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Mechanochemical synthesis of stable, quantum-confined CsPbBr$_3$ perovskite nanocrystals with blue-green emission and high PLQY

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Abstract

Cesium lead halides are a family of bright, visible-light emitting materials with near-unity photoluminescence quantum yield (PLQY) in nanocrystals (NCs). The usual way to achieve visible light-emission tunability is by mixing halides, which often leads to phase separation and poor stability. While the NCs should also show size-dependent PL emission, reports on strong quantum confinement in these materials are scarce. Here, we report the synthesis of quantum-confined cesium lead bromide (CsPbBr$_3$) NCs via a facile, environment-friendly, and scalable high-energy mechanochemical synthesis route. The PLQY measured is $\sim$85%, even after 90 days of synthesis, and the emission wavelength is shifted from green, 520 nm, to blue, 460 nm by quantum confinement in NCs of size 3–5 nm. Micro-PL optical spectroscopy and atomic force microscopy confirm the size tunability of PL on a single-dot scale. Our work demonstrates the potential of mechanochemical synthesis in the medium-scale production of bright luminescent quantum-confined NCs that could be extended to other materials as well.

1. Introduction

Cesium lead halide perovskites are well known for their excellent optical properties, tunability of light in the visible range and ease of synthesis [1–3]. Blue, green, and red emitting lead-halide phosphors have been synthesized via hot injection [3, 4], mechanochemical [5, 6], and ultrasonication methods [7, 8]. Near-unity photoluminescence (PL) quantum yield (QY) is claimed in bromide [9], iodide [9, 10], and chloride perovskites [9], but chlorides and iodides, and mixed halides are not very stable due to weak interactions between the halides [11] and detachment of ligands leading to degradation of the nanocrystals (NCs) [12, 13] and phase separation [13]. To increase the stability of the NCs and tune the PL emission in the entire visible range of the spectrum, mixing of Cl/Br/I halides [14–16], doping with transition metals [17–19] and size reduction [11] have been tried in the past. Encapsulation of NCs and ligand modification have been tried as well in the past to increase the stability of NCs [20–23]. Mixing the halides, i.e. bromides and chlorides, allows tuning the PL emission between green and blue; however, this typically affects the stability and PLQY [24–26], and mixed halides often tend to phase separate [26]. Another way to tune the PL emission is by quantum confinement; this has been achieved in the past via various synthesis methods [11, 27, 28]. Yet, the scalability of the synthesis method to obtain higher material yield for practical applications is still under active research. Furthermore, quantum-confined NCs can exhibit deteriorated electronic properties due to an excess of large-size organic cations and over-capped ligands [14].

Previous studies have classified the quantum confinement in perovskite NCs in three regimes: weak, intermediate and strong confinement with decreasing NC size [29]. Nevertheless, due to the possibility of
tuning the band gap of lead-halide perovskites by halide mixing, the effect of quantum confinement on the optical properties has received limited attention. Furthermore, the uniform size distribution achieved with controlled synthesis techniques such as the hot-injection method has facilitated band-gap tuning by halide mixing and doping [3]. Small, blue-emitting CsPbBr$_3$ NCs targeting 70% PLQY have been reported [30], but typically the PLQY goes down with smaller sizes [11, 30].

Mechanochemistry is a powerful method to synthesize larger amounts of nanomaterial, and it has been used in the past to synthesize cesium-lead halide perovskites [5, 6, 31, 32]. However, there is no report to our knowledge on high PLQY and strong quantum confinement in perovskite NCs prepared by mechanochemistry. Mechanochemistry is used for synthesis due to its gram-scale synthesis capability [33, 34], great control over stoichiometry [34] and solvent-free green approach [33, 34]. Herein, we report the synthesis of blue and green (∼460 and 505 nm) emitting CsPbBr$_3$ NCs by high-energy ball milling with high PLQY of ∼85%, stable over at least 90 days at ambient conditions. The two emission peaks are associated with two distinct size distributions, present in the sample after mechanochemical synthesis. The quantum-confined small sizes (<7 nm) and resultant PL blue shift are confirmed using micro-PL and atomic force microscopy (AFM) techniques. The high PLQY blue-emitting 3D quantum-confined CsPbBr$_3$ NCs synthesized by a scalable synthesis technique could help in realizing blue perovskite light emitting diodes (LEDs).

2. Materials and methods

All the chemical reagents were at least of analytical grade and used as received without further purification. Lead (II) bromide (PbBr$_2$, 99%), cesium bromide (CsBr, 99%), oleic acid (OA, technical grade 90%), oleylamine (OAm, 90%), were all purchased from Sigma Aldrich. Toluene was obtained from Honeywell.

We used a custom-built attritor type high-energy ball mill to do mechanochemical synthesis of CsPbBr$_3$ NCs. This ball mill is very different from the commercially available planetary ball mills also used in the past in such synthesis [6]. This design enabled us to do synthesis in controlled gas atmosphere and with continuous water cooling to take away extra heat from the system, helping in synthesizing good quality NCs. CsBr and PbBr$_2$ were loaded in the stoichiometric ratio (0.2 mmol) in a stainless-steel vessel. Twenty microliters of OA and OAm both were added to the vessel. Stainless steel balls of balls-to-powder weight ratio of 250:1 were added to the reaction vessel. An equal weight of balls of 10 mm and 5 mm was used in the process. The chamber has provisions for continuous nitrogen gas flow, to allow milling under nitrogen atmosphere. Throughout the milling process, the milling vessel was continuously water cooled to take away the access heat generated by collision of the balls. The milling was performed for 1 h continuously at 500 rpm. After the completion of milling, we added a mixture of OA and OAm (50 µl each) and 8 ml of toluene in the reaction vessel. We recovered NCs dispersion after 2 min of continuously mixing.

The resultant solution was bright green in color under daylight, suggesting the formation of CsPbBr$_3$ perovskites. The dispersion of the milled powders was centrifuged for 10 min at 12 000 rpm twice to get rid of unreacted ligands and precursors. We collected the precipitate and redispersed the precipitate in the toluene and stored the dispersion in the dark at ambient conditions.

To separate the two populations of nanoparticles, we used a combination of ultra-centrifugation and sonication. We centrifuged the redispersed precipitate obtained at 12 000 rpm for 5 min and collected the supernatant of it. The precipitate was again redispersed in toluene for further use. To study the stability of the NCs, we stored them in a cuvette used to measure PL on day 1 in ambient conditions and remeasured PL after 90 days.

Scanning transmission electron microscopy (STEM) imaging was conducted on FEI Verios 460 using Cu grids as support materials (available online at stacks.iop.org/JPMater/5/024005/mmedia). For STEM imaging, the samples were drop casted onto the Cu grids and then dried under vacuum for a whole day.

X-ray diffraction (XRD) was performed on a Rigaku MiniFlex benchtop x-ray diffractometer. Dispersions of the collected nanomaterials were drop casted on a zero-background silicon substrate multiple times to obtain a relatively dense dried coating. Samples were scanned in an angular range 2Θ from 10° to 60° with a scan rate of 0.05 rad s$^{-1}$ using Cu Kα ($\lambda = 1.54$ Å) x-rays.

High-resolution transmission electron microscopy (HRTEM) was conducted on Tecnai T20 G2 electron microscope coupled TVIPS XF416 CCD camera. Samples were drop casted on Cu grids and dried in air before the measurements.

A LAMBDA 950 UV/VIS/NIR spectrophotometer (PerkinElmer), was used to measure the absorbance/optical density in an excitation range of $E_{\text{det}} = 0.4–5.6$ eV. Here, the absorption spectrum of the solvent (i.e. toluene) is measured separately and subtracted from the spectrum. A Fluorolog spectrofluorometer (Horiba Jobin Yvon) is used to measure the PL excitation. As an excitation source, a
450 W Xe lamp (250–700 nm; type: short arc lamp, Ushio Inc., Japan) coupled to a monochromator is used providing a range of excitation wavelengths. The emission from the sample is always collected in a right-angle geometry to prevent the light source directly entering the detector. All spectra are corrected for the spectral sensitivity of the spectrofluorometer. The PLQY is measured by placing the sample in an integrating sphere (type: Newport 819C-1S-5.3). Here, a 150 W Xe lamp coupled to a spectrometer (Solar, MSA130) is used as an excitation source, providing a selection of excitation wavelengths. The excitation and emission light are scattered diffusively in the integrating sphere. The spectra are recorded by a CCD camera (type: 155S10141-1108S, Hamamatsu) coupled to another spectrometer (Solar M266). The calculation of the PLQY was done using a method and equation reported in the literature \[35\]. The time-resolved PL measurements are performed using a LifeSpecII time correlated single photon counting spectrometer (Edinburgh Instruments). It has a 230–850 nm detection range (MCP-PMT). A diode laser with excitation wavelength \(\lambda_{\text{exc}} = 375\) nm (EPL-375, Edinburgh Instruments) provides a 100 ps pulse. A right angle between the excitation and emission beam paths is maintained to avoid detection of scattered excitation light. For single-nanoparticle PL measurements, a highly diluted sample of perovskite NCs in UV-grade toluene was drop-casted onto a quartz coverslip (SPI supplies—25 mm diameter; thickness: 0.15–0.18 mm). The drop-casted sample was left to dry in a fume-hood at room temperature for a few minutes. We used an optical micro-spectroscopy setup coupled to an AFM (Nanowizard 3, JPK Instruments) for the measurements. A spectrometer (Princeton Instruments, Acton SP2300) coupled with a CCD (Princeton Instruments, Pylon 400B) was used to detect the PL emission. The sample was excited by diode lasers (405 nm and 445 nm, Becker and Hickl GmbH, BDL-405-SMN; BDL-445-SMN). The emitted light was collected using a 100× objective (Zeiss, Epiplan-Neofluar with NA of 0.75). A bandpass filter (Semrock, BLP01-405R-25; BLP01-445R-25) was used to filter the scattered excitation light. All the recorded PL spectra were corrected for spectral sensitivity in all the setups (Fluorolog; PLQY setup; and microscope). We studied the effect of the size of the NCs on the PL emission using this correlative AFM-micro-PL spectroscopy setup. The AFM was used in the tapping mode with an Al-coated silicon tip (NanoWorld Point probe silicon SPM sensor; resonant frequency \(\sim 320\) kHz). JPK software was used to capture scans and analyze the size of individual particles.

3. Results and discussion

The PL and absorption spectrum, together with a photograph of the as-synthesized sample are shown in figure 1(a) (right inset). We observe an emission peak at \(\sim 505\) nm and strong green fluorescence, together with an absorption edge at 505 nm. After letting the sample settle for a few days, we observe the supernatant fluoresces with bright blue color instead of the initial green fluorescence, which we associate with size-dependent settling of the particles. To fully investigate this effect, we centrifuged the NCs suspension and found that indeed, in contrast to the as-synthesized sample, the centrifuged sample exhibits strong blue fluorescence as shown in the photograph in the left inset. Analyzing the PL spectrum of the centrifuged sample in detail, we find that it shows two emission peaks: green emission with wavelength \(\sim 505\) nm and blue emission with wavelength \(\sim 460\) nm. These two peaks suggest the presence of two populations of NCs in the sample. Further evidence of the two populations comes from the presence of sharp absorption edges with corresponding Stokes shift in the main panel (black line). There are two sharp absorption edges, indicating the presence of the two different populations that absorb simultaneously. To obtain further evidence for the absorption and emission from the two populations, we performed PL excitation spectroscopy. The excitation of the green-emitting population of particles begins at \(\sim 520\) nm, while that of the blue-emitting particles starts at \(\sim 470\) nm, as shown in figure 1(b). At \(\sim 460\) nm, there is a sharp increase in the excitation of the blue emitting population and concomitant decrease in the excitation intensity of the green emitting particles. The presence of the two different excitation bands for the two PL peaks gives another evidence of the presence of two strongly emitting populations in the sample.

Remarkably, we observe that after 90 days of storage, the PL emission has even considerably increased, see figure 1(c). We also observe a small red shift. This is true for both blue and green emitting NCs: both peak intensities increase significantly, and the peaks shift slightly to the red.

This PL intensity increase is most clearly reflected in a drastic increase of the PLQY: the green emitting sample showed a PLQY of \(\sim 22\)% at the time of synthesis, while after 90 days, the same sample showed a PLQY of \(\sim 89\)% (figure S1(a), supplementary materials). During the 90 days, the sample was stored in a dark closet under room conditions. We have observed the increase in PLQY of green emitting sample to peak in five days from the synthesis. This suggests that with time, non-radiative relaxation channels have been passivated. We speculate that the disappearance of these non-radiative channels is due to healing of the material associated with the relaxation of ball milling-induced stresses. Initially, the NCs contain a considerable number of defects stemming from the mechanochemical synthesis, which heal over time,
Figure 1. Optical properties of mechanochemically synthesized sample. (a) PL and absorption spectra of the size-separated CsPbBr$_3$ sample. Two PL peaks at $\sim$460 nm and $\sim$505 nm are visible. Corresponding absorption curve shows presence of absorption edges for both PL peaks suggesting presence of two emitting populations. Left inset: size-separated sample under UV light showing blue emission. Right inset: non-size separated sample showing green emission and absorption/PL spectra with emission peak at $\sim$505 nm. (b) PL excitation spectra of the small sized NCs for PL$@$460 nm (in black), and PL$@$505 nm (in red). (c) Comparison of PL emission from original and size-separated sample 90 days after synthesis. Red shift and PL intensity increase suggest aggregation and stress relaxation of particles with time.

relaxing the internal stresses, and leading to efficient radiative emission after material healing. In addition, temperature could also play a role in accelerating the healing process. However, the limited phase stability of NCs under conditions of higher temperatures, humidity and continuous air exposure could affect the stability, and needs to be taken into account.

For the centrifuged sample, the PLQY is already high immediately after synthesis, $\sim$82%, and further increases to $\sim$85% after 90 days (figure S1(b), supplementary materials). To our knowledge, this is the highest PLQY for blue-emitting perovskite NCs following Li et al, who tabulated the synthesis efforts of blue-emitting perovskite NCs of various groups with corresponding PLQY [30]. Our measured PLQY is higher than these reported values. The PLQY and stability of blue-emitting mixed halide perovskites is the current bottleneck in realizing blue perovskite LEDs [36–38]. Our results of quantum-confined blue emission from perovskite NCs provide an alternative to mixed halide perovskites and, together with its enhanced stability, could be useful in the realization of blue perovskite LEDs. The PLQY for the green emitting NCs is also high, though rather comparable to other synthesis method [39–41]. Yet, the advantage of the mechanochemical synthesis method is the high material yield, providing grams of NCs in a one-pot synthesis in just 1 h.

To obtain more insight into the origin of the two emission peaks, we studied both samples with SEM and XRD. A SEM image of the original sample is shown in figure 2(a). The presence of nice cubic-shaped particles agrees with the literature [42]. Furthermore, the observation of ordered structures suggests a narrow size distribution. We measured particle sizes directly from the images using image analysis (ImageJ open-source software); the resulting size distribution, shown in the inset, reveals a reasonably narrow particle size distribution with average particle size of $\sim$7.5 nm. This distribution is somewhat broadened due to the visual presence of a second layer of particles resulting in some bigger random clusters (in white contrast). Particles with sizes of $\sim$7–8 nm are expected to show weak quantum confinement; indeed, this is reflected in the PL spectrum measured on this sample, showing an emission peak at $\sim$505 nm (inset, figure 1(a)) [11, 43], slightly blue shifted with respect to the expected bulk peak at 520 nm. In contrast, the SEM image of the size-separated sample shows a population of much smaller NCs, as shown in figure 2(b). The corresponding particle size distribution reveals the presence of very small particles with sizes in the range of 3–8 nm, suggesting that quantum confinement effects may be the origin of the blue shift as has been theoretically calculated previously [6]. Additional HRTEM imaging (figure S2, supplementary
Figure 2. CsPbBr$_3$ NCs obtained by ball milling. (a) SEM micrograph of the mechanochemically synthesized sample. Cubic-shaped NCs with narrow size distribution are observed. Inset: particle size distribution indicating average particle size $\sim$7.5 nm. (b) SEM micrograph of the minor population of very small NCs extracted by size separation. Inset: particle size distribution indicating presence of particles of size $<$6 nm. Particle size distribution in both micrographs is obtained using ImageJ software. Error of the size determination is of the order of $\sim$1 nm due to the uncertainty in detecting the NC edges. (c) X-ray diffraction patterns of the NCs before (black, large peaks) and after size separation (red, small peaks). The former show broad but clear peaks matching previous reports [34, 45]. The latter show very broad peaks reflecting the small NC sizes.

materials) provided more insights into the presence of small and large sizes. The HRTEM images show cubic-shaped NCs in the aged samples, and confirm the two different size populations. Interestingly, the freshly prepared samples show presence of distorted NCs exhibiting rough edges, which are not present in the aged sample. This supports our hypothesis of healing of the NCs over time. The PL blue shift can then be understood by a particle in a box model of quantum confinement, as also explained by Lin et al [44].

To further elucidate this point and distinguish size confinement effects from structural changes, we use XRD to study the crystal structure of the NCs. The XRD spectrum of the as-synthesized sample (figure 2(c), black data) shows the characteristic peaks of the CsPbBr$_3$ phase though due to the small NC dimensions, the peaks are broadened. Both cubic and orthorhombic phases have diffraction peaks within the broadened peaks [30, 36, 45] so we conclude that indeed the CsPbBr$_3$ perovskite phase was synthesized successfully. We indexed major peaks of the XRD spectrum as per most accepted orthorhombic crystal structure. We thus conclude that we have synthesized stabilized CsPbBr$_3$ NCs in a 1 h ball milling process, which have previously been reported after 14 h of mechanochemical synthesis [6]. The XRD pattern of the size-separated NCs (figure 2(c), red data) shows main peaks at the same positions, indicating that the small NCs exhibit the same perovskite phase. While some peaks are not visible due to lower concentration of the sample, the matched peaks at $2\Theta \sim 15^\circ$, 21$^\circ$ and 31$^\circ$ indicate consistent perovskite crystal structure of the large and small NCs.

To further elucidate the PL mechanism, we performed time-resolved PL spectroscopy on aged sample. The original suspension shows biexponential PL decay with lifetimes $\sim$5.1 $\pm$ 1 ns and 51 $\pm$ 1 ns. We associate this bi-exponential decay with the presence of the two populations. Indeed, the longer decay time is comparable to the reported literature on large ball-milled perovskite NCs [6]. Furthermore, the size-separated sample shows fast, near mono-exponential decay that matches the initial fast decay of the original suspension very well. We determine a lifetime of 6.3 $\pm$ 0.5 ns for the blue PL peak ($\sim$460 nm), consistent within measurement accuracy with the fast lifetime of the original suspension, and a somewhat longer decay time of 10.2 $\pm$ 1 ns for the 505 nm PL. Interestingly, when we measure time-resolved PL
Figure 3. Time resolved PL spectroscopy measurements on the (a) average PL decays curves for both PL peaks of size separated and large NCs (non-size separated) sample. The raw data is shown in the light-colored background with corresponding fits (solid bold lines). An arrow indicates increase in the PL lifetime with decrease in PL peak energy. Both PL peaks of size separated samples shows mono-exponential decay while bulk sample shows biexponential decay. The PL lifetimes are tabulated in the inset.
(b) Size separated sample. PL decay curves corresponding to their PL peak wavelengths are shown various colors. The lifetime extracted from mono-exponential fits are show in the inset in function of PL peak wavelengths. An increase in PL lifetime is observed with increasing PL peak wavelengths.

spectroscopy on freshly prepared samples (figure S3, supplementary materials), we observe the opening of an additional faster PL decay component that is not present in the aged sample that we associate it with non-radiative relaxation channels (defects). In addition, we also observe a shortening of the main radiative decay components. The opening of these fast relaxation channels and relatively shorter PL lifetimes is in line with the lower QY measured for the fresh samples and supports our hypothesis that defect healing after synthesis leads to closing of non-radiative decay channels.

To study the dependence of PL lifetime on emission wavelength of the aged samples in more detail, we focus on the size separated sample and measure time-dependent PL for various PL emission wavelength, as shown in figure 3(b). The curves show near mono-exponential decays with lifetimes in the range 5.5–12 ns, shortening with decreasing emission wavelength. In smaller NCs, the relatively enhanced presence of surface defects or trap states could lead to shorter radiative lifetimes. This is in qualitative agreement with the somewhat smaller PLQY observed for the smaller NCs, though the latter was observed to change only moderately from 89% of the large NCs to 85% of the smaller ones. A similar effect of the NC size on the radiative rate of quantum-confined perovskite NCs was observed in [6].

In fact, when we performed the mechanochemical synthesis without the presence of ligands, and added the ligands at the end of the reaction only, we observed no blue emission at all (figure S4, supplementary materials). We therefore associate the high PLQY of the small, quantum-confined NCs with the presence of ligands during the milling process, which may allow the particles to get stabilized after reaching a critical size during the reaction. Forde et al observed a lowering of the PLQY with decreasing NCs size, and related this to non-radiative decay channels opening up with increase in surface area [46]. In our ball-milled synthesized sample with ligands, we do not see such drop in the PLQY, which may be due to well-passivated NCs, preventing the formation of surface traps acting as non-radiative channels. We note that a completely dry milling process (without addition of ligands and solvent) resulted in agglomerated cubic-shaped NCs (figure S5, supplementary materials). In this case, the milling weld particles together but we observed that particles deagglomerated upon ultrasonication.

To further elucidate the role of quantum confinement in the observed blue shift of the PL emission, we performed micro-PL spectroscopy with correlated AFM. An inverted microscope coupled to a spectrometer and CCD was used to detect PL emission from the perovskite NCs, while an AFM installed on the same setup was used to measure the height of the particles with a resolution of 0.1 nm. Figure 4 shows AFM scans and corresponding particle size distribution ((a), (b)), together with a micro-PL map under excitation by a diode laser with wavelength 445 nm (c). While it is difficult to correlate both maps due to deterioration of the NCs under unprotected environment and intense laser power, we managed to measure PL spectra and sizes of quantum-confined NCs separately. The sizes of the NCs measured with AFM are mostly below 10 nm, as shown in figure 4(b). We measured the PL spectra of individual NCs before they were bleached at a low laser power of 5 µW cm−2. The individual PL spectra after Gaussian fitting are shown in figure 4(d), and their raw data with fits are presented in supplementary figure S5. The ensemble PL spectrum is shown for comparison.
Figure 4. Micro-PL-particle size correlative measurement of quantum confined cesium lead bromide NCs. (a) AFM image of an area of $40 \times 40 \, \mu m$ showing presence of quantum confined particles from size $\sim 3 \, nm$ and above. Some clusters of particles are present as well showing incapability of centrifugation and filtration to take out big particles/clusters out of the samples. (b) The distribution of height measured by AFM in the corresponding scan image (figure (a)) showing presence of $<10 \, nm$ sized particles. (c) 2D PL map of the $80 \times 80 \, \mu m$ area shows presence of brightly luminescent NCs excited by 405 nm laser. The PL map was acquired in 3 s with the scan rate of 1 MHz. Presence of big clusters overwhelming the PL signals from the small sized NCs and also scattering some background noise. (d) PL spectra of some representative single NCs measured on the microscope by integrating the signal for 5 s under continuous 405 or 445 nm laser excitation at scan rate of 50 kHz, using grating of 300 grooves mm$^{-1}$, showing presence of the particles in the sample emitting across the ensemble PL. The apparent single NCs could also be clusters of single NCs. The inset figure is showing a histogram of the peak wavelengths of emitting NCs.

The single-dot PL spectra (bottom of figure 4(d)) clearly show how the ensemble PL spectrum is built up from the individual contributions. We observe PL spectra peaking between 450 nm and 520 nm, in agreement with the ensemble PL spectrum. Furthermore, a histogram of the single-dot PL emission wavelength (inset) shows prevalence of particles emitting close to 460 nm and 505 nm, in good agreement with the ensemble PL peak positions. The corresponding single-dot PL spectra are shown in supplementary figure S7. This again suggests that the two PL peaks are due to the presence of two distinct populations, with the majority of the particles emitting either close to $\sim 460 \, nm$ or close to 505 nm. Furthermore, there are also particles emitting in between these peaks, i.e. there is a continuous emission of particles in a range between 450 and 520 nm that roughly corresponds to the measured NC size distribution measured by AFM. Together with the XRD measurements indicating the same phase of the small and larger NCs, this indeed confirms that quantum confinement effects related to the small NC sizes underlie the observed blue shift.

Nevertheless, the reason for the two distinct populations remains unclear. We can understand the mechanochemical synthesis of perovskite NCs using a ductile-ductile system as example. Upon mixing of the two precursors, initially, the reaction will proceed in two steps: first, downsizing of the precursors, and
second, reaction between the precursors causing the formation of CsPbBr$_3$, i.e. their nucleation and growth. Once the NCs are formed, in a ductile-ductile system such as this one, the NCs upon milling crush and with increasing milling time, the work-hardened particles become increasingly brittle and finally break down into small particles [47, 48]. Bimodal particle distributions obtained by mechanochemical synthesis are not uncommon and have been reported for various materials [49, 50]. Specifically, the appearance of blue PL emission (PL peak at ~460 nm) together with PL emission at longer wavelength has been observed by Umemoto et al in MAPbBr$_3$ perovskites synthesized by ultrasound-assisted bead milling [50]. They attributed these peaks to mechanical shear-force induced size separation and corresponding quantum confinement effects. Besides the CsPbBr$_3$ NCs presented here, we observe a very similar two-peaked PL emission in the mechanochemical synthesis of iodide-based CsPbI$_3$ NCs (figure S8, supplementary materials); these iodide-based NCs also show two populations in their size distribution, suggesting that this phenomenon may be more general.

4. Conclusions

We have demonstrated the successful mechanochemical synthesis of blue and green emitting CsPbBr$_3$ NCs with record PLQY for the blue emitting population. The blue shift in the PL emission was related to quantum confinement effects associated with significantly smaller particles in the ensemble. The results of time-resolved PL, micro-PL, SEM and XRD measurements all direct towards a second population of smaller particles of the same perovskite phase that emit in the blue due to size-related quantum confinement effects. The high PLQY with good stability even after 90 days of synthesis would be helpful to realize cesium lead halide perovskite-based blue LEDs using gram-scale mechanochemical synthesis method. We could easily extend the synthesis to 1.4 g material synthesis in one batch, indicating the potential of this technique for industrial scale up. The high-energy mechanochemical method can then help in the reduction of carbon footprints in large-scale nanomaterial synthesis.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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References

[1] Roo J D, Ibáñez M, Geiregat P, Nedelcu G, Walravens W, Maes J, Martins J C, van Driessche I, Kovalenko M V and Hens Z 2016 Highly dynamic ligand binding and light absorption coefficient of cesium lead bromide perovskite nanocrystals ACS Nano 10 2071–81
[2] Nedelcu G, Protesescu L, Yakunin S, Bodnarchuk M I, Grotheer M J and Kovalenko M V 2015 Fast anion-exchange in highly luminescent nanocrystals of cesium lead halide perovskites (CsPbX$_3$, X = Cl, Br, I) Nano Lett. 15 5635–40
[3] Protesescu L, Yakunin S, Bodnarchuk M I, Kröig F, Caputo R, Hendon C H, Yang R X, Walsh A and Kovalenko M V 2015 Nanocrystals of cesium lead halide perovskites (CsPbX$_3$, X = Cl, Br, and I): novel optoelectronic materials showing bright emission with wide color gamut Nano Lett. 15 3692–6
[4] Tong J, Wu J, Shen W, Zhang Y, Liu Y, Zhang T, Nie S and Deng Z 2019 Direct hot-injection synthesis of lead halide perovskite nanocubes in acrylic monomers for ultrastable and bright nanocrystal–polymer composite films ACS Appl. Mater. Interfaces 11 9317–25
[5] Zhu Z Y, Yang Q Q, Gao L F, Zhang L, Shi A Y, Sun C L, Wang Q and Zhang H L 2017 Solvent-free mechanochemical synthesis of composition-tunable cesium lead halide perovskite quantum dots J. Phys. Chem. Lett. 8 1610–4
[6] Protesescu L, Yakunin S, Nazarenko O, Dirin D N and Kovalenko M V 2018 Low-cost synthesis of highly luminescent colloidal lead halide perovskite nanocrystals by wet ball milling ACS Appl. Nano Mater. 1 1300–8
[7] Jang D M, Kim D H, Park K, Park J, Lee J W and Song J K 2016 Ultrasound synthesis of lead halide perovskite nanocrystals J. Mater. Chem. C 4 10625–6
[8] Tong Y et al 2016 Highly luminescent cesium lead halide perovskite nanocrystals with tunable composition and thickness by ultrasonication Angew. Chem., Int. Ed. 55 13887
Dutta A, Behera R K, Pal P, Baitalik S and Pradhan N 2019 Near-unity photoluminescence quantum efficiency for all CsPbX$_3$ (X = Cl, Br, and I) perovskite nanocrystals: a generic synthesis approach Angew. Chem., Int. Ed. 58 5552

Hassanabadi E, Latifi M, Reyes A F G, Masi S, Voon S J, Poyatos M, López B J and Seró I M 2020 Ligand & band gap engineering: tailoring the protocol synthesis for achieving high-quality CsPbI$_3$ quantum dots Nanoscale 12 14194–203

Swamkar A, Marshall A R, Sanehira E M, Chernomordik D B, Moore D T, Christians J A, Chakrabarti T and Luther J M 2016 Quantum dot-induced phase stabilization of α-CsPbI$_3$ perovskite for high-efficiency photovoltaics Science 354 92–95

Zhang J R, Hodes G, Jin Z W and Liu S 2019 All-inorganic CsPbX$_3$ perovskite solar cells: progress and prospects Angew. Chem., Int. Ed. 58 15596–618

Xiang W, Liu S and Tress W 2021 A review on the stability of inorganic metal halide perovskites: challenges and opportunities for stable solar cells Environ. Sci. 12 2090–113

Karlsson M et al 2021 Mixed halide perovskites for spectrally stable and high-efficiency blue light-emitting diodes Nat. Commun. 12 361

Zarich H F, Soetan N, Erwin W R and Bardhan R 2018 Mixed halide hybrid perovskites: a paradigm shift in photovoltaics J. Mater. Chem. A 6 5507–37

Knight A J, Borchert J, Oliver R D J, Patel J B, Radaelli P G, Snaith H J, Johnston M B and Herz L M 2021 Halide segregation in mixed-halide perovskites: influence of A-site cations ACS Energy Lett. 6 799–808

Wang R, Zhang H, Han S, Wu Y, Hu Z, Zhang G, Liu H, He Q and Zhang X 2021 Cadmium doping for improving the efficiency and stability of carbon-based CsPbBr$_3$, all-inorganic perovskite solar cells New J. Chem. 45 9243–50

Liu C, Sun J, Tan W L, Lu J, Gengenbach T R, McNeill C R, Ge Z, Cheng Y R and Bach U 2020 Alkali cation doping for improving the structural stability of 2D perovskite in 3D/2D PSCs Nano Lett. 20 1240–51

Wang G, Lei M, Liu J, He Q and Zhang W 2020 Improving the stability and optoelectronic properties of all inorganic less-Pb perovskites by B-site doping for high-performance inorganic perovskite solar cells Sol. RRL 4 2000528

Li X, Cai W, Guan H, Zhao S, Cao S, Chen C, Liu M and Zang Z 2021 Highly stable CsPbBr$_3$ quantum dots by silica-coating and ligand modification for white light-emitting diodes and visible light communication Chem. Eng. J. 419 129531

Mo Q, Chen C, Cai W, Zhao S, Yan D and Zang Z 2021 Room temperature synthesis of stable zirconia-coated CsPbBr$_3$ nanocrystals for white light-emitting diodes and visible light communication Laser Photon. Rev. 15 2100278

Mo Q, Shi T, Cai W, Zhao S, Yan D, Du J and Zang Z 2020 Room temperature synthesis of stable silica-coated CsPbBr$_3$ quantum dots for amplified spontaneous emission Photon. Res. 8 1605–12

Guo H, Zhao S, Wang H, Yan D, Wang M and Zang Z 2020 Room temperature synthesis of stable single-silica-coated CsPbBr$_3$ quantum dots combining tunable red emission of Ag–In–Zn–S for high-CRI white light-emitting diodes Nano Energy 67 104279

Li G et al 2016 Highly efficient perovskite nanocrystal light-emitting diodes enabled by a universal crosslinking method Adv. Mater. 28 3528–34

Zhang X et al 2020 Chlorine vacancy passivation in mixed halide perovskite quantum dots by organic pseudohalides enables efficient Rec. 2020 blue light-emitting diodes ACS Energy Lett. 5 793–8

Knight A J and Herz L M 2020 Preventing phase segregation in mixed-halide perovskites: a perspective Energy Environ. Sci. 13 2024–46

Lu M, Zhang Y, Wang S, Guo J, Yu W W and Rogach A I 2019 Metal halide perovskite light-emitting devices: promising technology for next-generation displays Adv. Funct. Mater. 29 1902008

Liu X K, Xu W, Bai S, Jin Y, Wang J, Friend R H and Gao F 2021 Metal halide perovskites for light-emitting diodes Nat. Mater. 20 10–21

Becker M A et al 2018 Bright triplet excitons in caesium lead halide perovskites Nature 553 189–96

Li J, Gan L, Fang Z, He H and Ye Z 2017 Bright tail states in blue-emitting ultrasmall perovskite quantum dots J. Phys. Chem. Lett. 8 6002–8

Palazon F, Ajjouri Y E, Luna P S, Laucello S, Manna L and Bolink H J 2019 Mechanochemical synthesis of inorganic halide perovskites: evolution of phase-purity, morphology, and photoluminescence J. Mater. Chem. C 7 11406–10

Askar A M, Karmakar A, Bernard G M, Ha M, Terskikh V V, Wiltshire B D, Patel S, Fleet J, Shankar K and Michaelis V K 2018 Composition-tunable formamidinium lead mixed halide perovskites via solvent-free mechanochemical synthesis: decoding the Pb environments using solid-state NMR spectroscopy J. Phys. Chem. Lett. 9 2671–7

Goyal A and Soni P R 2018 Functionally graded nanocrystalline silicon powders by mechanical alloying Mater. Lett. 214 111–4

Palazon F, Ajjouri Y E and Bolink H J 2020 Making by grinding: mechanochemistry boosts the development of halide perovskites and other multinary metal halides Adv. Energy Mater. 10 1902499

Valenta J 2014 Determination of absolute quantum yields of luminescing nanomaterials over a broad spectral range: from the integrating sphere theory to the correct methodology Nanosci. Methods 3 11–27

Nagadesh S B, Luo B, Pu Y C, Schwartz Z, Hollingsworth W R, Lindley S A, Brewer A S, Ayzen A L and Zhang J Z 2019 Size dependence of charge carrier dynamics in organometal halide perovskite nanocrystals: deciphering radiative versus nonradiative components J. Phys. Chem. C 123 4610–9

Guadlón-Reyes A F, Masi S and Mora-Seró I 2021 Progress in halide-perovskite nanocrystals with near-unity photoluminescence quantum yield Trends Chem. 3 499–511

Kumawat N K, Liu X K, Kabra D and Gao F 2019 Blue perovskite light-emitting diodes: progress, challenges and future directions Nanoscale 11 2109–20

Grisorio R et al 2021 Size-tunable and stable cesium lead-bromide perovskite nanocubes with near-unity photoluminescence quantum yield Nanoscale Adv. 3 3918–28

Zu Y et al 2019 Ultra-stable CsPbBr$_3$ nanocrystals with near-unity photoluminescence quantum yield via postsynthetic surface engineering J. Mater. Chem. A 7 26116–22

MacLaughlin C M 2019 Opportunities and challenges in perovskite-based display technologies: a conversation with Andrey Rogach and Haibo Zang ACS Energy Lett. 4 977–9

Huang H, Bodnarchuk M I, Kershaw S V, Kovalenko M V and Rogach A I 2017 Lead halide perovskite nanocrystals in the research spotlight: stability and defect tolerance ACS Energy Lett. 2 2071–83

Brennan M C, Zima J and Kuno M 2017 Existence of a size-dependent stokes shift in CsPbBr$_3$ perovskite nanocrystals ACS Energy Lett. 2 1487–8

Lin J, Gomez L, de Weerd C, Fujiwara Y, Gregorkiewicz T and Suenaga K 2016 Direct observation of band structure modifications in nanocrystals of CsPbBr$_3$ perovskite Nano Lett. 16 7198–202

Persson K 2014 Materials data on CsPbBr$_3$ (SG:62) by materials project (https://doi.org/10.17188/1273967)
[46] Forde A, Fagan J A, Schaller R D, Thomas S A, Brown S L, Kurtti M B, Petersen R J, Kilin D S and Hobbie E K 2020 Brightly luminescent CsPbBr\textsubscript{3} nanocrystals through ultracentrifugation J. Phys. Chem. Lett. 11 7133–40

[47] Benjamin J S and Volin T E 1974 Metall. Trans. 5 1929–34

[48] Rojas-Hernandez R E, Rubio-Marcos F, En’squez E, de la Rubia M A and Fernandez J F 2015 A low-energy milling approach to reduce particle size maintains the luminescence of strontium aluminate RSC Adv. 5 42559

[49] Taskiran M U, Demirkol N and Capoglu A 2006 Influence of mixing/milling on sintering and technological properties of anorthite-based porcelainised stoneware Ceram. Int. 32 325–220

[50] Umemoto K et al 2020 Simple production of highly luminescent organometal halide perovskite nanocrystals using ultrasound-assisted bead milling ACS Sustain. Chem. Eng. 8 16469–76