



Facile Method for Synthesis of CsPbBr₃ Perovskite at Room Temperature for Solar Cell Applications

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Abstract

Inorganic metal halide perovskites CsPbX₃ (X = Cl, Br, and I) has achieved extensive attention in recent years for photovoltaics because of their unique properties like tunable band gap, high charge carrier mobility, high absorption coefficient, *etc.* and which makes it suitable for optoelectronic applications. In this work, we have reported a facile synthesis method of inorganic CsPbBr₃ nanoparticles (NPs) at room temperature using cesium bromide (CsBr) as a Cs source, lead bromide (PbBr₂) as Br source, oleic acid, and Oleylamine as capping ligands. Nucleation starts immediately after the injection of a precursor solution into the toluene. Synthesis of CsPbBr₃ NPs was confirmed by X-Ray diffraction pattern, UV-Visible spectroscopy, photoluminescence (PL), scanning electron microscopy (SEM), and atomic force microscopy (AFM). X-ray diffraction pattern reveals mainly the monoclinic crystal structure of CsPbBr₃ NPs. The UV-Vis absorption spectra and PL spectra show a strong absorption peak at 509 nm, emission peak at 505 nm, and the band gap of CsPbBr₃ to be 2.2 eV. The synthesized CsPbBr₃ exhibit regular cuboid like structure with a particle size of approximately 400-500 nm. The surface roughness morphology of CsPbBr₃ NPs was studied using AFM, and it shows the roughness of the CsPbBr₃ films was around 260 nm. These results provide a facile synthesis method, and CsPbBr₃ NPs are a suitable candidate for the optoelectronic and photovoltaic device's application.

Keywords: CsPbBr₃; Thin films; Capping ligands; Room temperature synthesis; Green emission.

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1. Introduction

Photovoltaic conversion of solar energy has emerged to be one of the ultimate ways of meeting the increasing energy demands of the future in a time when conventional sources of energy are getting depleted. Solar energy is everlasting and is radiated to the earth everywhere, and the use of photovoltaics for direct conversion of solar energy introduces no direct pollution of the environment. For 30 years, massive efforts have been taken to understand and fabricate the semiconductor solar cell devices and enhance their efficiency. The present-day solar photovoltaic industry is dominated by silicon. The researchers have spent more than 30 years achieving efficiency by more than 25 % and have now reached near the thermodynamic limit.^[1-4] The cost of the semiconductor grade silicon required for solar cells limits the mass-scale deployment of technology and further reduction in cost. Therefore, many alternatives have been sought after by

researchers worldwide. The emergence of perovskite solar cells has achieved power conversion efficiency (PCE) by more than 20 % in a matter of years and has a lower manufacturing cost.^[5-7] Organic-inorganic hybrid lead halide perovskite CH₃NH₃PbX₃, (X = Cl, Br, I) got the attention of scientists because of promising efficiencies of 22.1 % within a few years.^[8] Despite extraordinary optoelectronic properties, this material has a limitation of poor material stability. The primary reason behind the poor stability of organic-inorganic hybrid lead halide perovskite is the volatile nature of the CH₃NH₃ organic component. Hence replacement of CH₃NH₃ organic component was in demand, and consequently, this organic component is replaced by inorganic component Cs⁺ and this inorganic component has better thermal stability.^[9] Moreover, the CsPbX₃ perovskite is used in several other applications, including photodetector, laser and light-emitting diode,^[10,11] and so on.

The CsPbX₃ metal halide perovskite has unique properties like tunable bandgap, high charge carrier mobility, high absorption coefficient, *etc.* These peerless properties of CsPbX₃ make them special for practical applications in solar cells. Two colloidal synthesis methods are popular for synthesizing metal halide perovskite nanocrystals. First is a

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hot injection approach, and another is the colloidal synthesis of CsPbX_3 at room temperature. The hot injection approach is a widely used method for the synthesis of well-structured CsPbX_3 NPs. In the hot injection approach, a Cs-oleate precursor is prepared and rapidly injected into a Pb-oleate precursor. Maksym V. Kovalenko and their group^[12-13] successfully synthesized all inorganic CsPbX_3 perovskite NCs by the hot injection (HI) method. However, this method has some disadvantages, like high-temperature reaction under an inert atmosphere (argon or nitrogen). It may limit the output of mass production. The low batch-to-batch reproducibility and surfactant must be used to prevent the agglomeration of CsPbBr_3 NPs, which markedly decreases the photoluminescence quantum yield (PLQY). Hence overall, looking at the increased cost and limitation of this technique, this method is unsuitable for future applications. Thus, there is an urgent need to find a facile, low-temperature synthesis method with high optical merits, high-yield, and stable synthesis routes to synthesize the CsPbX_3 NPs.

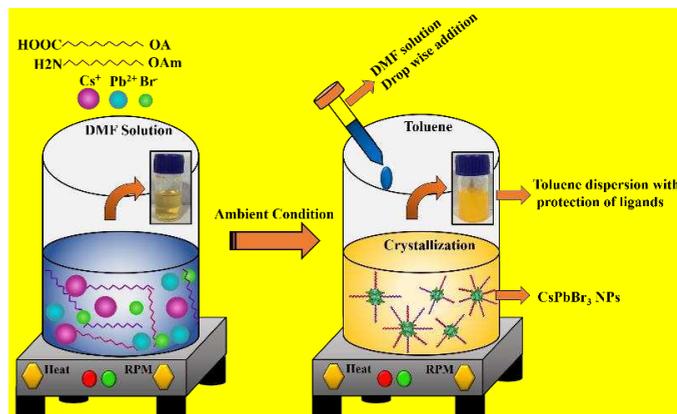
Thus, different research groups have developed an alternative route to synthesize CsPbX_3 NPs at room temperature without inert gas protection. To overcome the limitations of the HI method, Zeng's group^[14] invented the supersaturated recrystallization (SR) technique and made it possible to synthesize high-quality CsPbBr_3 NPs at room temperature. Herein, we report a high-quality CsPbBr_3 NPs synthesized at room temperature from oleic acid and oleylamine ligands by a simple ligand assisted supersaturated recrystallization (LASR) method. Further, the structural, morphological, topological, compositional, and optoelectronic properties have been investigated with various analytical techniques.

2. Materials and Experimental Section

The Cesium Bromide (CsBr , 99.999 %), Lead Bromide (PbBr_2 , 99.999 %), Oleylamine (OAm, 70 %), Oleic acid (OA, 90 %) were used with the purity level as mentioned in parenthesis. The chemicals mentioned above used for the synthesis of CsPbBr_3 were procured from Sigma-Aldrich and used without further purification and processing. The N, N-Dimethylformamide (DMF 99.8 %), dimethyl sulfoxide (DMSO, 99.8 %), and toluene (99.5 %) were purchased from HPLC India with AR grade.

2.1 Preparation of CsPbBr_3 Nanoparticles and Thin Film

The CsPbBr_3 material was synthesized at room temperature by a simple method using two different precursors, solvents and ligands. Nucleation starts immediately after the injection of a polar and less polar solvent. The CsBr (0.4 mmol) and PbBr_2 (0.4 mmol) were dissolved in 5 ml of DMF and stirred for 3 hrs at ambient temperature. Later, 0.5 ml of OAm and 1 ml of OA were added to the precursor solution to stabilize it, and the total volume is 6.5 ml in a beaker. Subsequently, all the precursor solution injected drop-wise into antisolvent, such as toluene (10 ml), under continuous stirring. Within 5-10 s, the yellow suspension was obtained. We have provided a detailed reaction procedure and growth mechanism in [Schematic 1](#) of CsPbBr_3 NPs.



Schematic 1. Illustration of the reaction procedure and growth mechanism. (a) Stable precursor in DMF solution (with actual image) (b) Reaction processed with the addition (drop-wise) of DMF solution in to toluene solution (with actual image).

2.2. Purification of CsPbBr_3 Material

The solution prepared by the procedure mentioned above containing CsPbBr_3 was then taken out and centrifuged at 3000 rpm for 10 min. The centrifuge sediment was given twice a toluene wash, and the final sediment of CsPbBr_3 was then dried under an IR lamp and collected for further characterizations. The soda-lime glass was used as a substrate to deposit a thin film of CsPbBr_3 . The substrates were carefully cleaned sequentially in piranha solution, double distilled water, acetone, and ethanol. The obtained CsPbBr_3 powders were re-dissolved in DMSO with a concentration of 20mg/ml. This solution was put in an ultrasonic bath until a transparent solution was formed. The prepared mixture of CsPbBr_3 and DMSO was deposited on the soda-lime substrate by drop cast method, and the films were dried at 120 °C for 1 hr and used for further characterizations.

2.3. Characterization of CsPbBr_3

The films of CsPbBr_3 have been investigated by different characterization techniques to study structural, optical, composition, and surface properties. The XRD patterns were recorded on Bruker D8 Advance X-ray diffractometer with $\text{Cu K}\alpha$ (1.54 Å) radiation. The UV-visible absorption spectra were recorded using a JASCO, V-670 UV-Visible spectrophotometer range of 300-1200 nm. The steady-state photoluminescence (PL) spectra were recorded using Edinburgh Instruments FLS 980 spectrophotometer. The samples were excited using 350 nm line for recording steady-state PL. Atomic force microscope (AFM; model: Asylum Research Cypher) was applied to study the surface morphology of the CsPbBr_3 samples. The surface morphology of the CsPbBr_3 films is investigated using scanning electron microscopy (JEOL JSM-6360 A).

3. Results and Discussion

3.1 Growth Mechanism of CsPbBr_3 Nanoparticles

[Schematic 1](#) systematically represents the growth mechanism of CsPbBr_3 NCs. There are two different precursors (CsBr and PbBr_2) and ligands (OLA and OA) and two different solutions (DMF and Toluene), nucleation starts immediately (within

few seconds) after mixing the polar (DMF solution) and nonpolar (toluene) solvents. The DMF solution was added drop-wise in the toluene solution. At the initial stage, 0-10 s as DMF solution added into toluene solution, and numerous crystal nuclei appear rapidly as the primary nanoparticles. At the initial stage, precursor concentration is too low to permit the growth of CsPbBr₃ nanoparticles, and no nucleation process occurs at this stage. Then at 10-20 s, more precursor solution added into toluene, which can provide essential nutrients for crystallization and growth of larger CsPbBr₃ nanoparticles. There is a substantial difference between Cs⁺, Pb²⁺, and Br⁻ in DMF and toluene solution. Therefore, pouring the DMF solution into a large amount of toluene will induce supersaturated recrystallization of CsPbBr₃ particles.

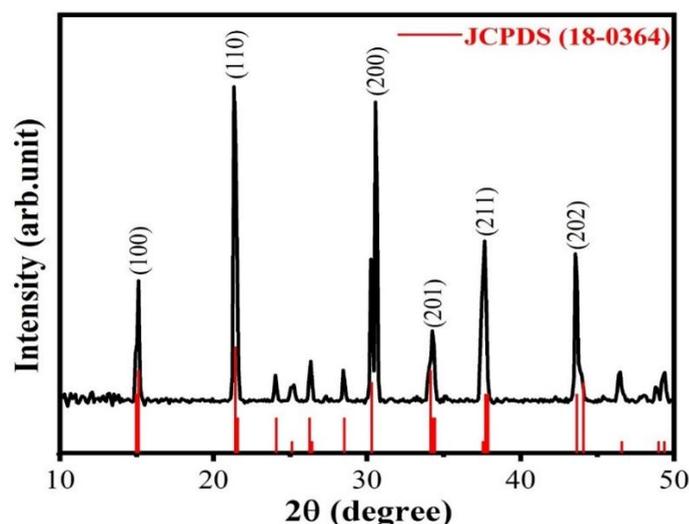


Fig. 1 X-ray diffraction pattern of CsPbBr₃ film deposited on the soda-lime substrate by drop-cast method.

3.2 X-Ray Diffraction Analysis

The structural phase of the as-synthesized CsPbBr₃ material was characterized by the XRD technique. The XRD pattern (Fig. 1), the major peaks at $2\theta \sim 15.09^\circ, 21.30^\circ, 30.58^\circ, 34.18^\circ, 37.67^\circ, 43.57^\circ$ are assigned to the (100), (110), (200), (201), (211) and (202) planes demonstrated the monoclinic crystal structure of the CsPbBr₃ with lattice parameter $a = b = c = 5.82 \text{ \AA}$. The results are well-matched with the previous reports and the JCPDS file no. (#18-0364).^[15] The monoclinic CsPbBr₃ shows polycrystalline nature, and there are no secondary phases of Cs₄PbBr₆ and CsPb₂Br₅ are observed. The diffraction peaks are sharp and narrower, indicating the increased and better crystallinity of the material.

3.3 UV-Visible and Photoluminescence Spectroscopic Analysis

The colloidal solution of CsPbBr₃ NPs was used for UV-Visible and PL spectroscopic measurements. The UV-Visible absorption spectra of CsPbBr₃, as shown in Fig. 2(a) shows a strong peak at 509 nm. The optical band gap was estimated using the relation of $(\alpha h\nu)^2$ vs. $h\nu$. (where α is an absorbance, h is Planck constant and ν is frequency). The effective optical band gap of CsPbBr₃ is 2.2 eV. The wavelength of PL emission spectra is 505 nm with a narrow full width half

maximum (FWHM) of 29.87 nm are observed, as shown in Fig. 2(b). A similar emission was observed by Weiqiang Yang *et al.* and Hanguang Lu *et al.* at 505 nm and 510 nm, respectively.^[16-17]

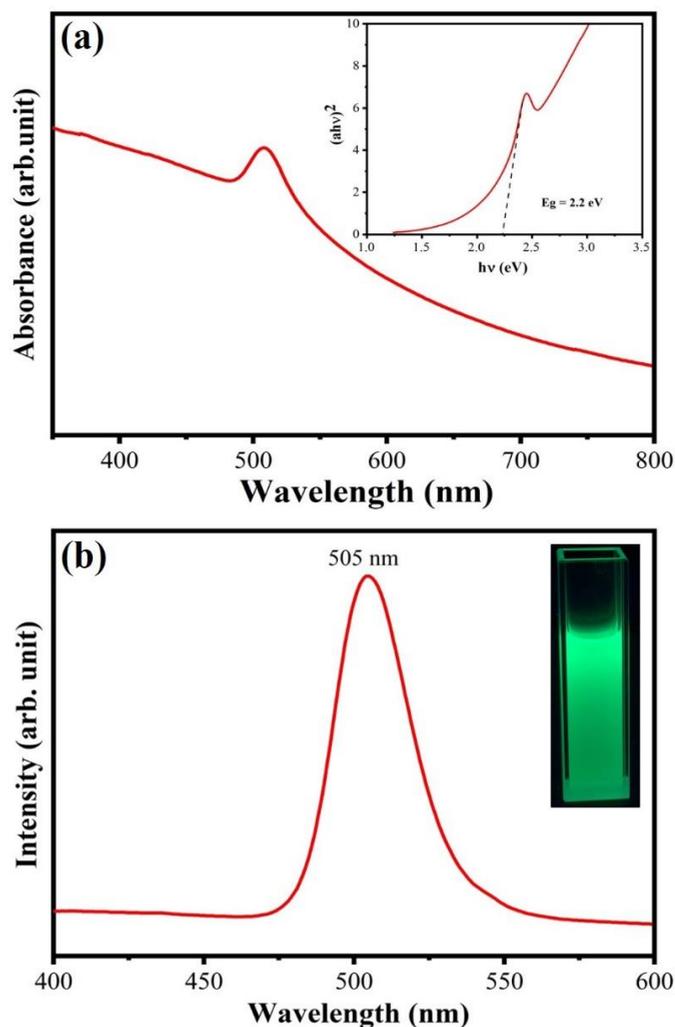


Fig. 2 (a) UV- Visible absorption and the inset shows the Tauc plot of CsPbBr₃ (b) Photoluminescence (PL) emission spectra and the digital image of CsPbBr₃ solution under the 365 nm UV lamp.

3.4 Morphology and Composition Analysis of CsPbBr₃ Nanoparticles

The morphology and composition analysis of CsPbBr₃ samples are shown in Fig. 3. The SEM shows that the CsPbBr₃ particles have 400-500 nm in size with regular cuboid morphology shown in Fig. 3(a-b). The EDAX pattern in Fig. 3(c) shows that the atomic ratio of Cs/Pb/Br is 16.83:19.24:63.92, indicating that the atomic Cs:Pb:Br ratio is close to the stoichiometry.

3.5 Atomic Force Microscopy

The 2-dimensional (2D) and 3-dimensional (3D) AFM images of CsPbBr₃ thin films are shown in Fig. 4. The surface topography of the as-prepared CsPbBr₃ thin films on a soda-lime glass substrate was examined under an atomic force microscope (AFM). All AFM images show the formation of

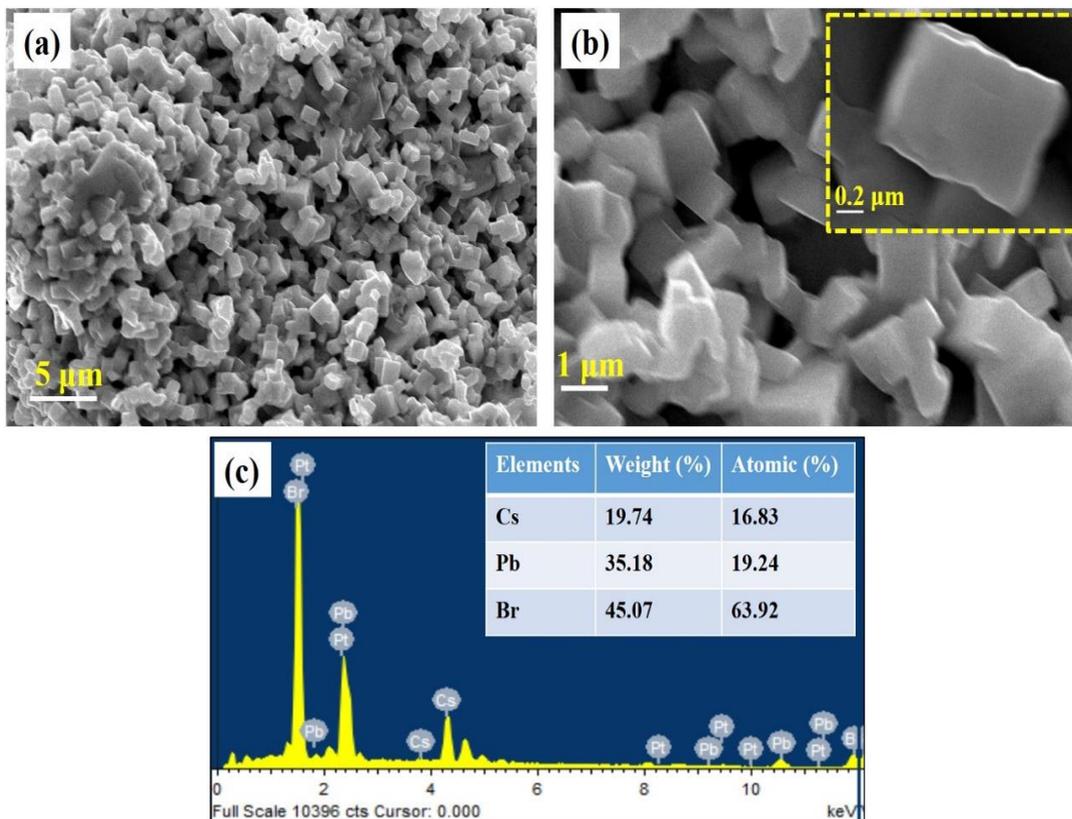


Fig. 3 (a-b) SEM images of CsPbBr₃ NPs (c) EDAX pattern of CsPbBr₃ NPs.

smooth, continuous, and dense CsPbBr₃ thin films without defects such as cracks and pinholes. Roughness variation of CsPbBr₃ thin film surface found using Scanning Probe Image Processor (SPIP) software is shown in Fig. 4. The total scan area of the CsPbBr₃ thin film was 2 and 5 μm². The CsPbBr₃ thin film surface roughness was observed between 95 nm to 250 nm.

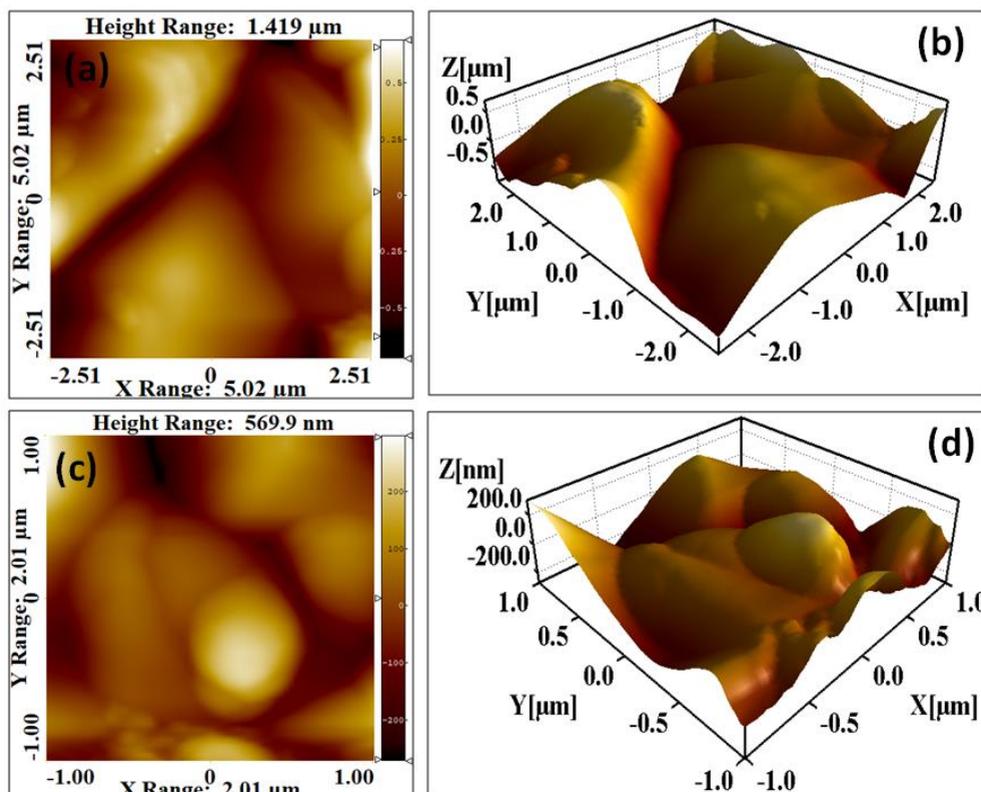


Fig. 4 AFM images of CsPbBr₃ film deposited on sola lime substrate by drop cast method.

4. Conclusion

We have successfully synthesized the CsPbBr₃ NPs at room temperature using a facile colloidal synthesis method. The UV-Visible spectroscopic analysis shows a strong absorption peak at 509 nm. The estimated bandgap of CsPbBr₃ was found to be 2.2 eV. The monoclinic structural phase of CsPbBr₃ material was observed in the XRD patterns and exhibited a cuboid-like structure with size ~ 400-500 nm. The wavelength of PL emission spectra at 505 nm with a narrow FWHM of ~ 29.87 nm have been observed. Controlled room-temperature synthesis and formation of thin films of CsPbBr₃ NPs with promising properties can open a novel path for low-cost optoelectronic devices.

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Supporting Information

Not applicable

Conflict of Interest

There are no conflicts to declare.

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