Supplementary Materials

Electron-beam-induced degradation of halide-perovskiterelated semiconductor nanomaterials

Zhiya Dang (党志亚)^{1*}, Yuqing Luo (罗余庆)¹, Xue-Sen Wang (王学森)², Muhammad Imran³, and Pingqi Gao (高平奇) ^{1**}

¹ School of Materials, Sun Yat-sen University, Guangzhou, 510006, China

² Department of Physics, National University of Singapore, Singapore 117551, Singapore

³ Department of Nanochemistry, Istituto Italiano di Tecnologia, Via Morego 30, Genova 16163, Italy

*Corresponding author: dangzhy3@mail.sysu.edu.cn

**Corresponding author: gaopq3@mail.sysu.edu.cn

Synthesis of Cs₃CoCl₅ nanowires (NWs)

All syntheses were carried out in the air and without any pre-dried chemicals or solvents. $0.325~g~Cs_2CO_3$ was dissolved in 5~mL oleic acid (OA) by using a heat gun until all Cs_2CO_3 reacted with OA. In a typical synthesis, 0.4~mmol of $CoCl_2$ was dissolved in 2~mL ODE, 1~mL OA, and 1~mL oleylamine (OLA) in a 20~mL vial on a hotplate at 100~C. After complete dissolution of the halide precursors, $500~\mu L$ of CsOA was added to the solution at optimized temperature. After 5~minutes, the reaction mixture was slowly cooled to room temperature using a water bath. To collect the NWs, the solution was then centrifuged at 3800~rpm for 10~min. After centrifugation, the supernatant was discarded and the NWs were redispersed in 4~mL hexane or toluene.

2. Sample information

Table S1. The composition, morphology and size of the nanomaterials of all-inorganic halide perovskite-related compounds used in this study.

Composition	Morphology	Size	
		Edge-8 nm	
CsPbBr ₃	Nanocubes	Edge-20 nm	
	Nanosheets	Thickness-3 nm	
Cs ₄ PbBr ₆	Nanocrystals	Edge-50 nm	
Cs ₃ CoCl ₅	Nanowires	Width-5~8 nm	
Cs ₃ Bi ₂ I ₉	Nanocrystals	Edge- 8~12 nm	

3. The composition analysis of metal nanoparticle formation and Br desorption on CsPbBr3 nanocubes

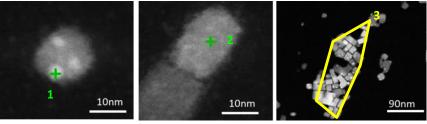


Fig. S1. HAADF-STEM images of three selected regions of interest containing CsPbBr₃ nanocubes for carrying out the EDS measurements and analysis

Fig. S1 shows HAADF-STEM images of three selected regions of interest containing CsPbBr₃ nanocubes. The EDS measurement is carried out at the two points labelled by green number "1" and "2" and the area enclosed by yellow line "3". The quantitative results are presented in Table S2. The point analysis carried out at the spot "1" located on a bright nanoparticle shows a Pb-rich composition, together with HRTEM results confirming that the content of the nanoparticles formed on the CsPbBr₃ nanocubes is Pb. The composition at point "2" is more Br-deficiency compared to area 3. This is because electron irradiation at such a high magnification in the region of interest "2" is more intensive, which causes a more severe Br loss.

Table S2. The composition results obtained from the EDS analysis of above regions of interest shown in Fig. S1

Sample	Dot (1)	Cube (2)	Multiple cubes (3)
Cs	18.3%±12.6%	22.9%±11.5%	18.3%±13.7%
Pb	33.3%±11.3%	23.7%±11.3%	20.2%±13.1%
Br	48.4%±6.3%	53.4%±5.3%	61.5%±6.6%

Fig. S2 shows the elemental mapping revealing the nature of Pb nanoparticles formed on the CsPbBr3 nanocubes.

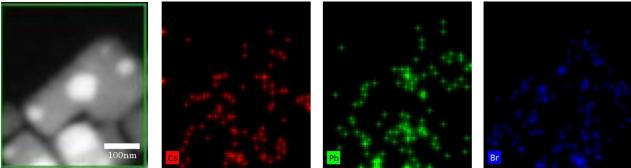


Fig. S2. Elemental maps of CsPbBr3 nanocubes under electron beam irradiation

Effect of incident electron energy

We measured and quantified the EDS spectra for two incident electron energies (E = 80 keV and 200 keV) with respect to the imaging time for the same electron dose rate of $2.0 \times 10^8 \text{ e} \cdot \text{A}^2 \text{s}^{-1}$. According to the bromine loss obtained from the EDS data in Fig. S2, a more significant compositional change is observed at a lower incident electron energy (Br atomic concentration (at.%) drops from 55% to 40% for 80 keV electrons) compared to that at a higher incident electron energy (from 57% to 52% for 200 keV). This result reveals that the overall process is dominated by radiolysis effect [1].

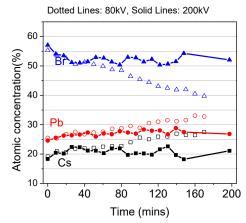


Fig. S3. Composition changes of 3 nm thick $CsPbBr_3$ nanosheet with prolonged irradiation at room temperature by incident electrons of energy of 80 keV and 200 keV (adapted from [2]).

References

1. R. F. Egerton, P. Li, and M. Malac, "Radiation damage in the TEM and SEM," Micron 35(6), 399-409 (2004).

Z. Dang, J. Shamsi, F. Palazon, M. Imran, Q. A. Akkerman, S. Park, G. Bertoni, M. Prato, R. Brescia, and L. Manna, "In Situ Transmission Electron Microscopy Study of Electron Beam-Induced Transformations in Colloidal Cesium Lead Halide Perovskite Nanocrystals," ACS Nano 11, 2124-2132 (2017).