Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Material

Localized Exciton Emission in $CsPbBr_3$ Nanocrystals synthesized with Excess Bromide Ions

Wenqiang Liu,[†,‡] Guodong Yuan,[,†,‡] Yang Zhang,[*,§] Qi Wang,[†,‡] Shuai Zhao,[†,‡] Zhiqiang Liu,[†,‡] Tongbo Wei,[†,‡] Junxi Wang,[†,‡] Jinmin Li[†,‡]*

†Center for Semiconductor Lighting, Institute of Semiconductors, Chinese Academy of Sciences, State Key Laboratory of Solid State Lighting, Beijing Engineering Research Center for the 3rd Generation Semiconductor Materials and Application, Beijing 100083, P. R. China

‡Center of Materials Science and Optoelectronics Engineering , University of Chinese Academy of Sciences, Beijing 100049, P. R. China

§ Department of Physics, Henan University, Kaifeng, Henan 475004, P. R. China

X-ray Photoelectron Spectroscopy (XPS) measurements of $CsPbBr_3$ perovskite nanocrystals (NCs)

To determine the molar ratios of elements in $CsPbBr_3$ perovskite NCs, XPS investigations were carried out. Full survey XPS spectra of $CsPbBr_3$ perovskite NCs were obtained with different Br/Pb molar ratios of 3.0, 3.6, and 4.5 in starting solutions. Figure S1 shows the full survey XPS spectra of $CsPbBr_3$ perovskite NCs obtained with Br/Pb molar ratios of 3.0, 3.6, 4.5 in starting solutions, corresponding to samples 1#, 2#, 3#, respectively. It can be seen that the characteristic peaks of Cs, Pb and Br in all samples. The peak at 285 eV is attributed to C 1s due to the pollen templates.

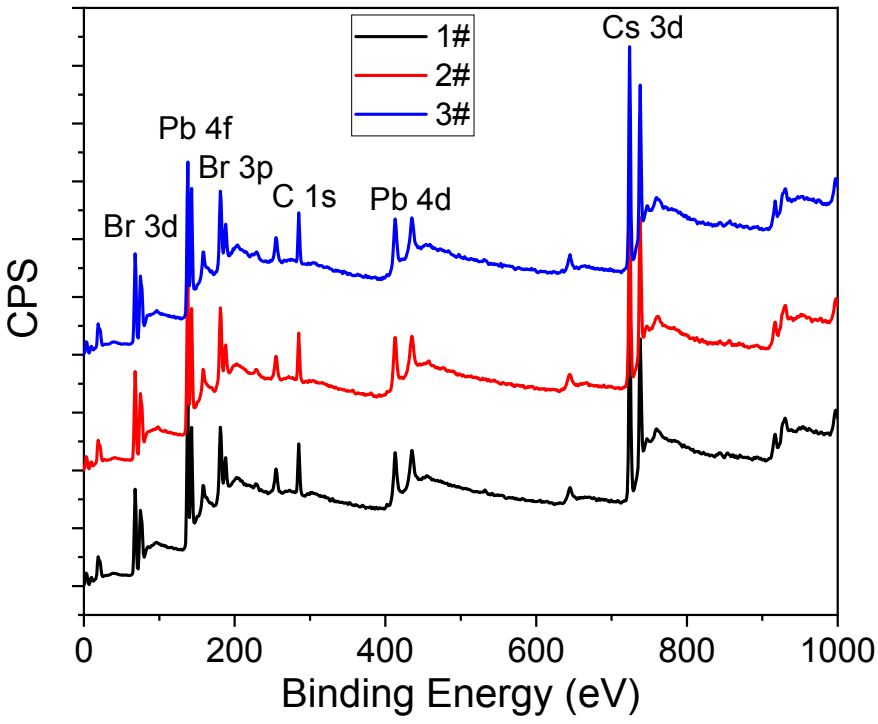

Figure. S1. Full scan survey XPS spectra of $CsPbBr_3$ perovskite NCs obtained with different Br/Pb molar ratios of 3.0/1 (sample 1#), 3.6/1 (sample 2#), 4.5/1 (sample 3#) in starting solutions.

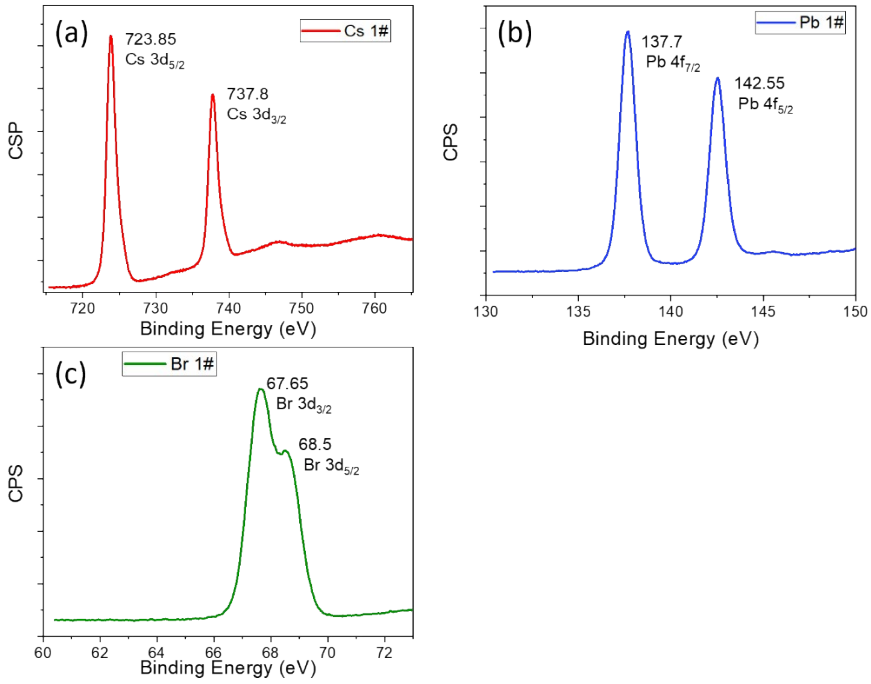

Figure S2. High-resolution XPS spectra of the Cs 3d (a), Pb 4f (b), and Br 3d (c) signals for sample 1# (Br/Pb molar ratio of 3.0/1).

To further investigate the quality and composition, high-resolution XPS spectra of the Cs 3d (a), Pb 4f (b), and Br 3d (c) signals for sample 1# obtained with Br/Pb molar ratio of 3.0/1 in starting solution, as shown in Figure S2. Figure S2 (a) shows the two peaks at 723.85 eV and 737.8 eV, corresponding to Cs 3d5/2 and Cs 3d3/2. The two peaks at 137.7 eV and 142.55 eV in Figure S2 (b) are attributed to the Pb 4f7/2 and Pb 4f5/2. The peak at 138.8 eV attributed to Pb 4f7/2 in $PbBr_2$ is not observed, indicating that there are no $PbBr_2$ from starting reactant in the as-prepared $CsPbBr_3$ NCs.[1] That is, there is no residue of the reactant of $PbBr_2$. In Figure S2 (c), there are two peaks at 67.65 eV and 68.5 eV, originating from Br 3d3/2 and Br 3d5/2, respectively. There is

no characteristic peak at 66.8 eV corresponding to the Br 3d3/2 in CsBr.[2] This result indicates that there is no residue of the reactant of CsBr. Therefore, there are no residue of the reactants of $PbBr_2$ and CsBr in the as-prepared $CsPbBr_3$ NCs. On the other hand, the relative atomic amounts in the as-prepared $CsPbBr_3$ NCs are estimated according to the relative area ratios of different atomic characteristic peaks and their relative sensitivity factors, using the following empirical formula.

$$n_i = \frac{I_i/S_i}{\sum T_i I_i/S_i}$$

where I is the peak area, S is atomic sensitivity factor, T is analyzer transmission efficiency. Casa XPS software was used for detailed data processing. A ratio of Cs, Pb and Br of sample 1# is roughly 1:0.98:3.01 (±0.05% due to peak area uncertainty).

For sample 2# obtained with Br/Pb molar ratio of 3.6/1 in starting solution, high-resolution XPS spectra of the Cs 3d, Pb 4f, and Br 3d are shown in Figure S3. In Figure S3 (a), the two peaks at 723.75 eV and 737.7 eV, corresponding to Cs 3d5/2 and Cs 3d3/2 are observed. In Figure S3 (b) two characteristic peaks attributed to Pb 4f7/2 and Pb 4f5/2 are at 137.65 eV and 142.5 eV. There is no peak at 138.8 eV due to Pb 4f7/2 in $PbBr_2$. In Figure S3 (c), two peaks at 67.65 eV and 68.4 eV are attributed to Br 3d3/2 and Br 3d5/2, respectively. There is also no characteristic peak at 66.8 eV of Br 3d3/2 in CsBr. Therefore, there is also no residue of the reactant of CsBr. It can be concluded that there are no residue of the reactants of $PbBr_2$ and CsBr in sample 2#. The relative atomic amounts in sample 2# are calculated with Casa XPS software. A ratio of Cs, Pb and Br of sample 2# is about 1:0.98:3.03 (±0.05% due to peak area uncertainty). In contrast, the percent value of the relative atomic of Br in sample 2# is greater than that

of in sample 1#.

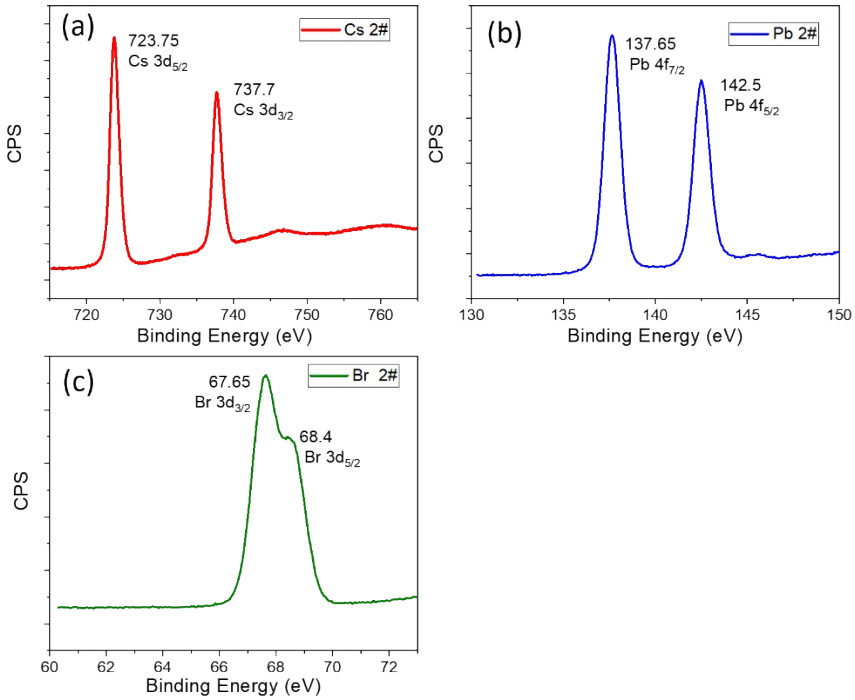

Figure S3. High-resolution XPS spectra of the Cs 3d (a), Pb 4f (b), and Br 3d (c) signals for sample 2# (Br/Pb molar ratio of 3.6/1).

For sample 3# prepared by Br/Pb molar ratio of 4.5/1 in starting solution, high-resolution XPS spectra of the Cs 3d, Pb 4f, and Br 3d are shown in Figure S4. In Figure S4 (a), the two characteristic peaks corresponding to Cs 3d5/2 and Cs 3d3/2 are at 723.8 eV and 737.8 eV, respectively. In Figure 4S (b) two characteristic peaks attributed to Pb 4f7/2 and Pb 4f5/2 are located at 137.7 eV and 142.55 eV. Meanwhile, there is also no peak at 138.8 eV from Pb 4f7/2 in $PbBr_2$. In Figure S4 (c), two characteristic peaks are located at 67.65 eV and 68.55 eV of Br 3d3/2 and Br 3d5/2, respectively. No characteristic peak at 66.8 eV of Br 3d3/2 in CsBr is visible. That is, there is also no residue of the reactant of CsBr. There are no residue of the reactants of $PbBr_2$ and CsBr

in sample 3#. The relative atomic amounts in sample 3# are also calculated with Casa XPS software. A ratio of Cs, Pb and Br of sample 3# is about 1.01:0.98:3.06 (±0.05% due to peak area uncertainty). Compared with samples 1# and 2#, the percentage of the relative atomic of Br in sample 2# is the greatest among all samples. However, the obtained atomic ratios in three samples are close to the ideal Cs:Pb:Br atomic ratio of 1:1:3. In other words, the crystal structure of $CsPbBr_3$ does not change with the increase in Br contents in samples 2# and 3#. This result is in agreement with XRD data (as shown in Figure 1a in manuscript).

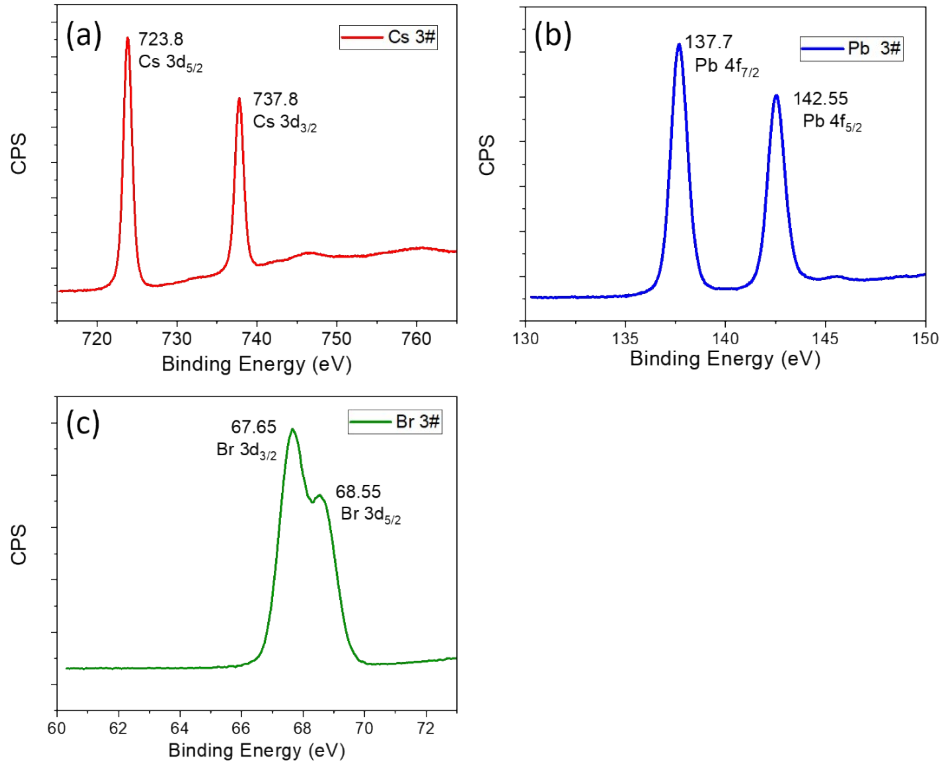

Figure S4. High-resolution XPS spectra of the Cs 3d (a), Pb 4f (b), and Br 3d (c) signals for sample 3# (Br/Pb molar ratio of 4.5/1).

References

S1 L.R. Pederson, *J Electron Spectrosc Relat Phenom*, 1982, **28**, 203-209.

S2 M Kamada, O Aita, K Ichikawa, M Okusawa, K Tsutsumi, *Phys. Rev. B*, 1992, **45**, 12725.