

Tuning the Optical Properties of MAPbBr₃ Perovskite Nanocrystals via Alkali Metal Ions Doping

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Halide perovskite nanocrystals (PeNCs) have emerged as a class of excellent semiconductors in the past few years for their high-performance optoelectronic applications. These materials have received considerable attention due to efficient charge carrier mobility, high photoluminescence quantum yields (PLQYs) and near theoretical efficiencies for green emitters. However, methylammonium (MA) cation-based perovskites exhibit their inherent instability such as high sensitivity to light, heat, oxygen, and moisture which influence their performance in practical applications. Their low in production cost and ease of synthesis make them suitable candidate for upcoming technologies. In this research, we study the doping of Cs and Rb cations into MAPbBr₃ PeNCs to optimize their morphology, crystal structure, and optical properties. It is found that rubidium cations doping can greatly enhance the photoluminescence intensity of the MAPbBr₃ PeNCs, whereas cesium cations can improve the structural stability owing to the increased valence bond intensity. This work provides useful thoughts for the synthesis of high-performance optoelectronic devices based on mixed-cation PeNCs.

Introduction

In recent years, researchers have shown an increased interest in metal halide perovskite nanocrystals (NCs) for optoelectronic applications in various fields, including light-emitting and light-harvesting devices, photodetectors and lasers. The superior performance of perovskite nanocrystals (PeNCs) is mainly attributed to high photoluminescence quantum yields (PLQYs), and their tunable bandgaps through the precise mixing of halogens and particle size [1-3]. The first PeNCs were synthesized by Schmidt in 2014, and since then, there has been a growing body of literature that recognises the importance of these materials [4]. The general structural formula of perovskites is ABX₃, where A is a methylammonium (CH₃NH₃⁺; MA⁺), formamidinium (CH (NH₂)₂⁺; FA⁺) or cesium (Cs⁺) cation; B is a divalent cation (mostly Pb²⁺ (lead)); and X is a halide anion (Cl⁻, Br⁻, or I⁻) [5]. Metal halide perovskites (MHPs), particularly the methylammonium lead halide (CH₃NH₃PbX₃; X = Cl⁻, Br⁻, I⁻), which show superior optoelectronic properties from excellent efficiency of detection of photons to photovoltaic

applications [6,7]. However, the potential concern of MA-cation-based perovskites is their inherent instability such as high sensitivity to light, heat, oxygen, and moisture which reduces their future applications [8]. Thus far, several reports have shown that the stability of MAPbBr₃ NCs could be enhanced by replacing MA cations with other smaller-size cations or compositional engineering [9]. For example, Bing Xu *et al.* reported for the first time the fabrication of PeNCs by mixing the organic cation (MA) with inorganic cation (Cs) to use as an emission layer for perovskite light-emitting diodes (LEDs). The high-performance LEDs based on these PeNCs showed a maximum luminance of 24500 cd/m², a current efficiency of 4.1 cd/A, and external quantum efficiency of 1.3% [10]. Another study was reported about the incorporation of rubidium (Rb⁺) ions into MAPbBr₃-based LEDs. The addition of Rb ions partially replaced the MA cations and showed excellent electroluminescent behaviour with a current efficiency of 9.45 cd/A and the luminance of 7694 cd/m². A 19-fold increase in current efficiency and a 10-fold increase in luminance were demonstrated in Rb cations doped LEDs compared to pristine MAPbBr₃-based

perovskite devices [11]. In this work, we study the incorporation of Cs and Rb cations into MAPbBr₃ PeNCs to optimize their morphology, crystal structure and optical properties. The RbBr and CsBr are used as a dopant to partially replace the MA cations. Band-gap engineering of mixed-cation PeNCs has been demonstrated during the fabrication process, by replacing the MA cations with alkali metal ions (Cs and Rb), with different concentrations.

Experimental

Materials

Lead bromide (PbBr₂) (99.9%), cesium bromide (CsBr) (99.9%), rubidium bromide (RbBr) (99.6%), oleic acid (90%), oleylamine (70%), dimethylformamide (DMF) (99.8%), hexane (95%), and toluene (99.8%) were purchased from Sigma-Aldrich. Methylammonium bromide (MABr) (98%) was purchased from Ossila Ltd.

Material synthesis

The MAPbBr₃ PeNCs were fabricated by ligand-assisted re-precipitation (LARP) technique. Briefly, 0.122mmol of PbBr₂ and 0.098mmol of MABr were dissolved in 5ml of DMF. In a separate glass vial, 500μl oleic acid and 50μl oleylamine were mixed and injected into the precursor solution. After that, 500μl precursor solution was dropped into vigorously stirred 10ml toluene at room temperature to initiate the crystallization of nanocrystals, which was observed by strong greenish-yellow PL emission. For the MA_{0.7}Cs_{0.3}PbBr₃ synthesis, 0.098 mmol of MABr was replaced by 0.068 mmol of MABr and 0.029mmol of CsBr.

The crude solution was centrifuged at 4000rpm for 10 min to remove bulk and unreacted materials, and the resultant precipitate was re-disperse in 1ml of hexane. After another centrifugation at 4000rpm for 5 min to remove precipitates, a bright green solution was obtained for further characterization.

For the rubidium-doped MA_{0.6}Rb_{0.4}PbBr₃ synthesis, 0.098mmol of MABr was replaced by the 0.059mmol of MABr and 0.039mmol of RbBr.

Characterizations

Transmission electron microscopy images were captured on a JEOL-JEM TEM machine operating at an accelerating voltage of 200 kV. X-ray diffraction data were collected by using PANalytical XpertPro diffractometer with Cu Kα radiation over the 2θ range from 10° to 60°. The ultraviolet-visible (UV-Vis) spectrum was measured with the LAMBDA 35 PerkinElmer spectrometer. Photoluminescence (PL) spectra were recorded at room temperature by using a fluorescence spectrometer (FLS920, Edinburgh Instruments).

Results and discussion

To study the effect of Rb and Cs cations doping on the structure and optical properties of MAPbBr₃, the LARP method was used to form highly crystalline and monodisperse PeNCs. This method is a simple and versatile technique to fabricate NCs at room temperature via solvent-mixing approach by introducing ligands on the surface.

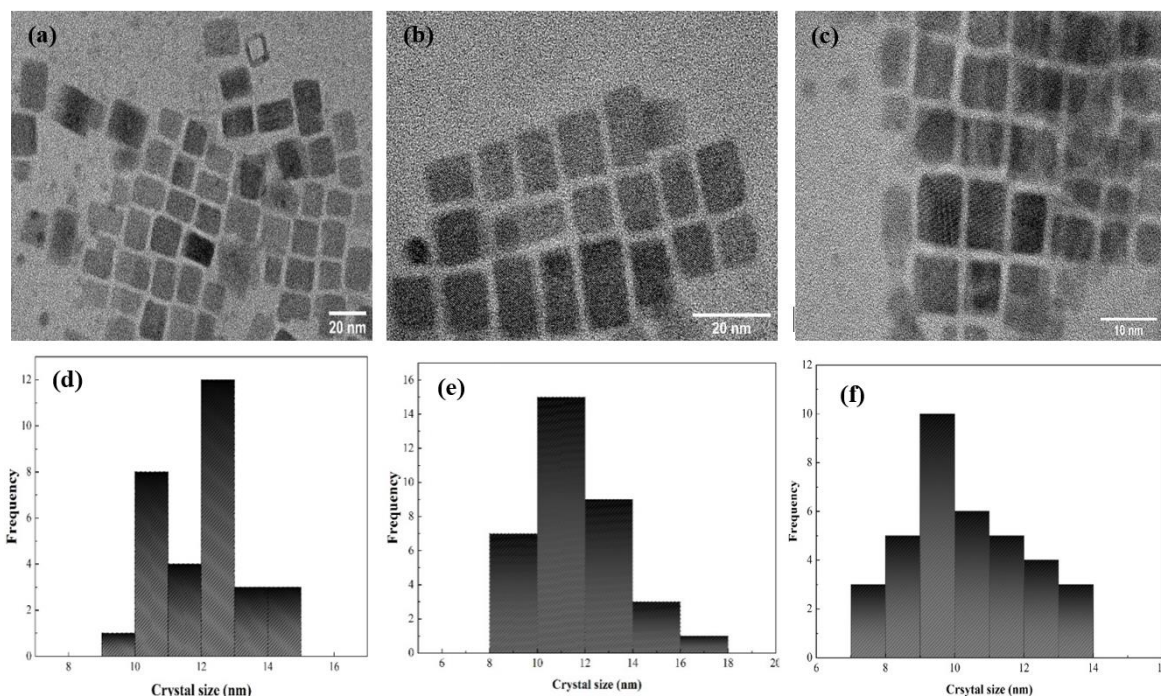


Fig. 1. (a) TEM image of the MAPbBr₃ PeNCs (b-c) Morphology of MAPbBr₃ PeNCs doped with Cs and Rb cations with different concentrations (d) Histogram of as-prepared MAPbBr₃ PeNCs (e) Histogram of MA_{1-x}Cs_xPbBr₃ when x=0.3 for Cs cations (f) Histogram of MA_{1-x}Rb_xPbBr₃ PeNCs when x=0.4 for Rb ions.

We found that the optimal doping level of Cs and Rb cations to achieve excellent PL for $MA_{1-x}Cs_xPbBr_3$ and $MA_{1-x}Rb_xPbBr_3$ is $x=0.3$ and $x=0.4$ relative to MA cations respectively [10,11]. The as-synthesized $MAPbBr_3$ PeNCs are predominantly single crystalline with sizes varying from 9nm to 15nm as shown in Fig. 1(a). All the PeNCs have a cubic shape with no substantial change in shape after doping Cs or Rb ions into the pristine samples as displayed in Fig. 1(b-c). The TEM histograms as presented in Fig. 1(d-f) reveal a small degree of size reduction for the alkali metal ions (Cs and Rb) doped PeNCs.

To study the changes in the optical band gap of alkali metal ions (Cs and Rb) doped PeNCs, we performed UV-Vis absorption spectroscopy measurements. As demonstrated in Fig. 2(a), the absorption spectra were blue-shifted from 535nm to 527nm upon Cs cations doping into the $MAPbBr_3$ NCs. This absorption band was further blue-shifted to 521nm after Rb cations doping into the pristine PeNCs.

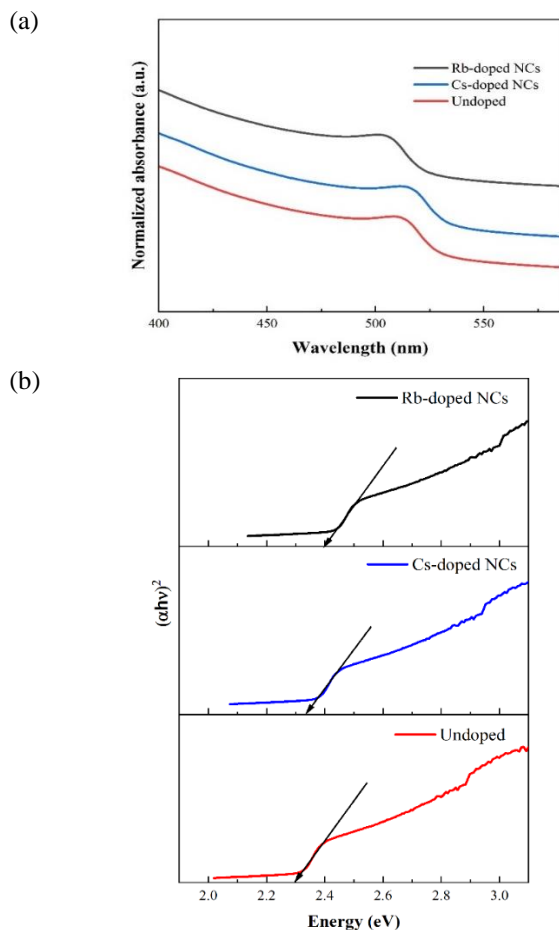


Fig. 2. (a) The absorption spectra of $MAPbBr_3$ and alkali metal ions (Cs and Rb) doped PeNCs. (b) Optical band gap energy calculation (Tauc's plot) of the undoped and doped PeNCs.

The band gap of such materials is the minimum required energy that outermost electrons get rid of the valence band. The valence bond strength depends on the lattice constant as the smaller the atomic spacing, the

greater the force between neighbouring atoms. The optical band gap of these undoped and doped samples was calculated by the following Tauc's formula which is given by $ah\nu = A(h\nu - Eg)^n$ where $h\nu$ is photon energy, α is the absorption constant, A is the proportionality constant, and Eg is the value of band gap. The value of $n=1/2, 3/2, 2,$ and 3 is used for direct, direct-forbidden, indirect, and indirect-forbidden bandgaps, respectively [12].

As depicted in Fig. 2(b), the decrease in lattice constant due to the insertion of smaller size cations (Cs and Rb), shows the potential in the increased value of the band gap from 2.23eV to 2.40eV.

In addition, Fig. 3(a) presents the dependence of PL characteristics of $MAPbBr_3$ PeNCs on Cs and Rb cations doping. As we can see from the PL spectra, with alkali metal ions incorporation, the intensity of each PL spectrum was increased. Furthermore, compared with $MAPbBr_3$ PeNCs, the peak position of Cs and Rb cations doped samples, PL spectra was blue shifted from 532nm to 526nm, showing that alkali metal ions can slightly change the luminance spectra. The presence of Stokes shift may be because when a system absorbs photons with high energy and is directed to the excited state, followed by the rapid relaxation to the ground state. The system would come to the original condition with the loss of energy due to vibrational and relaxation dissipation which causes the redshift of the emission spectrum compared with the absorption spectrum [13].

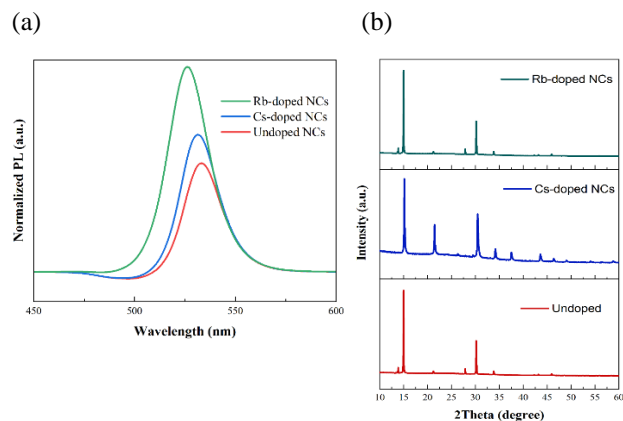


Fig. 3. (a) PL spectra of alkali metal cations doped $MAPbBr_3$ PeNCs. (b) X-ray-diffraction patterns of alkali metal cations doped $MAPbBr_3$ PeNCs.

To confirm the composition and crystallization of the NCs, the x-ray diffraction (XRD) measurements were recorded with Cs and Rb ions treated with $MAPbBr_3$ perovskite NCs. The as-prepared NCs showed highly crystalline behavior, as depicted from the XRD patterns in Fig. 3(b) It can be noticed that the intensity of (100) peak decreases and the intensity of (110) peak gradually increases because of Cs ions doping into the crystal lattice. Interestingly, we also observe that the Rb-doped PeNCs did not show any significant changes in the XRD spectra because of their small size.

Conclusion

In this study, we have synthesized Cs and Rb cations doped MAPbBr₃ perovskite NCs via the LARP method. The alkali metal ions doping replaces the MA cations and affects the crystal lattice of MAPbBr₃, hence tuning the optical properties of MAPbBr₃ PeNCs in turn. The results of this study have shown that there are no significant changes in the morphology of PeNCs, whereas alkali metal ions doped PeNCs show reduction in size due to crystal lattice contraction. We found that PL intensity increases to a higher value with Rb cations doping than that with Cs due to the more tolerance of the PeNCs for higher doping of smaller size alkali metal ions. These findings describes an advancement in understanding the chemistry and structural stability of perovskite NCs essential for various optoelectronic applications. Considerably more work will need to be done to determine the long-term effects of alkali metal ions treatments for halide PeNCs.

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Conflict of interest

There are no conflicts of interest to declare.

Keywords

Perovskite nanocrystals; Alkali metal ions; optical band-gap, structural stability.

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Author biography



Madeeha Tabassum is a Ph.D. candidate in the school of engineering and materials science of the Queen Mary University of London. She has a B.Sc. (2013) and M.Sc. (2016) degree in Textile Engineering. Her research involves the synthesis of perovskite nanostructures for application in optoelectronics

Graphical abstract

