



Low temperature synthesis of high-quality all-inorganic cesium lead halide perovskite nanocrystals in open air and their upconversion luminescence



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ABSTRACT

In this work, a single-step and low-cost synthesis of all-inorganic cesium lead halide perovskite nanocrystals was developed. PbX₂ and Cs₂CO₃ were added to a mixture containing 1-octadecene (ODE), oleic acid (OA) and oleylamine (OLA), and heated at 80–100 °C for 15–30 min in air. The resultant high-quality cube-like CsPbX₃ nanocrystals are monodisperse with dimensions of 7–15 nm, and display strong photoluminescence (PL) with a narrow, tuneable emission band of 14–43 nm and a high quantum yield (~90%). The mechanisms of nucleation and growth were investigated by testing the effects of temperature and surface ligands (OA/OLA) on the crystal morphology and PL intensity. The high quality of the CsPbX₃ nanocrystals was further confirmed by efficient upconversion PL with high energy gain, observed here for the first time for colloidal CsPb(Br/I)₃ nanocrystals, with an energy gain higher than 430 meV that was mainly attributed to anti-stokes generation rather than the multiphoton effect.

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1. Introduction

All-inorganic cesium lead halide (CsPbX₃, X = Cl, Br, I) perovskite nanocrystals were first reported by Kovalenko and co-workers in 2015 [1], and increasing attention is now being placed upon them due to their excellent optical and electronic properties [2–5]; they are color-tuneable across the entire visible and infrared region, have a high PL quantum yield (PLQY), and a narrow emission width [6–10]. These properties make them useful for potential applications as light emitting diodes (LEDs) and other optoelectronic devices [11–15]. To date, perovskite nanocrystals with different shapes, such as nanocubes [16], nanowires [17], and nanosheets [18], have been prepared by hot injection, anion exchange, solvothermal, room-temperature re-precipitation, and ultrasonication [19–23].

Hot injection is the most popular method for preparing high-quality all-inorganic perovskite nanocrystals. Kovalenko and co-workers first synthesized all-inorganic CsPbX₃ perovskite

nanocrystals using this approach by preparing the Cs-oleate precursor then rapidly injecting it into the Pb-oleate precursor. The resulting CsPbX₃ nanocrystals were synthesized in less than 10 s at high temperature (140–200 °C). Due to the high temperature, the reaction system was protected under an argon or nitrogen atmosphere. Additionally, the nucleation of CsPbX₃ nanocrystals at high temperature was so fast that it was difficult to control. The inorganic-organic hybrid halide perovskite film in solar cells is treated at ~100 °C to create a large crystalline grain (>1 μm) [24–27], suggesting CsPbX₃ perovskite nanocrystals may also be prepared in this temperature range. This would be beneficial because a protected atmosphere and high boiling point solvents such as 1-octadecene (ODE) would not be needed, which would simplify the preparation process and reduce the cost greatly.

The synthesis of CsPbX₃ nanocrystals at lower temperatures therefore represents a significant challenge. Although some reports on the synthesis of CsPbX₃ nanocrystals at room temperature have been made, this involved pre-synthesis of cesium and lead precursors under an inert atmosphere at higher temperatures [28–30]. Fortunately, the ultrasonication method explored by Alexander S. Urban and co-workers offers some hope. In this process, PbX₂ and Cs₂CO₃ were added into mixture of ODE, oleic acid (OA) and oleylamine (OLA), and CsPbX₃ nanocrystals were synthesized

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directly in open air without any temperature control. Actually, temperature did have a large effect on nucleation of CsPbX₃ nanocrystals in this process, even though temperature control was not performed during ultrasonication. We found that nucleation of CsPbBr₃ nanocrystals only occurred when the temperature was higher than 70 °C during ultrasonication. Then, we further found that CsPbBr₃ nanocrystals were also nucleated without ultrasonication, as long as the temperature was kept higher than 70 °C.

Herein, for the first time, we reported a new thermal process to synthesize monodisperse cubic CsPbX₃ nanocrystals by heating a mixture of ODE/OA/OLA containing PbX₂ and Cs₂CO₃ at 80–120 °C in air within 15–30 min. The nucleation, growth and properties of CsPbX₃ nanocrystals were subsequently investigated. Meanwhile, efficient upconversion PL with high energy gain of CsPbX₃ nanocrystals were measured and investigated.

2. Experimental

2.1. Materials

Cs₂CO₃ (cesium carbonate, 99.9%), PbX₂ (X = Cl, Br, I, 99.9%), 1-octadecene (ODE, technical grade 90%), oleic acid (OA, technical grade 90%), oleylamine (OLA, technical grade 70%) and trioctylphosphine (TOP, technical grade 90%) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Hexane and acetone were bought from Tianjin Damao Chemical Works. All chemicals were used without further purification.

2.2. Synthesis of CsPbX₃ nanocrystals

CsPbX₃ nanocrystals were prepared by a thermal method. Cs₂CO₃ (0.1 mmol) and PbX₂ (0.3 mmol, X = Cl, Br, I) were added

into a 100 ml flask, and a mixture of 10 ml ODE, 0.25–2 ml OA, and 0.25–2 ml OLA were added, and 0.5–1 ml TOP was added based on the PbCl₂ content in CsPbBr_{3-x}Cl_x nanocrystals. The flask was heated to 80–90 °C in a water bath or to 100–120 °C in an oil bath. All reactions were carried out in the open air without any protective inner atmosphere. Colloidal nanocrystals were obtained after 15–40 min, and were dissolved in 15 ml acetone, centrifuged at 9000 rpm for 10 min, and nanocrystal precipitates were redispersed in 10 ml hexane. The dispersion was further centrifuged at 3000 rpm to remove large nanocrystals.

2.3. Characterisation of CsPbBr₃ nanocrystals

All UV/vis spectra were recorded at 25 °C using a Hitachi U-2800 spectrophotometer (Hitachi, Tokyo, Japan) with a quartz cuvette. Photoluminescence (PL) spectra were measured using an OCEAN QS65000 spectrofluorimeter (Ocean Optics, Dunedin, FL, USA) with UV excitation at 400 nm. The UV excitation was 10 mW and the concentration of all measured samples were 0.02 mol/L for the PL measurement. Time-resolved fluorescence measurements were carried out with a Fluorolog-3 steady-state spectrofluorimeter equipped with a time-correlated single photon counting (TCSPC) system. The PL quantum yield (PLQY) was measured directly using a Fluorolog Horiba spectrofluorimeter. The morphology of crystals was assessed using a Joel JEM-1230 transmission electron microscope (TEM; JEOL, Tokyo, Japan) at an acceleration voltage of 100 kV and the size was calculated by Image J software. X-ray diffraction (XRD) patterns of CsPbX₃ nanocrystal powders were acquired using a Bruker D8 Discover X-ray diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Digital photographs were taken with a HUAWEI P9 phone equipped with a LEICA dual-camera.

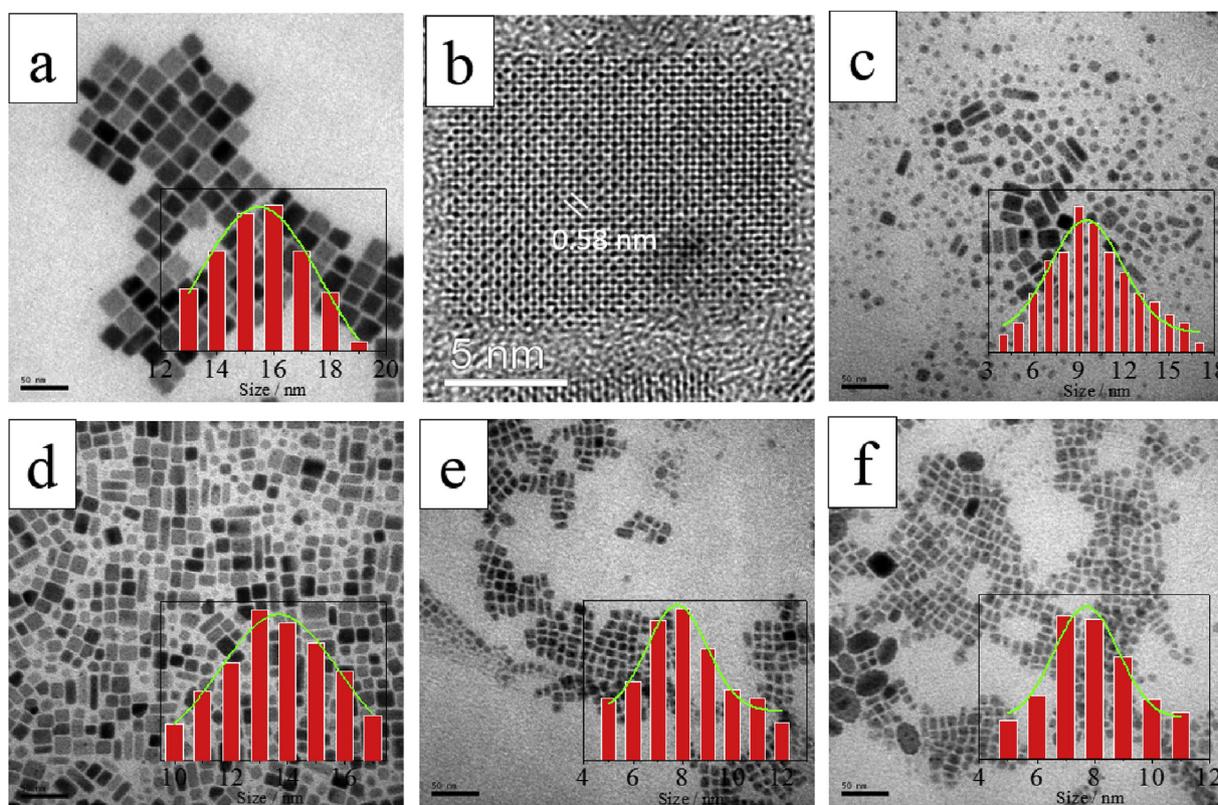


Fig. 1. Morphology of CsPbBr₃ nanocrystals visualised by (a) TEM and (b) HRTEM. (c) TEM morphology of CsPbCl₂Br, (d) CsPbCl₂Br, (e) CsPbBr₂I and (f) CsPbBr₂I. Scale bars = 50 nm. The insets were the responding size distribution of the nanocrystals.

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