Low-Temperature Electron Beam-Induced Transformations of Cesium Lead Halide Perovskite Nanocrystals

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ABSTRACT: Cesium lead halide perovskite (CsPbX₃, with X = Br, Cl, I) nanocrystals have been found to undergo severe modifications under the high-energy electron beam irradiation of a transmission electron microscope (80/200 keV). In particular, in our previous work, together with halogen desorption, Pb²⁺ ions were found to be reduced to Pb⁰ and then diffused to form lead nanoparticles at temperatures above −40 °C. Here, we present a detailed irradiation study of CsPbBr₃ nanocrystals at temperatures below −40 °C, a range in which the diffusion of Pb⁰ atoms/clusters is drastically suppressed. Under these conditions, the irradiation instead induces the nucleation of randomly oriented CsBr, CsPb, and PbBr₂ crystalline domains. In addition to the Br desorption, which accompanies Pb²⁺ reduction at all the temperatures, Br is also desorbed from the CsBr and PbBr₂ domains at low temperatures, leading to a more pronounced Br loss, thus the final products are mainly composed of Cs and Pb. The overall transformation involves the creation of voids, which coalesce upon further exposure, as demonstrated in both nanosheets and nanocuboids. Our results show that although low temperatures hinder the formation of Pb nanoparticles in CsPbBr₃ nanocrystals when irradiated, the nanocrystals are nevertheless unstable. Consequently, we suggest that an optimum combination of temperature range, electron energy, and dose rate needs to be carefully chosen for the characterization of halide perovskite nanocrystals to minimize both the Pb nanoparticle formation and the structural decomposition.

INTRODUCTION

Research interest in lead halide perovskites, with the chemical formula APbX₃ (with A⁺ = CH₃NH₃⁺, NH₂CH=NH⁺, Cs⁺, and X⁻ = Cl⁻, Br⁻, I⁻), has surged exponentially over the last few years due to their remarkable performance in both photovoltaics¹–³ and optoelectronics.⁴–⁵ However, halide perovskites are known to undergo rapid degradation under irradiation from several sources (UV and visible light, X-rays, electrons), heating, or exposure to moisture.⁶–¹² In a recent work from our group, we studied the electron beam-induced transformations of CsPbX₃ nanocrystals,¹³ by means of in situ transmission electron microscopy (TEM), and found that high-energy (80–200 keV) electron irradiation induces a radiolysis process in which both the halogen desorption and Pb²⁺ reduction to Pb⁰ occur. Our results were similar to those of the previous works that reported electron-stimulated desorption processes.¹⁴–¹⁷ We found that two factors, the incident electron energy and the substrate temperature, are important in the transformation process of CsPbX₃ nanocrystals: (i) 200 keV electrons induce less damage than 80 keV electrons and (ii) the rate at which the Pb⁰ species aggregate into Pb nanoparticles depends on the temperature. Finally, no Pb nanoparticles were observed below −40 °C.¹³

In the present study, we focus on the electron beam-induced transformations in CsPbBr₃ nanocrystals at T ≤ −40 °C, with an incident electron energy of 200 keV. We demonstrate that the electron beam induces the decomposition of CsPbBr₃ and the nucleation of crystalline domains of various compositions and phases, including CsBr, CsPb, and PbBr₂. The CsBr and PbBr₂ domains are unstable under irradiation. It is known that in alkali halides (e.g., CsBr), stimulated halogen desorption can be induced by UV laser,¹⁸ electron,¹⁹,²⁰ or ion irradiation.²¹ Halogen loss also occurs for PbX₂ under light and electron irradiation.²²,²³ In the present CsPbBr₃ nanocrystals, in addition to the Br loss accompanying Pb²⁺ reduction, electron irradiation induces the desorption of Br from the CsBr and PbBr₂ domains. These two combined processes result in an exceptionally high Br...
loss at low temperatures. Our data show that the CsPbBr₃ nanocrystals are unstable even when irradiated at low temperatures, that is, even if the formation of Pb nanoparticles is hindered under these conditions. These findings suggest that caution should be taken in the characterization of halide perovskites involving radiation sources even at low temperatures, and that an appropriate temperature range needs to be chosen for the specimen to minimize both Pb nanoparticle formation and structure decomposition. For instance, for 200 keV electrons in the dose rate range of 10⁶–10⁷ e⁻/Å²/s, the optimum temperature is −40 °C.

RESULTS AND DISCUSSION

We studied in detail the transformations induced in the CsPbBr₃ nanocrystals with two different morphologies, namely nanosheets (rectangular shaped, ~3 nm thick, with lateral sizes ranging from hundreds of nanometers up to a few micrometers) and nanocuboids (an edge length of 20–40 nm), to appreciate the possible effects of the surface-to-volume ratio, reported to affect the damage rate in our recent work. The details of the synthesis procedures are reported in the Experimental Section.

Electron Irradiation of CsPbBr₃ Nanosheets (Two-Dimensional (2D) Case).

High-angle annular dark-field scanning TEM (HAADF-STEM) images of a CsPbBr₃ nanosheet were acquired by increasing the electron dose, that is, increasing the exposure time with a fixed dose rate (see Figure 1).

To elucidate the nature of the nanometer-sized domains in the porous structure, the evolution of selected area electron diffraction (SAED) patterns from the nanosheets at increasing irradiation doses throughout the whole investigated temperature range were acquired and are summarized in Figure S2 of the SI. The results of these analyses indicate that, as long as the sample temperature was below −40 °C, the samples underwent similar transformations under irradiation.

The azimuthal integrations (Figure 2a) of four sequential SAED patterns (A–D in Figure 2b) of a single nanosheet at −120 °C show that the nanosheet loses its perovskite structure rapidly, with new diffraction peaks appearing. The comparison with the reference data from the ICSD database reveals that, among the new peaks (labeled in Figure 2a), peak 1 mainly arises from CsBr, peak 2 corresponds to CsPb, and peaks 3 and 4 result from both CsPb and PbBr₂. In particular, CsPb is an equiatomic semiconducting Zintl alloy, in which each Cs is tetrahedrally coordinated with a [Pb₄]⁴⁺ tetrahedral polyanion cluster, and the valence electrons of the Cs atoms are transferred to the lead clusters. The formation of CsPb likely arises from the bonding of the Pb₄ clusters with the surrounding Cs⁺ ions. This is because the Pb diffusion is drastically reduced below −40 °C, favoring the clustering process instead, with the formation of CsPb particles. In the studied temperature range, it is known that no phase transitions occur in CsBr, CsPb, and PbBr₂. The powder-diffraction X-ray diffraction data from the ICSD database for these three compounds, which were taken at room temperature (RT), are a good approximation of the crystal structure below −40 °C. (See more about the crystal structure of CsBr nanocrystals at different temperatures in Figure S3 of the SI.)

High-resolution TEM (HRTEM) analyses further confirmed the formation of CsPb, CsBr, and PbBr₂ domains (Figure 2c). Br and Pb atoms at the corners and edges of CsPbBr₃ nanosheets have a lower coordination, and their electronic configuration can be more easily altered by electron irradiation. As a result, the CsPb crystals appeared first at the edge of nanosheets and later in the inner regions (Figure 2c). The decomposition and recrystallization of CsPbBr₃ into these nanodomains is driven by the organization of the system into a more favorable state through the ionizing radiation-induced elemental diffusion. This type of behavior is not at all limited to CsPbBr₃ because various works on different materials have reported the decomposition and crystallization under electron irradiation from the starting single crystals into nanodomains. These nanodomains could have either the original composition and crystal structure of the initial crystal, or even different ones.

Among the new peaks appearing in Figure 2a, the intensity of the dominant peak from CsBr (peak 1) decreases when increasing the electron dose. This is due to the decomposition of the CsBr domains upon further electron irradiation (see Figure S4 of the SI). The instability of CsBr under electron irradiation at the same temperature and at the same level of electron irradiation was investigated with the experiments conducted on pure CsBr nanocrystals, for which the syntheses are found in the Experimental Section. These were found to turn into hollow particles under electron irradiation, accompanied by the loss of Br, with only the Cs species remaining. The reader is referred to Figures S5 and S6 for the structural evolution and electron-stimulated Br desorption from pure CsBr nanocrystals. The PbBr₂ domains are also not stable under further electron irradiation (see Figure S7 of the SI). Consequently, the Br loss from the CsPbBr₃ nanosheet below −40 °C was much more significant than at higher temperatures (such as −10 °C and RT),...
as demonstrated by the energy-dispersive X-ray spectrometry (EDS) study later in the article. Figure 3 reports the variation in Br concentration (in atom %) from the quantification of the EDS spectra obtained by increasing the electron dose on a single CsPbBr₃ nanosheet (see Figure S8 of the SI). The Br concentration decreased from 58% to 20% when the temperature was below −40 °C; for comparison, variations in the Br concentration at −10 °C and at RT are also shown in Figure 3: it is evident that the concentration remained around 58% in those cases.

One may argue that the decomposition may be due to electron beam induced contamination. In a TEM, the electron beam causes the formation of hydrocarbon ions by reacting with stray hydrocarbons in the path, which then condense into a carbon-rich polymerized film. The local decrease in temperature would accelerate this deposition of the contamination on top of the sample surface, which could help to increase the decomposition rate. However, in the present work, the presence of contaminants from the residual gas is strongly reduced by a liquid nitrogen−cooled cryogenic trap close to the objective polepieces. Moreover, the contamination is mostly removed by irradiating the sample at low magnification before the measurements (namely beam showering) via hydrocarbon cracking.²⁹ There-

Figure 2. Structural evolution of CsPbBr₃ nanosheets with increases in the electron dose at low temperatures. (a, b) SAED patterns (A−D) of a single nanosheet at −120 °C and their azimuthal integration compared with the reference cards for the orthorhombic CsPbBr₃ phase (ICSD: 97851), CsBr (ICSD: 236387), CsPb (ICSD: 627071), and PbBr₂ (ICSD: 202134). (c) Zoomed-in view of the white-boxed regions in high-resolution TEM (HRTEM) images (inset) performed on a corner region at −60 °C, showing the appearance of CsPb, CsBr, and PbBr₂ crystalline domains.

Figure 3. Br content (atom %) for a CsPbBr₃ nanosheet under an increasing electron dose at RT, −10, −60, −90, −120, and −160 °C, as evaluated by EDS.
fore, the acceleration of decomposition at lower temperatures is not likely contributed by the contaminants.

Overall, we conclude that under electron irradiation below $-40^\circ C$, the CsPbBr$_3$ nanosheets transformed into randomly oriented CsBr, PbBr$_2$, and CsPb domains. Subsequently, CsBr and PbBr$_2$ decomposed under further irradiation and resulted in a porous morphology.

**Electron Irradiation of CsPbBr$_3$ Nanocuboids (Three-Dimensional (3D) Case).** To generalize the above electron beam-induced transformation of CsPbBr$_3$ nanocrystals at low temperatures, we also conducted the same study on a different morphology. Figure 4a reports the evolution of CsPbBr$_3$ nanocuboids under electron irradiation at $-60^\circ C$, at which an interesting morphological change occurred. The CsPbBr$_3$ nanocuboids first became rounder due to the preferential Pb$^{2+}$ reduction and Br desorption occurring at the undercoordinated sites at the corners. Then, the nanocrystals transformed into hollow nanostructures under further irradiation. The transformation of nanocuboids at all of the temperatures below $-40^\circ C$ followed a similar path, as reported in Figure S9 in the SI. In analogy with the 2D case, CsBr, CsPb, and PbBr$_2$ domains were formed, which is shown in the zoomed-in view of several subsequently acquired HRTEM images of a CsPbBr$_3$ nanocuboid (Figure 4b). The HRTEM analysis indicated that the CsPbBr$_3$ nanocuboids were enclosed by the {001}, {110}, and {11̅0} facets with the orthorhombic phase (Figure S10). The models for various crystal structures involved were built using VESTA$^{30}$ and are shown in Figure 4c. In particular, the CsBr domain has an epitaxial relationship with the parent lattice in the CsPbBr$_3$ structure: CsBr (100)//CsPbBr$_3$ (200) and CsBr [01̅1]//CsPbBr$_3$ [001]. The models illustrate that the “reshaping” process of the nanocuboids is enabled by the formation of new crystalline domains. The effect is more noticeable in the 3D case than in the 2D case (nanosheets) due to the presence of extended surfaces in all of the three orthogonal directions in the 3D case. Similar to the 2D case, the overall elemental analysis of the nanocuboids indicates that, under electron irradiation below $-40^\circ C$, the Cs/Pb/Br ratio (atom %) changed from the initial stoichiometry (1:1:3) to 1:1:0.3, corresponding to a Br loss of as high as 90%.

A question may arise whether the different illumination conditions have different damage behaviors on the perovskite nanocrystals: HRTEM (wide-beam illumination) and STEM (scanning probe). The local dose in HRTEM conditions is lower, but the sample is under continuous exposure, whereas the local dose in the STEM is much higher, but the structure can relax before the probe reaches that point again. This is evaluated by observing the evolution of nanocuboids, which is reported in Figure S11 of the SI, under different illumination conditions. It is found that the nanocuboids evolve into hollow morphologies at low temperatures in all of the cases. However, a slight difference was observed: the hollow structure is round in shape in the STEM mode, whereas the edges of the hollow structure tends to be faceted in the HRTEM mode. This is because the electrons continuously impact on the sample in the HRTEM mode, and the decomposed products crystallize, which gives rise to the faceted edges.

At higher temperatures (i.e., RT), the nanocuboids with 20–40 nm edges experienced much less damage (i.e., Br loss) than the 3 nm thick nanosheets, whereas the damage at lower temperatures (below $-40^\circ C$) was equal for these two morphologies due to the hollowing process. A brief comparison

**Figure 4.** Evolution of CsPbBr$_3$ nanocuboids with increases in the electron dose at $-60^\circ C$. (a) HAADF-STEM images. (b) Zoomed-in view of the white-boxed region of the HRTEM images (inset) demonstrating the four domains formed on a CsPbBr$_3$ nanocuboid under irradiation (at the condition of imaging). (c) Crystal structure models of the initial perovskite structure and the four domains generated.
shows that the effect of surface-to-volume ratio of the perovskite nanocrystal does not play a relevant role with regards to the electron beam-induced damage at low temperatures.

**CONCLUSIONS**

In conclusion, the transformation process of CsPbBr₃ nanocrystals under electron beam irradiation at low temperatures reveals a very different scenario to that of the higher temperatures. The formation of Pb nanoparticles reaches a possible (final) stable stage at T > ~40 °C. However, at T ≤ ~40 °C, the decomposed products crystallize into several compounds under electron irradiation, including CsPb, PbBr₂, and CsBr, favored by the limited diffusion of Pb. Electron irradiation further causes the desorption of Br from the CsBr and PbBr₂ domains. The Br loss is consequently much more significant than in the high-temperature case. Voids are formed and coalesce, and finally give rise to porous and hollow morphologies, both in the 2D case (nanosheets) and the 3D case (nanocuboids). The present findings will most likely apply to other types of perovskite and perovskite-related materials.

**EXPERIMENTAL SECTION**

**Chemicals.** Cobalt(II) bromide (CoBr₂, 99%), cesium carbonate (Cs₂CO₃, reagentPlus, 99%), 1-octadecene (ODE, technical grade, 90%), oleylamine (OLAm, 70%), oleic acid (OLAc, 90%), and toluene (anhydrous, 99.8%) were purchased from Sigma-Aldrich. All of the chemicals were used without any further purification.

**Synthesis.** Rectangular CsPbBr₃ nanosheets ~3 nm thick, with lateral sizes ranging from hundreds of nanometers up to a few micrometers, were synthesized by a colloidal procedure reported elsewhere. CsPbBr₃ nanocuboids with an edge length of 20–40 nm were synthesized by a colloidal procedure similar to the one reported recently, with the difference being that the synthesis was performed at room temperature (RT). CsBr nanocrystals were synthesized by a colloidal approach in which 0.087 g CoBr₂ was dissolved in 2 mL ODE together with 1 mL OLAm and 1 mL OLAc at 100 °C. Then, after the complete solubilization of CoBr₂ salt, a 0.5 mL Cs-oleate solution (0.325 g Cs₂CO₃ dissolved in 5 mL oleic acid) was quickly injected. Five minutes later, the reaction mixture was cooled by immersing the flask in a water bath. After centrifugation, the supernatant was discarded and the particles were redispersed in toluene.

**Transmission Electron Microscopy (TEM).** The nanocrystals were deposited on an ultrathin carbon film supported on a holey carbon film coating 400 mesh TEM copper grids. The electron beam irradiation experiments were conducted in a 200 kV TEM (JEOL JEM-2200FS) equipped with a spherical aberration corrector (CEOS) for the objective lens and an in-column image filter (Ω-type). A Gatan cryotransfer holder (model 626) with liquid nitrogen cooling, equipped with a Model 900 Smartset cold stage controller, was used for observing the electron beam-induced transformation at different temperatures in the range of −180 °C < T < 25 °C. The use of a direct detection camera could significantly reduce the dose rate and slow down the damage process reported here, but the damage could not be removed completely. Because we aimed at observing the effect of irradiation, a CCD camera with 2048 × 2048 pixel (UltraScan 1000, Gatan Inc.) resolution was calibrated using the following method: acquire a TEM image of the STEM probe on UltraScan 1000, read the counts C (number of electrons per pixel in the acquisition dwell time) and pixel number N, probe current I is calculated by the equation

\[ I = \frac{CNt}{A} \]

With a spot size of 1.5 nm and a convergence semiangle of 16 mrad, the probe current is 68 pA (corresponding to a current density of 3.8 × 10⁷ A/cm²).

The probe current can be changed by selecting the spot size. On the basis of the probe current and irradiation time t and scan area A, the accumulated dose D is calculated using the equation

\[ D = \frac{It}{A} \]

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01009.

Evolution of morphologies and SAED patterns of CsPbBr₃ nanosheets under electron irradiation at various low temperatures, SAED of CsBr at various temperatures, evolution of CsBr domains and PbBr₂ domains on a CsPbBr₃ nanosheet under electron irradiation, evolution of pure CsBr nanocrystals under electron irradiation at ~60 °C, evolution of EDS spectra under electron irradiation at various temperatures, crystal structure and evolution of CsPbBr₃ nanocuboids at different temperatures, comparison of the evolution of CsPbBr₃ nanocuboids in HRTEM mode and STEM mode (PDF).

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The manuscript was written through contributions of all of the authors. All of the authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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