Supporting Information for

Atomic-Scale Visualization of Metallic Lead Leak Related Fine Structure in $CsPbBr_3$ Quantum Dots

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Experimental Methods：

Nanocrystal Growth. $CsPbBr_3$ nanocrystals were synthesized using a hot-injection technique, as described by Protesescu et al[1]. ODE (5 mL) and $PbBr_2$ (0.069g, ABCR, 98%) were loaded into 25 mL 3-neck flask and dried under vacuum for 1h at 120 ºC. Dried oleylamine (0.5S2mL, OLA, Acros 80-90%) and dried OA (0.5 mL) were injected at 120 ºC under N_2. After complete solubilization of a PbX_2 salt, the temperature was raised to 140-200 ºC (for tuning the NC size) and Cs-oleate solution (0.4 mL, 0.125 M in ODE, prepared as described above) was quickly injected and, 5s later, the reaction mixture was cooled by the ice-water bath.

TEM sample preparation. The nanocrystals were deposited on a carbon support TEM grid by drop casting. The grids were pretreated by plasma cleaning in vacuum to remove surface impurities prior to STEM experiments before drop casting. The $CsPbBr_3$ quantum dots were dispersed in the toluene after hot-injection synthesis. The concentration of the quantum dots solution is 10mg/ml. Before drop casting, in order to make the quantum dots form a single

layer arrangement on the carbon film to facilitate electron microscopy capturing, we diluted the quantum dots solution ten times to 1mg/ml. Then we dropped casting two drops of 0.02 ml per drop each time on the ultra-thin carbon film covered copper grid with. Before the TEM characterization, we store the copper grid in the drying oven with steady temperature and humidity (20℃, humidity of 20%).

STEM Characterization. The STEM experiments were carried out using the aberration-corrected (equipped with fifth-order aberration corrector) JEOL GRANDARM 300F (operated at 300 kV). Gaussian blurring was used to smooth out the HAADF images to accurately determine the position of the respective atomic columns. Given the average size of the QDs is around 100nm, we set the electron accelerating voltage at 300 KV to get the best spatial resolution with TEM and STEM imaging. To minimize the radiolysis and radiation damage caused by the high-energy electron beam, the imaging beam is set at the lowest dose rate (10C for STEM imaging, $2e/Å^2s$ for TEM imaging). The overall incident electron beam dose is controlled below $30e/Å^2$ with low dose rate and limited imaging exposure time.

In-situ CL experiment. In-situ CL spectroscopy analysis was carried out using a Gatan Vulcan CL holder. Nano-CL experiments were performed on a JEOL GRAND ARM300F microscope equipped with a Gatan Vulcan CL system. The microscope operated at an accelerating voltage of 80kV with a probe current of ~200pA. The temperature of the sample in the Vulcan holder was set at ~ -170 °C. The incident electron beam of the microscope was then converged to 0.14 nm with a convergence angle ~ 18 mrad with 30um condenser lens aperture to scan the sample and stimulate the CL signal. Miniature elliptical mirrors were positioned above and below the specimen to provide a light collection angle of up to 7.2 sr. All CL spectra were acquired in 300s using a Gatan Vulcan cathodoluminescence detector. All data were collected and analyzed using Digital Micrograph.

PL experiment. The PL experiment was carried out in a spectrometer outside the electron microscope. A 50/50 nonpolarizing beam splitter was used to reflect the pulse beam into the

microscope objective (100X, NA=0.8). A series of neutral density filters were used to adjust the pulse beam's average power to about 2mW onto the $CsPbBr_3$ quantum dots. The excited PL signal was selected with a 750nm short pass filter and then guided into a spectrometer.

Computational Details. The first-principles modeling was based on DFT, as implemented in the Vienna Ab initio Simulation Package.[2] The Perdew–Burke–Ernzerhof exchange-correlation functional was used.[3] The plane-wave energy cutoff was set to 400 eV and the projector augmented wave method[4] was utilized with the following potentials: Cs_sv($5s^2 5p^6 6s^1$) for Cs, Pb_d($5d^{10} 6s^2 6p^2$) for Pb, and Br($4s^2 4p^5$) for Br. The orthorhombic structure of $CsPbBr_3$ as confirmed for its nanocrystals was adopted.[22] The supercell size of the phase boundary was about 11.9 × 49.6 × 35.8 $Å^3$. The Brillouin zone was sampled using Monkhorst–Pack k-points grid of 2 × 1 × 1 for the phase boundary. Two atomic layers parallel to the planar defect were fixed to their bulk positions to simulate the internal region of grains, while the remaining atoms were relaxed till the force on each atom is less than 0.02eV $Å^{-1}$.

Supplementary Figures

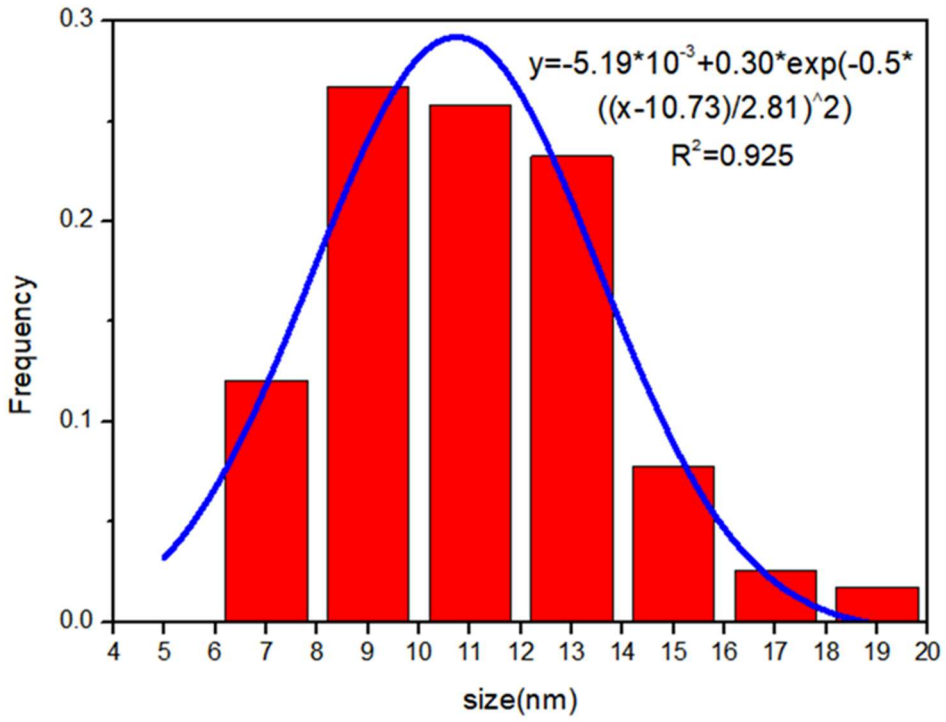

Fig. S1 Size distribution of the $CsPbBr_3$ quantum dots and its Gaussian fitting curve.

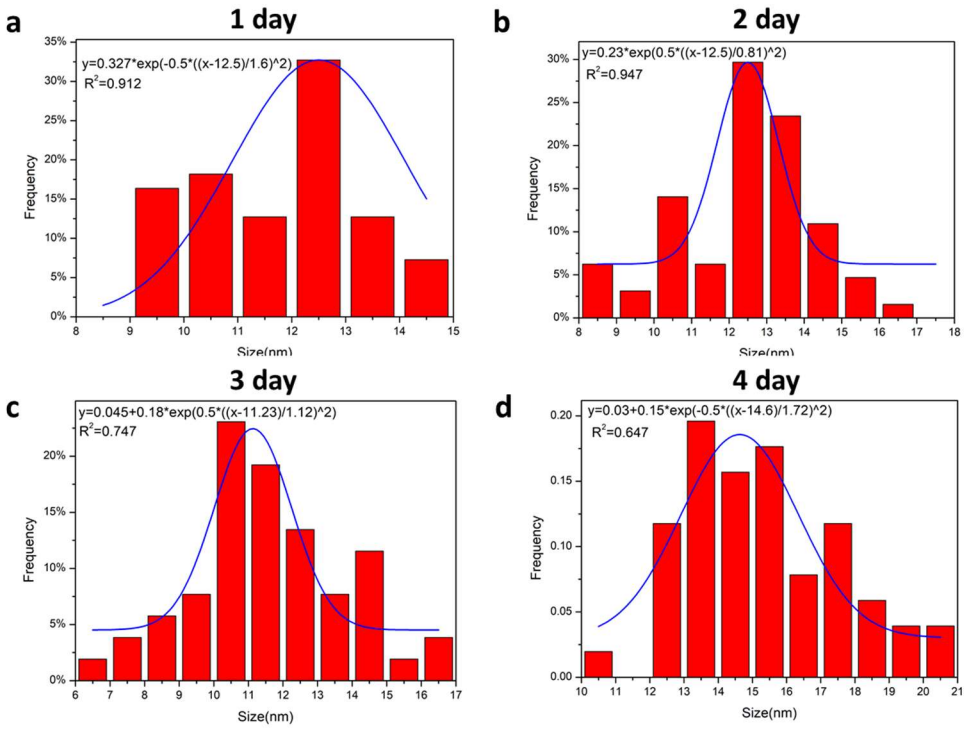

Fig. S2 Size distributions of the $CsPbBr_3$ quantum dots over storage time and the corresponding Gaussian fitting curves.

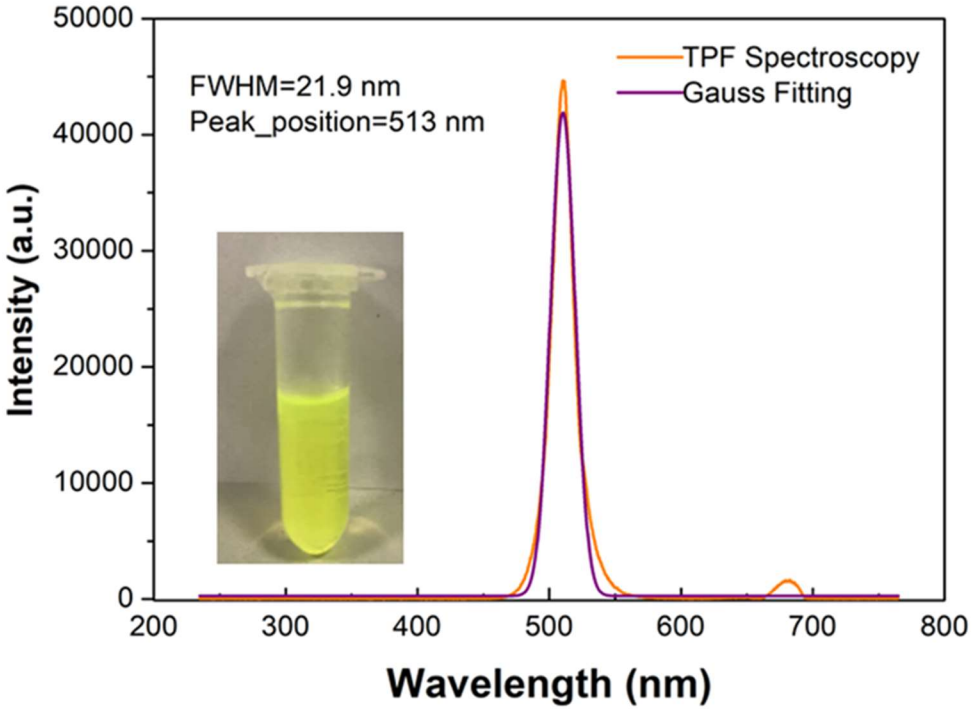

Fig. S3 Two-photon PL spectra of $CsPbBr_3$ and its Gaussian fitting curve.

Total	Mean	Standard Deviation	Sum	Minimum	Median	Maximum
30	1.052	0.0742	30.36	0.89	1.01	1.19

Table S1 Intensity ratio between A, B site of RP phase perovskite.

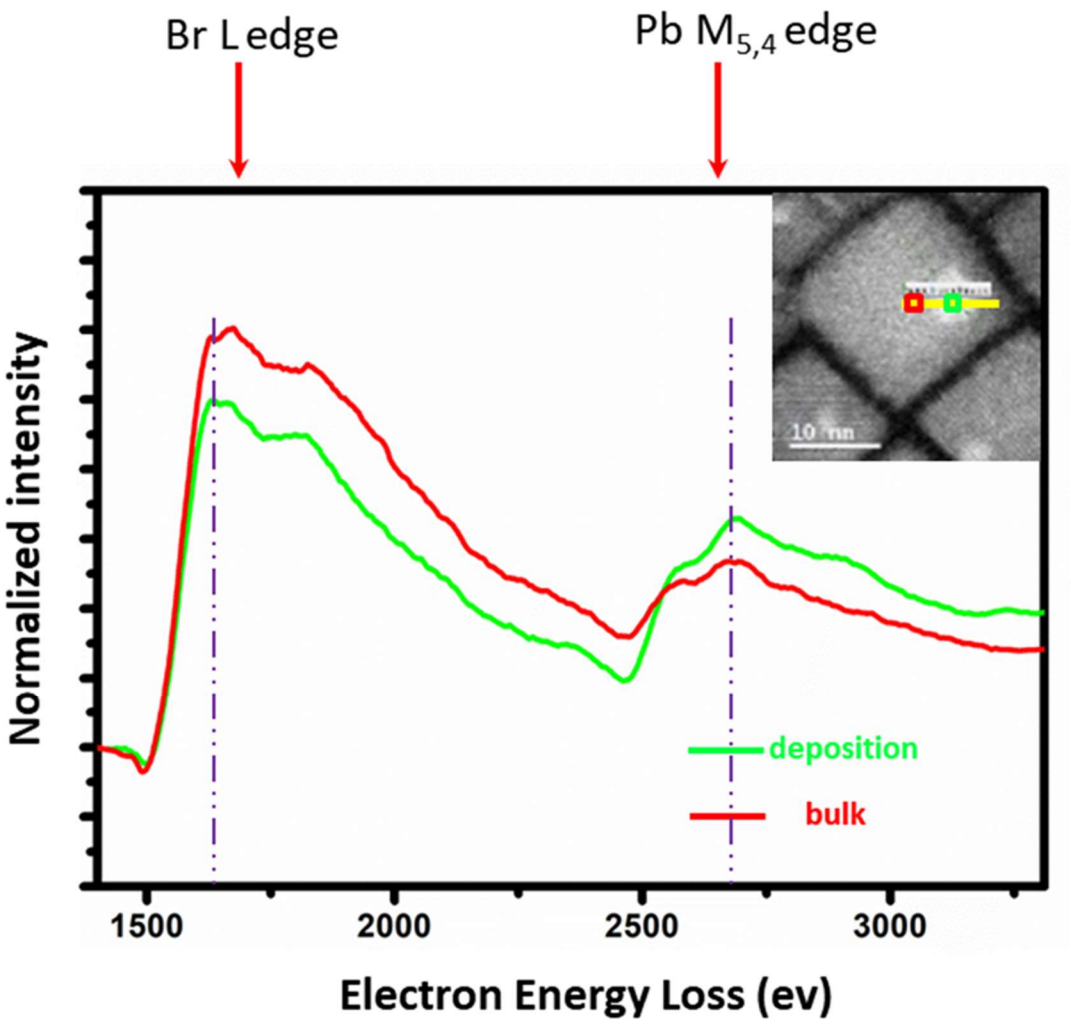

Fig.S4 STEM-EELS of the Br edges and the Pb-$M_{5,4}$ edges for the $CsPbBr_3$ QDs.

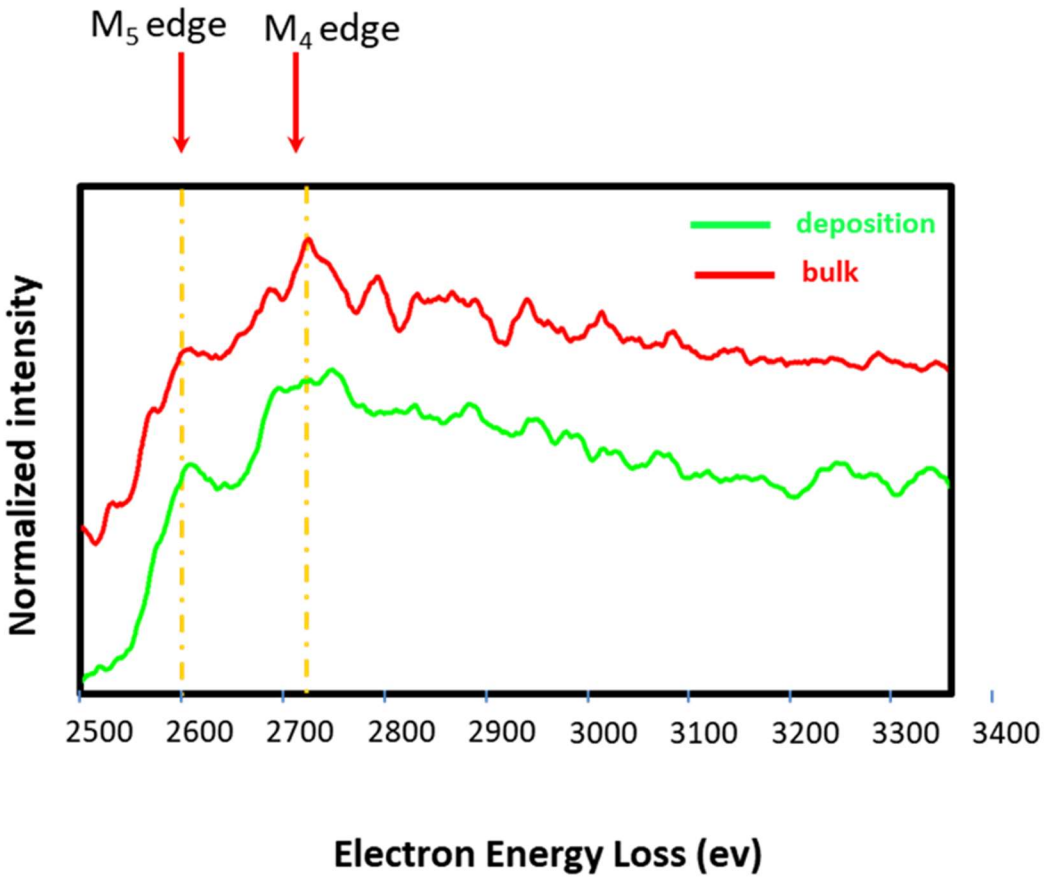

Fig. S5 STEM-EELS of Pb-$M_{5,4}$ edges for the $CsPbBr_3$ QDs.

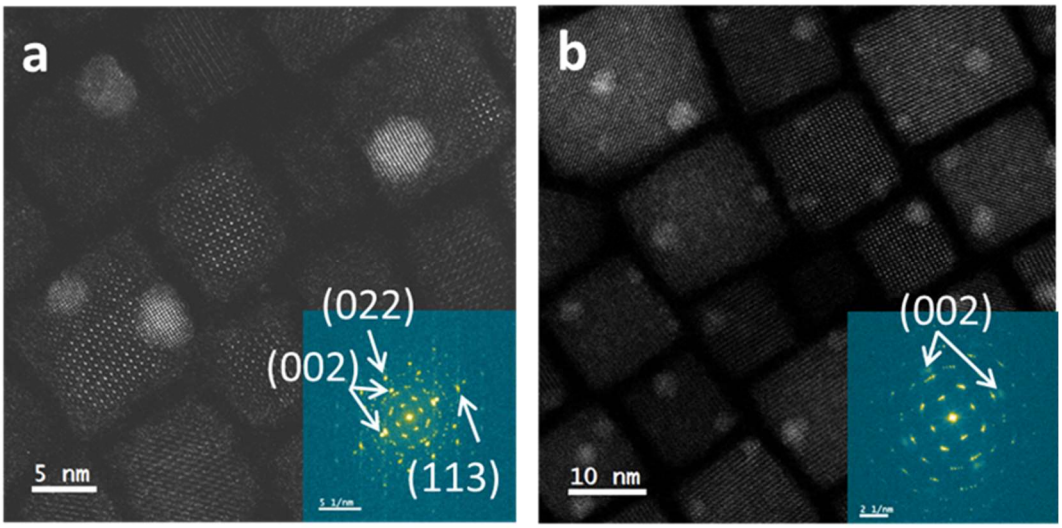

Fig. S6 (a), (b) STEM-HAADF image of $CsPbBr_3$ QDs with Pb nanocrystallites attachment. The insets show the FFT of the whole area. The white arrows give away the inverse space information of metallic lead among the diffraction pattern of orthorhombic perovskite $CsPbBr_3$.

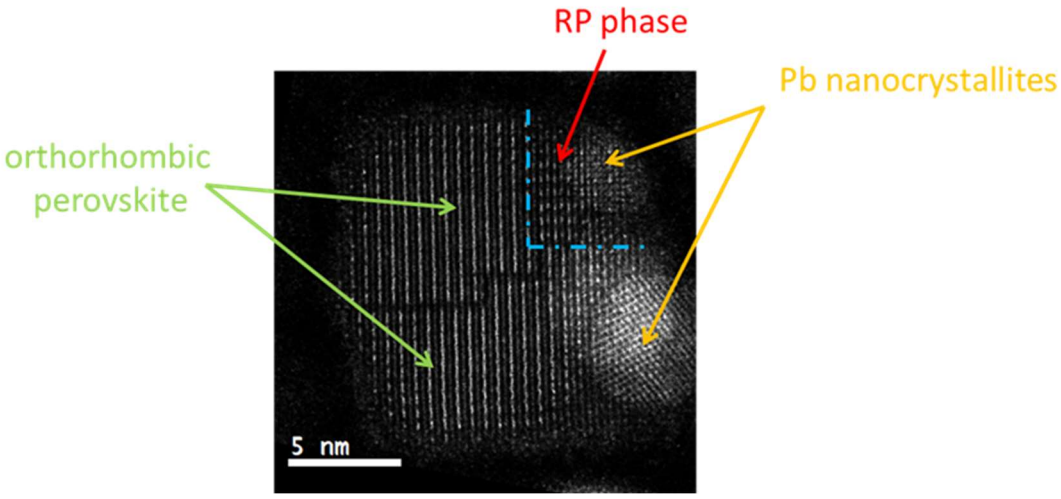

Fig. S7 STEM-HAADF image of $CsPbBr_3$ QDs off the zone-axis.

References

1. L. Protesescu, S. Yakunin, M. I. Bodnarchuk, F. Krieg, R. Caputo, C. H. Hendon, R. X. Yang, A. Walsh and M. V. Kovalenko, *Nano Letters*, 2015, **15**, 3692-3696.
2. G. Kresse and J. Furthmuller, *Physical Review B*, 1996, **54**, 11169-11186.
3. J. P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1996, **77**, 3865-3868.
4. P. E. Blochl, *Physical Review B*, 1994, **50**, 17953-17979.