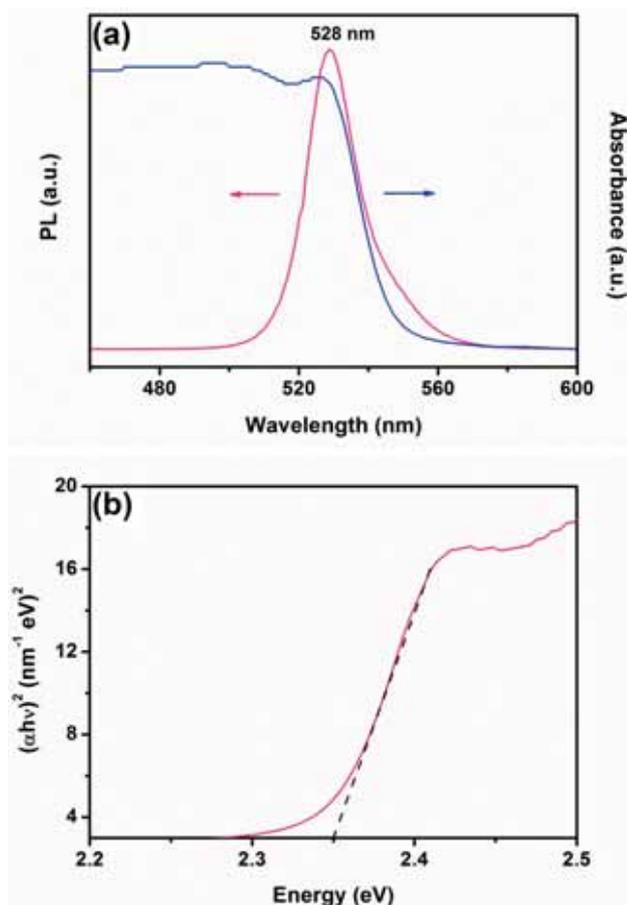


Figure 9. Absorption (right) and PL (left) spectra of (a) CsPbBr₃ powders, and (b) direct band gap Tauc plot of CsPbBr₃ from absorption spectrum. The PL under 473 nm excitation.

emission spectra of CsPbBr₃ powders. The absorption onset for the CsPbBr₃ is found to be 521 nm. The PL emission spectrum of CsPbBr₃ exhibits a peak at 528 nm with a narrow full-width at half-maximum (FWHM) of 16 nm, which is similar to the optical features of CsPbBr₃ nanocrystals [29]. The direct band gap Tauc plot of CsPbBr₃ from absorption spectrum gives a direct gap of 2.35 eV, as shown in figure 9b. The optical absorption and PL emission spectra of CsPb₂Br₅ powders are shown in figure 10a, from which we can see a small Stokes shift, and the highly symmetric PL peak centres at 527 nm with a narrow FWHM of 12 nm, indicating its potential application for lasing. According to the absorption spectrum, an indirect band gap of 3.01 eV is calculated (figure 10b), which is in accordance with the reported results [30].

The PL property of microsized CsPbBr₃ powders obtained in this work is different from that of QDs. Pan *et al* [17] prepared CsPbBr₃ QDs with average sizes of 8.2, 9.2 and 10.6 nm; the PL positions of these samples are 496, 503 and 512 nm, respectively, implying that PL peak shifts to longer wavelength when the size of QDs is increased. These results are due to the quantum confinement. The typical PL peak of

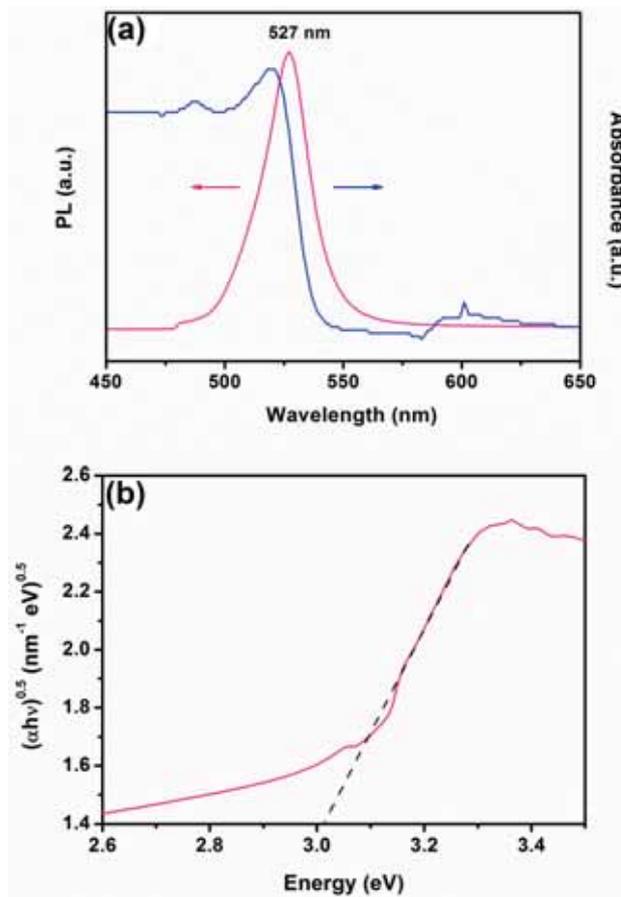


Figure 10. Absorption (right) and PL (left) spectra of (a) CsPb₂Br₅ powders, and (b) indirect band gap Tauc plot of CsPb₂Br₅ from absorption spectrum. The PL under 473 nm excitation.

the CsPbBr₃ QDs in their work is 512 nm. Besides, Song *et al* [18] reported that the typical PL peak of the CsPbBr₃ QDs was located at 510 nm. In this work, the microsized CsPbBr₃ powders present a PL emission of 528 nm. These results demonstrate that the PL emission wavelength of microsized CsPbBr₃ powders is longer than that of CsPbBr₃ QDs. However, there is no obvious difference between PL properties of microsized and nanosized CsPb₂Br₅ powders. Ruan *et al* [31] reported that PL emission spectrum of CsPb₂Br₅ nanowires showed a peak at 525 nm. Meanwhile, the PL emission peak position of CsPb₂Br₅ nanosheets was at 529 nm. The microsized CsPb₂Br₅ powders obtained in our work have a PL emission peak at 527 nm. It can be concluded that the PL property of microsized CsPb₂Br₅ powders is similar to that of nanosized CsPb₂Br₅ particles.

4. Conclusions

A facile and scalable method for the synthesis of highly luminescent CsPbBr₃ and CsPb₂Br₅ powders is reported. The Cs⁺/Pb²⁺ mole ratio has a significant effect on the phase

of final product in the synthesis process. Both CsPbBr₃ and CsPb₂Br₅ powders present a narrow emission line-width and PL emission at 528 and 527 nm, respectively. These CsPbBr₃ and CsPb₂Br₅ powders have potential applications in optoelectronic devices.

Acknowledgements

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