Temperature Dependent Study of Electron Beam-induced Transformation of Cesium Lead Halide Perovskite Nanocrystals

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Research interest on lead halide perovskites has surged exponentially in the last years, due to their remarkable performance in both photovoltaics and optoelectronics.[1] However, a major shortcoming of halide perovskites for application in devices is their rapid degradation under irradiation from several sources (light, X-rays, electrons), heating, or exposure to moisture.[2] Here we have studied the electron beam-induced transformations of CsPbBr₃ nanocrystals (in particular, 3 nm thick CsPbBr₃ nanosheets synthesized by a colloidal method[3]), by means of in-situ transmission electron microscopy (TEM), as shown in Figure 1(a). Two parameters play key role in the transformation process: incident electron energy (E₀) and substrate temperature (T).

Figure 1(b) reports compositional changes of the three elements of interest measured from EDS spectra at increasing irradiation times from scanning TEM (STEM) - energy-dispersive X-ray spectroscopy (EDS) analysis at E₀=80 keV and 200 keV. Upon irradiation, due to Br desorption, Br concentration decreases while Cs and Pb concentration increases. The results show that Br loss is more significant at E₀=80 keV than at 200 keV, indicating a radiolysis dominant process. In parallel with the Br loss, Pb²⁺ ions are reduced to Pb⁰ atoms. When T is high (above -40°C), the system stabilizes by the aggregation of Pb⁰ atoms into Pb nanoparticles (ICSD 96501, see high-resolution TEM (HRTEM) image in Figure 1(b)) at a rate that depends on the temperature (see high angular annular dark field (HAADF)- STEM images in Figure 1(c)). [4] This is similar to those of works that reported electron stimulated desorption processes and metal nanoparticle formation.[5] Meanwhile the locally Pb deficient perovskite structure becomes progressively amorphous, while the surrounding perovskite structure is maintained.

When T is below -40°C the Pb diffusion is drastically reduced, no Pb nanoparticles were visible; instead, the nanosheets turn porous under electron irradiation (see Figure 2(a)), losing the perovskite structure rapidly. New diffraction peaks appear, which correspond to CsBr (ICSD: 236387), CsPb (ICSD: 627071), and PbBr₂ (ICSD 202134) (see Figure 2(a, b)). Electron irradiation induced decomposition has been reported for various materials[6], for which the driving force is the reorganization of matter into a more favorable thermodynamic state[7]. PbBr₂ and CsBr domains further lose Br upon electron irradiation, leading to a higher Br loss at low temperatures (see Figure 2 (c)).

Our study further strengthens the understanding of the effect of electron beam irradiation on halide perovskites. The mechanism presented in this study governs the formation of high contrast particles observed in TEM images of lead halide perovskite, tin halide perovskite NCs, and other perovskite related materials such as CsPb₂Br₅, and it helps defining some precautions to follow. When dealing with halide perovskites characterization using electron microscopy, increasing the incident electron energy of the microscope can largely improve the stability of the sample. Low temperatures (below – 40 °C) hinder the formation of Pb nanoparticles in CsPbBr₃ nanocrystals when irradiated, the nanocrystals are nevertheless less stable than at higher temperatures (above – 40 °C) due to the high Br loss.
Figure 1. 3 nm thick CsPbBr$_3$ nanosheets under electron irradiation: (a) Schematics depicting an area being irradiated; (b) Atomic concentration (at.%) of Cs, Pb, Br versus electron irradiation time from quantitative EDS measurements at RT for both $E_0 = 80$ keV (open symbols) and 200 keV (solid symbols); (c) HRTEM of a Pb nanoparticle formed on CsPbBr$_3$ nanosheet (Scale bar: 2 nm, $E_0 = 200$ keV); (d) HAADF-STEM images at RT and 40 °C (Scale bar: 50 nm, $E_0 = 200$ keV).

Figure 2. Evolution of 3 nm thick CsPbBr$_3$ nanosheets under electron irradiation ($E_0 = 200$ keV): (a) HAADF-STEM images and selected area electron diffraction (SAED) at -90°C; (b) HRTEM performed on a corner region at -60°C, showing appearance of CsPb, CsBr and PbBr$_2$ crystalline domains; (c) Br concentration (at.%) with increasing electron dose at different temperatures.

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References: