

Supporting Information

α -CsPbI₃ Nanocrystals by Ultraviolet Light-Driven Oriented Attachment

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EXPERIMENTAL SECTION

Chemicals. All chemicals were used without purification, unless otherwise noted.

Cesium carbonate (Cs_2CO_3 , 99 %, Alfa Aesar), lead iodide (PbI_2 , 99.9985 %, Alfa Aesar), 1-octadecene (ODE, 90 %, Alfa Aesar), oleic acid (OA, 90 %, Alfa Aesar), and oleylamine (OAm, 80-90 %, Aladdin) and n-hexane (97.5 %, Innochem) dried with molecular sieves in resealable bottle.

Synthesis of Cs-oleate precursor. According to the modified previous procedures,^{40,51} 0.5 g Cs_2CO_3 , 2 mL OA and 50 mL ODE were added to a 100 mL 3-necked round bottom flask and degassed at 120 °C for 30 min under vacuum, then heated up to 150 °C under N_2 flow for 10 min. The heated process from vacuum to N_2 was repeated for 3 times totally, aiming to remove H_2O and O_2 in the solution. After that, the solution became clear, the Cs-oleate precursor solution was obtained due to the reaction of Cs_2CO_3 and OA, the solution was kept at 100 °C with protection of N_2 .

Synthesis of CsPbI_3 Quantum dots (QDs). 1 g PbI_2 and 50 mL ODE were added into another 100 mL 3-necked round bottom flask and degassed at 120 °C for 1 h under vacuum. Then 5 mL dried OAm and 5 mL OA were injected into the flask under N_2 flow. A pump was used to maintain the vacuum of the flask until the PbI_2 was completely dissolved, which showed a light-yellow clear solution and without gas generated. The temperature was raised to 150 °C via an oil bath and 8 mL Cs-oleate was swiftly injected into the reaction mixture with the protection of N_2 flow. As solution became turbid and turned to dark red, the flask was put into an ice bath after 5-8 s. The

obtained suspension was centrifugalized (10000 rpm for 5 min) to collect the solid products, and then resultants were dispersed into n-hexane.

Synthesis of CsPbI₃ film and illumination process. The CsPbI₃ QDs suspension were centrifugalized (10000 rpm for 5 min) to collect the upper solution. Indium Tin Oxide (ITO) with the size of 1 cm × 1 cm are prepared to drop-casting the obtained solution in glove box. Then the successfully prepared films are put under UV light in glove box and covered with diaphragms. The obtained films are put in the clean centrifuge tube, sealed well with parafilm, packed into sealing box and then took out from glove box to do the characterizations.

Quasi-in-situ TEM operation. The upper solution of centrifugalized suspension of CsPbI₃ QDs is diluted and dropped on coordinate micrograte in the glove box. After dried in the glove box under dark environment for 12 hours, the coordinate micrograte was taken for TEM characterization. The process was operated fast, and the coordinate micrograte was put in glove box again to be exposed under moderate UV light for 12 hours. This process was repeated until the characterization of TEM is completed.

Characterizations. Powder X-ray diffraction (XRD, PANalytical Empyrean diffractometer) with a Cu-K α source ($\lambda = 1.5406 \text{ \AA}$) measurements were used to analyze the crystal features of the samples. High-resolution transmission electron microscope (HRTEM) images and selected area electron diffraction (SAED) patterns were recorded on a probe Cs-corrected Titan G2 instrument with an accelerated voltage of 300 kV. Raman spectra were collected by a Renishaw InVia Reflex spectrometer

(Wotton-under-Edge, UK) with a 532 nm excitation length. X-ray photoelectron spectroscopy (XPS). The UV-vis absorption spectra were collected on a UV-vis spectrophotometer (UV-2600). Photoluminescence (PL) spectra and time-resolved PL (TRPL) were measured with an Edinburgh Instrument FLS 980 spectrophotometer. Excitation was provided by an Edinburgh EPL-510 ps pulsed diode laser. X-ray absorption fine structure (XAFS) from Beijing Synchrotron Radiation Facility (BSRF, 1W2B) was measured.

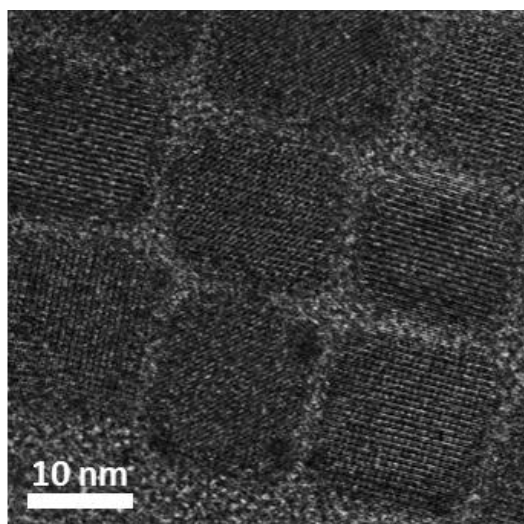


Figure S1. TEM image of α CsPbI₃ QDs synthesized following modified previous procedures.

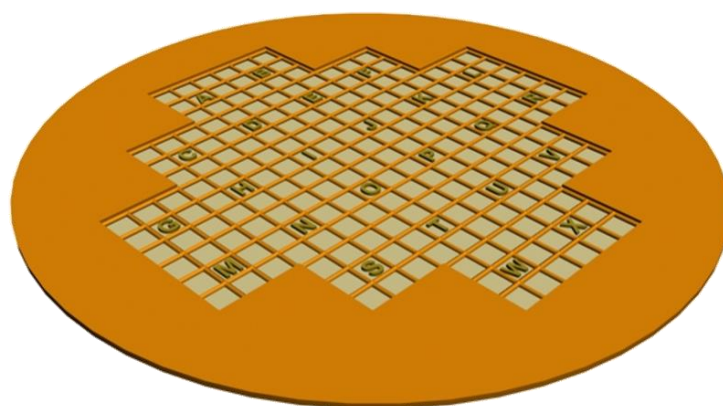


Figure S2. Schematic illustration of coordinate micrograte.

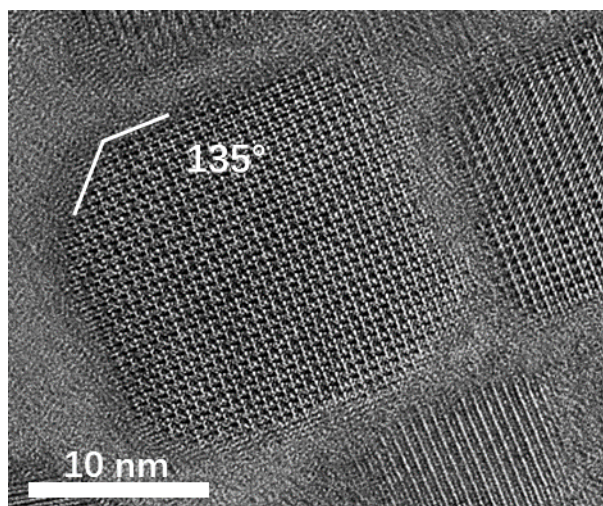


Figure S3. TEM image of a single CsPbI₃ quantum dot under illumination of moderate UV light for 24 hours.

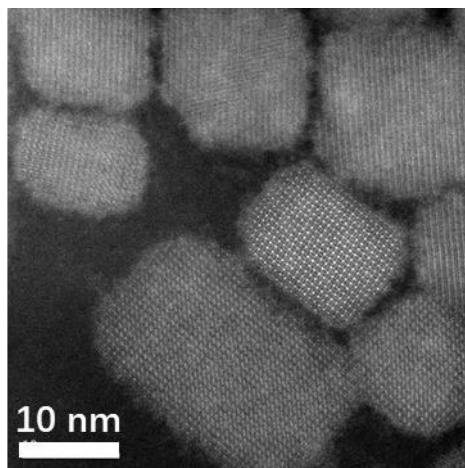


Figure S4. HRTEM image of CsPbI₃ QDs under illumination of moderate UV light for 48 hours.

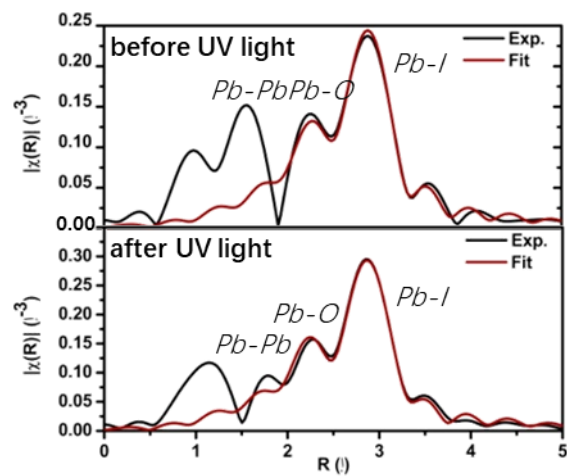


Figure S5. The magnitude R-space experimental EXAFS data and fits for CsPbI₃ QDs before and after UV-light.

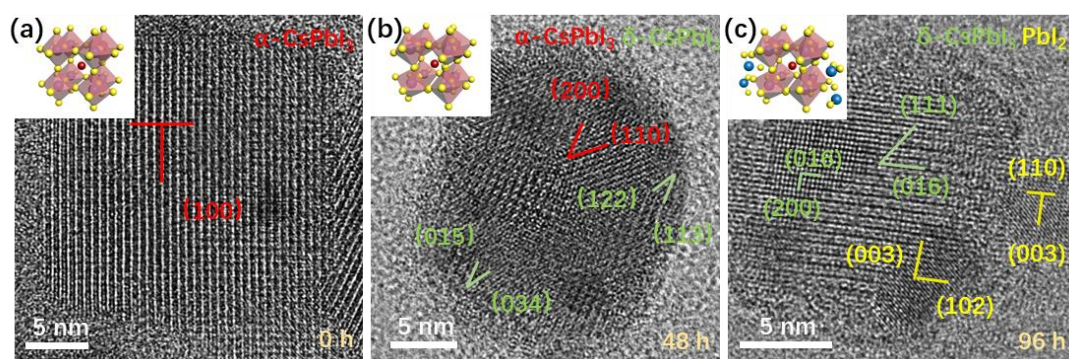


Figure S6. TEM images of a single CsPbI_3 quantum dot under high voltage UV-light with (a) 0 hour's illumination, (b) 24 and (c) 48 hours' illumination. Insets are corresponding illustrations of the degradation process of CsPbI_3 quantum dot.

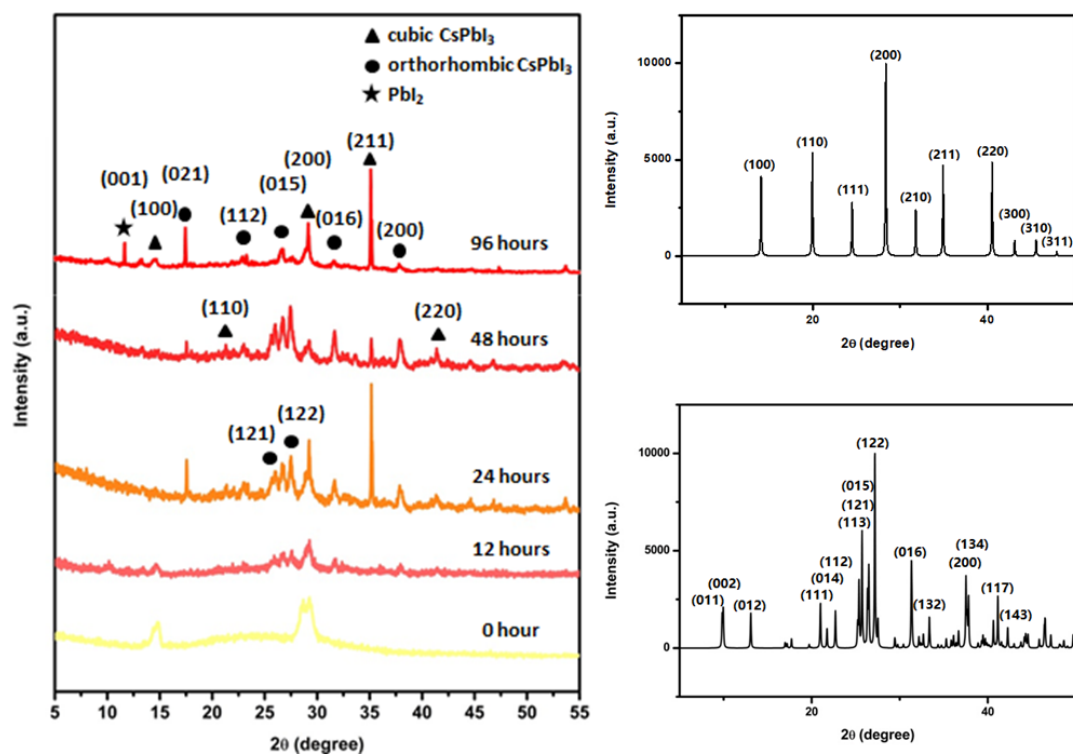


Figure S7. XRD patterns of CsPbI₃ QDs under high intensity UV light under different illumination durations and the standard XRD patterns of α -CsPbI₃ and δ -CsPbI₃.

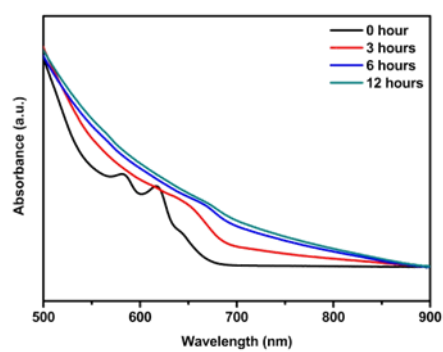


Figure S8. Absorption pattern of CsPbI₃ QDs under high voltage UV-light under different illumination durations.

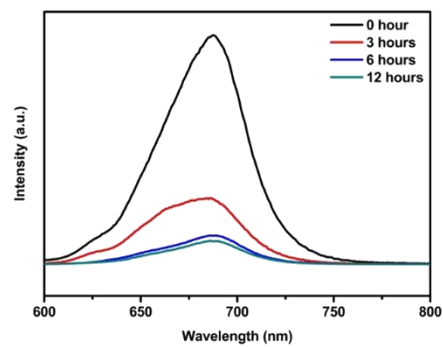


Figure S9. Emission pattern of CsPbI₃ QDs under high voltage UV-light under different illumination durations.

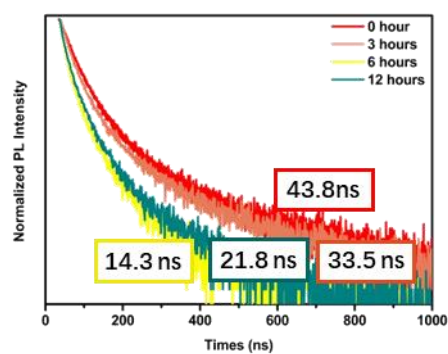


Figure S10. PL decay patterns of CsPbI₃ QDs under high voltage UV-light under different illumination durations.

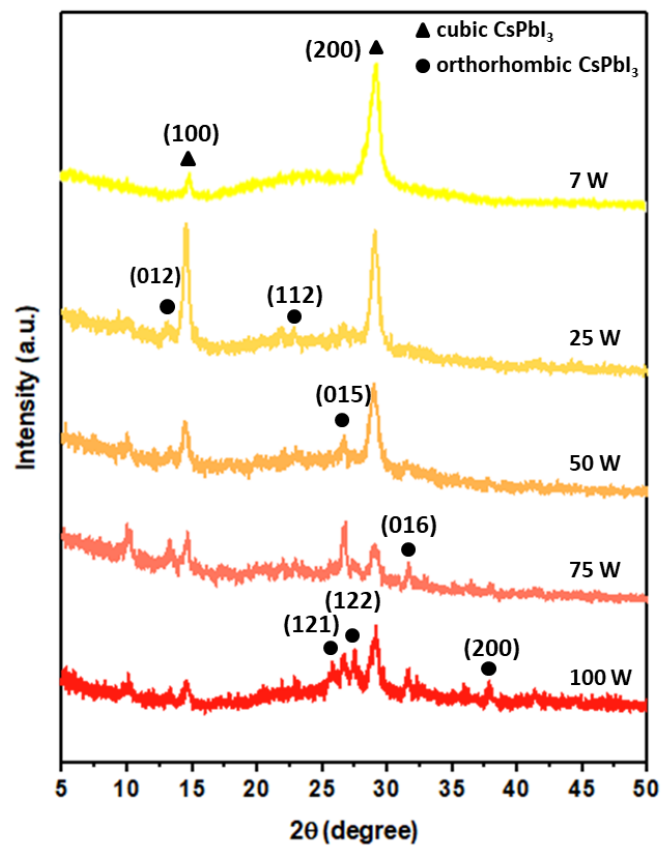


Figure S11. XRD patterns of CsPbI₃ QDs under different power densities of UV light for 12 hours.

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