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Kinetics of Cesium Lead halide perovskite Nanoparticle growth; Focusing and De-focusing of size distribution

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Abstract
In this work we study the kinetics of Cesium lead halide perovskite Nanoparticle (NP) growth; the focusing and de-focusing of the NP size distribution. Cesium lead halide perovskite NPs are considered to be attractive materials for optoelectronic applications. Understanding the kinetics of the formation of these all-inorganic perovskite NPs is critical for reproducibly and reliably generating large amounts of uniformly sized NPs. Here we investigate different growth durations for CsPbI\(_3\) and CsPbBr\(_3\) NPs, tracking their growth by High-resolution transmission electron microscopy and size distribution analysis. As a result, we are able to provide a detailed model for the kinetics of their growth. It was observed that the CsPbI\(_3\) NPs exhibit focusing of the size distribution in the first 20 seconds of growth, following by de-focusing over longer growth durations, while the CsPbBr\(_3\) NPs show de-focusing of the size distribution starting from the beginning of the growth. The monomer concentration is depleted faster in the case of CsPbBr\(_3\) than in the case of CsPbI\(_3\), due to faster diffusion of the monomers, which increases the critical radius and results in de-focusing of the population. Accordingly, focusing is not observed within 40 seconds of growth in the case of CsPbBr\(_3\). This study provides important knowledge on how to achieve a narrow size distribution of cesium lead halide perovskite NPs when generating large amount of these promising, highly luminescent NPs.

Introduction
Metal halide perovskites are under intense investigation for their utility in photovoltaic solar cells. The great majority of studies address the carrier transport and the long diffusion length\(^1,2\) of bulk hybrid organic-inorganic lead halide perovskites, such as CH\(_3\)NH\(_3\)PbI\(_3\), which have demonstrated a solar cell power conversion efficiency of 20.1% to date\(^3\). However, the nanoscale
properties of the lead halide perovskites have scarcely been studied. Recently, Protesescu et al. reported on a novel synthesis of all-inorganic cubic cesium lead halide perovskite nanocrystals. The solution process synthesis produced mono-disperse populations of colloidal CsPbBr$_3$, CsPbI$_3$, CsPbCl$_3$, and mixed halide perovskites. Follow up works have been conducted on the ion-exchange dynamics of CsPbX$_3$ nanoparticles. These have shown that post-synthetic treatment of CsPbX$_3$ NPs (X=Br or Cl or I) with halide donators (such as other CsPbX$_3$ NPs, lead halide salts, organo-metallic Grignard reagents, oleylammmonium halides, tetrabutylammonium halides, or octadecylammonium halides) can be used to determine the final halide presence in CsPbX$_3$ NPs. This presents a post-synthetic path to spectral tuning of the nanocrystals. In addition, the original synthesis was adjusted to yield CsPbX$_3$ nanowires, and the progression of nanowire development over time was analyzed. It was observed that reactions quenched between 10 and 180 minutes after precursor injection yielded varying ratios of orthorhombic-phased nanocubes, nanosheets, and nanowires.

CsPbX$_3$ perovskites are direct bandgap semiconductors with orthorhombic, tetragonal, and cubic crystal phases, the cubic phase forming at high temperatures (above 130 °C for CsPbBr$_3$). Theoretical band gap energy calculations predict band gaps of 2.00 eV and 1.44 eV for CsPbBr$_3$ and CsPbI$_3$ respectively, while experimental measurements are greater by 0.2 eV. The Bohr diameter of CsPbBr$_3$ is 12nm. Compositional alteration of the halides, as well as crystal size adjustment from the bulk, allows for optical tuning between 410 and 700 nm. CsPbX$_3$ nanocrystals have narrow emission and high quantum yields of up to 90%.

The above studies demonstrate the unique and interesting properties of cesium lead halide perovskite NPs and their potential to be used in optoelectronic applications.

In this work, we study the kinetics of Cesium lead halide perovskite NP growth; the focusing and de-focusing of the NP size distribution. It is important to understand the kinetics of these Cesium lead halide perovskite NPs in order to reproducibly and reliably generate large amounts of uniformly sized NPs. We investigate different growth durations for CsPbI$_3$ and CsPbBr$_3$ NPs, tracking their growth by High-resolution transmission electron microscopy and size distribution analysis. A model describing the kinetics of the growth is demonstrated. This study provides insight into how to successfully achieve a narrow size distribution of cesium lead halide perovskite NPs.
Experimental

Synthesis of CsPbX₃, X=Br, I.

CsPbBr₃ and CsPbI₃ nanocrystals were synthesized according to a previously published procedure⁴, slightly adjusted. PbX₂ (99.9%), Cs₂CO₃ (99.9%), octadecene (ODE, Tech. 90%), oleic acid (OA, Tech. 90%), and oleylamine (OLA, Tech. 70%) were purchased from Sigma Aldrich. Briefly, 0.188 mmol of PbBr₂ or PbI₂ was dissolved in 5 mL ODE, 0.5 mL OA, and 0.5 mL OLA in a three-necked-flask, and degassed at 120°C. 2.46 mmol (0.8 g) of Cs₂CO₃ was dissolved in 30 mL ODE and 2.5 mL OA in a three-necked-flask, and degassed at 120°C. The Cs-oleate flask was then raised to 150°C under Argon to ensure full solubility of Cs₂CO₃. A hot syringe was used to swiftly inject 0.4 mL of the Cs precursor into the lead halide precursor solution at elevated temperature (170°C for Br, 145°C for I), yielding a bright green (Br) or deep red (I) colloid. The reaction was quenched with an ice bath 1, 4, or 40 seconds after the injection of the Cs precursor. The CsPbBr₃ product could be washed with hexane, precipitated by addition of isopropanol, isolated by centrifuge, and re-dispersed in hexane. The CsPbI₃ product was isolated directly from the ODE by centrifuge, and re-dispersed in hexane.

Absorbance measurements were performed using a JASCO V670 UV-VIS-NIR spectrophotometer.

Photoluminescence (PL) was measured using a Varian Cary Eclipse Fluorescence spectrophotometer.

High resolution transmission electron microscopy (HR-TEM) and electron diffraction measurements were performed using a Tecnai F20 G2 operated at 200kV.

PL Quantum yield- (PL-QY) was measured using a Hamamatsu Quantaurus-QY system.

X-ray diffraction: X-ray diffraction measurements were performed using the D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) with a secondary graphite monochromator, 2° Soller slits and a 0.2 mm receiving slit. XRD patterns within the range 5° to 60° 2θ were recorded at room temperature using CuKα radiation (λ=1.5418 Å) with the following measurement conditions: a tube voltage of 40 kV, a tube current of 40 mA, step-scan mode with a step size of 0.02° 2θ and a counting time of 1–3 s per step. At the GIXRD (grazing incidence X-ray diffraction), the value of the grazing incidence angle was 2.5°.
Results and Discussion

In this work we performed a detailed investigation of the impact of growth duration on product size distribution in the synthesis of all-inorganic perovskite NPs in the form of: CsPbX$_3$ where X=Br or I. Four different growth durations were studied: 1 seconds, 4 seconds, 20 seconds and 40 seconds. We decided to study these growth durations based on a previous observation$^4$ that the majority of growth of the Cs lead halide NPs occurs within the first 1-3 seconds, such that we could analyze the distribution focusing and defocusing beyond the main growth stage, between 1 and 40 seconds.

First we synthesized CsPbBr$_3$ NPs over four different growth durations: 1 sec, 4 sec, 20 sec and 40 sec. The absorbance and photoluminescence (PL) of all products exhibit similar absorbance onset in the range of 515 nm-522 nm and sharp photoluminescence peak in the range of at 515 nm-525 nm (depends on their size) with Full Width Half Maximum (FWHM) of 20 nm and PL-QYs of 60%. Figure 1A shows the absorbance and PL of CsPbBr$_3$ NPs with growth duration of 4 sec compared to the absorbance of bulk CsPbBr$_3$ deposited by a one-step process$^9$ on the substrate (the absorbance and PL of products of the other growth durations are shown in figure 1S). It can be observed that the absorbance spectra of the NPs is more pronounced than the absorbance spectra of the bulk, due to the quantum size effect in these NPs, as reported earlier$^4$. The electron diffraction pattern of the CsPbBr$_3$ NPs is presented in figure 1B and the corresponding diffraction derived d-spacing is shown in figure 2A. The d-spacing match the cubic structure of CsPbBr$_3$. The XRD of the CsPbBr$_3$ NPs is presented in figure 2B further support the cubic structure.

![Graph A](image1.png)

Figure 1: (A) Absorption and photoluminescence spectra of CsPbBr$_3$, bulk and NP at 4 sec growth time. (B) Electron diffraction pattern of CsPbBr$_3$ NPs.
Figure 2: (A) d-spacing of CsPbBr₃ NPs obtained from electron diffraction and corresponding crystal planes. (B) X-ray Diffraction spectra of CsPbBr₃.

Figure 3 shows the growth duration variations between 1 and 40 seconds while all other synthesis parameters were held constant. The different growth durations yielded cubic CsPbBr₃ NPs with an average side length of 9.0nm for 1 second growth, 9.6nm for 4 seconds growth, 8.4nm for 20 seconds and 9.3nm for 40 seconds growth. HR-TEM measurements can be observed in figure 2A-2D, presenting the CsPbBr₃ NPs of different growth durations and the corresponding size distribution histograms (figure 2E-2H). (The size distribution histograms were calculated from data obtained using ImageJ software, the typical analysis population being 2000 NPs) It can be seen that the FWHM of the size distributions increase with the growth duration, implying a de-focusing process (Ostwald ripening), as will be discussed below.
**Figure 3:** HR-TEM images of CsPbBr$_3$ NPs allowed to grow for (A) 1 seconds, (B) 4 seconds, (C) 20 seconds, (D) 40 seconds. Inset- HR-TEM of a single NP. Normalized size distribution histograms for NP populations of each growth time; (E) 1 seconds, (F) 4 seconds, (G) 20 seconds, (H) 40 seconds. FWHM of the size distributions is indicated.

In order to further study the variation in size distribution of the Cs lead halide NPs, we synthesized CsPbI$_3$ NPs over four different growth durations: 1 sec, 4 sec, 20 sec and 40 sec. The absorbance and photoluminescence (PL) of all products exhibit similar absorbance onset in the range of 695 nm -705 nm and sharp photoluminescence peak in the range of at 684 nm-695 nm (depends on their size) with FWHM of 37nm and PL-QY in the range of 75-77%. Figure 4A shows the absorbance and PL of CsPbI$_3$ NPs with growth duration of 4 sec (the absorbance and PL of products of the other growth durations are shown in figure 2S). HR-TEM of a CsPbI$_3$ NP with lattice fringes is shown in figure 4B, corresponding to the (1,1,0) crystallographic plane. Analyzing the electron diffraction (figure 4B inset) provides the d-spacing which corresponds to the cubic crystal form of CsPbI$_3$, as detailed in figure 5A. The XRD of the CsPbI$_3$ NPs is presented in figure 5B further support the cubic structure.

![Figure 4](image)

**Figure 4:** (A) Absorption and photoluminescence spectra of CsPbI$_3$ NPs. (B) HR-TEM image of a particle with distinct lattice fringes and inset of electron diffraction pattern.
**Figure 5:** (A) d-spacing of CsPbI$_3$ and corresponding crystal planes; (B) X-ray Diffraction spectra of CsPbI$_3$, the XRD peaks are matching the crystallographic planes reported in ref.$^{10,11}$. 

Figure 6 shows the growth duration variations between 1 and 40 seconds while all other synthesis parameters were held constant. The different growth durations yielded cubic CsPbI$_3$ NPs with an average side length of 13.40nm for 1 second growth, 10.5nm for 4 seconds growth, 7.5nm for 20 seconds growth and 13.46nm for 40 seconds. HR-TEM measurements can be observed in figure 6A-6D, presenting the CsPbI$_3$ NPs at different growth durations and the corresponding size distribution histograms (figure 6E-6H). (Analysis was performed using ImageJ software.)

It can be seen that the FWHM decreases over 4 seconds and 20 seconds of growth, and increases again over 40 seconds of growth, implying de-focusing followed by focusing, followed by focusing, followed by de-focusing as will be discussed below.
Figure 6: HR-TEM images of CsPbI$_3$ NPs allowed to grow time of (A) 1 seconds, (B) 4 seconds, (C) 20 seconds, (D) 40 seconds. Inset- HR-TEM of single CsPbI$_3$ NP at the different growth time. Normalized size distribution histograms for NP populations of each growth time (E) 1 seconds, (F) 4 seconds, (G) 20 seconds, (H) 40 seconds. FWHM of the size distributions is indicated.

As indicated above, in the case of CsPbBr$_3$, we observe a widening of the size distribution between $t=1$ second and $t=40$ seconds of growth duration, however in the case of CsPbI$_3$, we observe first a narrowing of the size distribution between 1 and 20 seconds growth duration, and then a widening of the size distribution between 20 and 40 seconds.

It is expected that a burst of nucleation is followed first by a phase of distribution narrowing (focusing), and then by a second phase of distribution widening (de-focusing). The nucleation burst results in most particles being of similar size in an environment of high monomer concentration. (Monomer concentration is important because it is inversely related to the critical radius.) Initially, particles smaller than the critical radius dissolve into the existing pool of monomers, while particles above the critical radius grow with a rate depending on their size: particles only slightly larger than the critical radius grow faster, while ones relatively larger grow slower. Since particles close to the critical radius grow fastest, they "catch up" to the larger particles, bringing more of the particle population into the same size range, narrowing the distribution$^{12}$. The size dependent growth rate is depicted graphically in figure 7.
When monomer concentration is depleted as a result of growth (monomers leave solution as they add on to growing particles), the critical radius increases past the average size. In that case, a large fraction of the population is now below the critical radius and dissolving, their monomers adding on to larger, growing particles. During focusing, most particles were growing at a rate that allowed them to catch up in size to the larger particles. During de-focusing, most particles are shrinking/disappearing while some are growing, broadening the distribution. (Also named as Ostwald ripening) The formation of small particles is kinetically favored, while large particles are thermodynamically favored. However small particles have larger surface to volume ratio than large particles. When looking at the molecules on the surface of the particle they are energetically less stable than the molecules in the interior of the particle. Therefore small particles will attain a lower energy state if they will transform to large particles as happened in Ostwald ripening.

A schematic illustration of the focusing and de-focusing processes is illustrated in figure 8. In the case of CsPbI₃, we observed a moment of focusing at t= 20 seconds growth duration (stage 2 in figure 6), and subsequent defocusing at t= 40 seconds growth duration (stage 4 in figure 8). In the case of CsPbBr₃, only distribution widening (de-focusing) is observed (Stages 3 and 4 in figure 8).

The main reason for the difference in the focusing/de-focusing processes between these two perovskites (e.g. CsPbI₃ and CsPbBr₃) is related to the monomer concentrations. As stated earlier the monomer concentration is inversely proportional to the critical radius. The majority of

**Figure 7:** The size dependent growth rate. $r^*$ - critical radius. Reprinted with permission from reference 12.
growth of the Cs lead halide NPs occurs within the first 1-3 seconds, such that the growth after the first 3 seconds is mainly limited by the diffusion of the monomers. Previous reports show that the diffusion coefficient of Br is larger than the diffusion coefficient of I.\textsuperscript{13} In addition, the synthesis temperature of the CsPbBr\textsubscript{3} NPs was higher (170\textdegree C) than the synthesis temperature of CsPbI\textsubscript{3} (145\textdegree C), which also suggests faster diffusion of the monomers. Therefore it is assumed that after 4 seconds of growth the monomer concentration is more depleted in the case of CsPbBr\textsubscript{3} than in the case of CsPbI\textsubscript{3}, which increases the critical radius and results in de-focusing of the population.

**Figure 8:** Schematic illustration of the focusing and de-focusing processes. At stage 1, the reaction flask has a large population of mode-sized particles relative to that of smaller and larger particles, and monomer concentration is high. Small particles below the critical radius dissolve into the pool of monomers while mode-sized particles grow fast, resulting in focusing (stage 2). When monomer concentration is depleted due to growth, the critical radius is increased and mode-sized particles begin to dissolve, while the small population of large particles continues to grow, resulting in defocusing (stage 3). Over time, particles below the critical radius progressively dissolve while large particles progressively grow, accentuating the positive skew (stage 4).

**Conclusions**

In this work we investigated the kinetics of CsPbX\textsubscript{3} (where X=Br or I) NPs as their growth durations were varied by tracking the focusing and de-focusing of the NPs size distribution. In the case of CsPbI\textsubscript{3}, focusing of the size distribution was observed after 20 seconds of growth duration, while further increasing the growth duration results in de-focusing of the size distribution. In the case of CsPbBr\textsubscript{3}, no focusing of the size distribution was observed. The main reason for that is related to the monomer concentration, which is depleted faster in the case of
CsPbBr$_3$ than in the case of CsPbI$_3$, increasing the critical radius and resulting in de-focusing of the population. To conclude, narrow size distribution could be achieved by choosing the appropriate growth time in the case of CsPbI$_3$, while higher monomer concentration is probably beneficial in the case of CsPbBr$_3$ in order to have narrow size distribution. Understanding the kinetics of these attractive NPs is critical for future use of them in optoelectronic applications.

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