

Supporting Information

Phonon Mode Transformation in Size-evolved Solution-processed Inorganic Lead Halide Perovskite

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Preparation of Cs-oleate solution:

0.4 g Cs_2CO_3 and 1.2 mL OA were loaded into a 3-neck flask along with 15 mL ODE, degassed and dried under vacuum at 120 °C for 1h, and then heated under Ar gas to 150 °C until all Cs_2CO_3 reacted with OA.

Chemicals and

Cs_2CO_3 (99.9%, Aldrich), octadecene (ODE, 90%, Aldrich), oleic acid (OA, 90%, Aldrich), PbBr_2 (99.999%, Aldrich), oleylamine (OLA, Aldrich, 70%), toluene ($\geq 99.5\%$, Aladdin). All chemicals were used as received without further purification.

Synthesis of CsPbBr_3 nanocrystals:

5 mL of octadecylene (ODE) and 0.18 mmol of PbBr_2 were loaded into a 3-neck flask and degassed under vacuum for 1 h at 100 °C. Certain amount of OLA and OA were injected at 100 °C under Ar gas (typically, 0.5 mL of OLA, 0.5 mL of OA). The temperature was raised to 120 °C for 1 hour, which was allowed for complete dissolution of the PbBr_2 salt. For the synthesis of CsPbBr_3 nanocrystals, the solution was kept at 170 °C, and 0.5 mL as-prepared Cs-oleate solution was quickly injected. After a certain reaction duration, the reaction mixture was cooled by an ice-water bath. The size of cubes will increase with reaction duration across nano-cube to micro-cube. Reaction duration less than 10 seconds, there will almost be nano-cubes with length about 20 nm. The size of micro-cube could be more 10 μm with reaction duration about 20 hours.

Purification of CsPbBr_3 nanocrystals:

After quenching by ice water bath, the crude solution was cooled down to room temperature and centrifuged with toluene at 3000 rpm (rounds per minute) for 3 minutes to obtain supernatant. Then the supernatant was centrifuged with toluene at 8000 rpm for 5 minutes to obtain precipitation. After purification, the precipitation was dispersed into toluene to obtain solution.

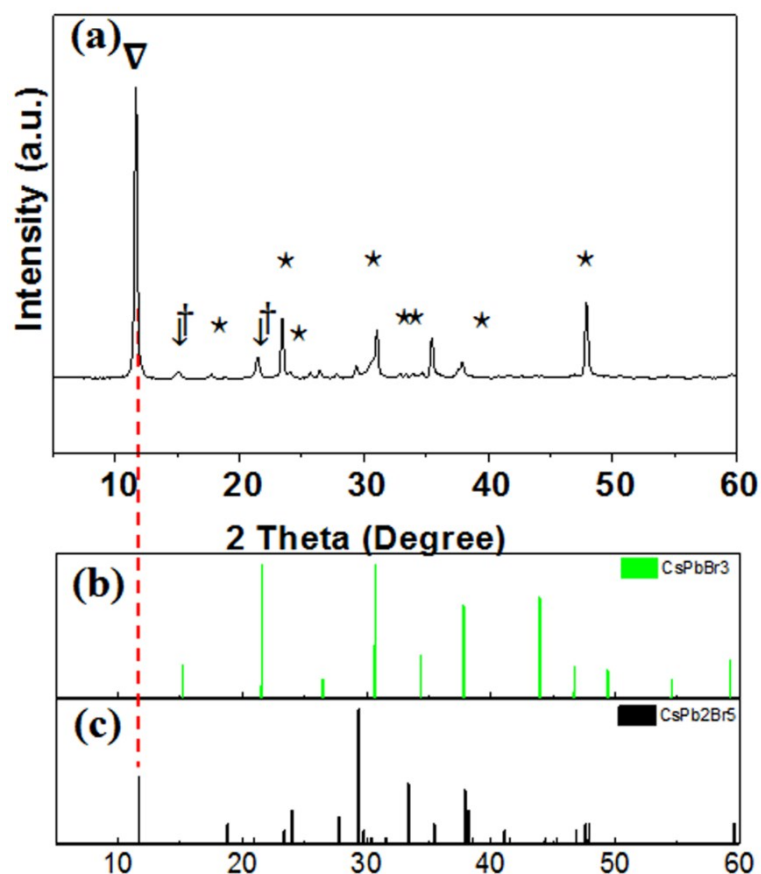


Figure S1: micro-cube perovskite sample (a), CsPbBr₃ cubic structure phase standard card (b), and CsPb₂Br₅ phase standard card (c). There are different symbols indicate the faces of the crystal structures phase of cubic 1 for CsPbBr₃ (arrow ↓), cubic 2 for CsPbBr₃ (cross ↑), orthorhombic for CsPbBr₃ (star ★), and tetragonal structure CsPb₂Br₅ (triangle ▽). The strongest peak belongs to facet (002) of CsPb₂Br₅ phase.

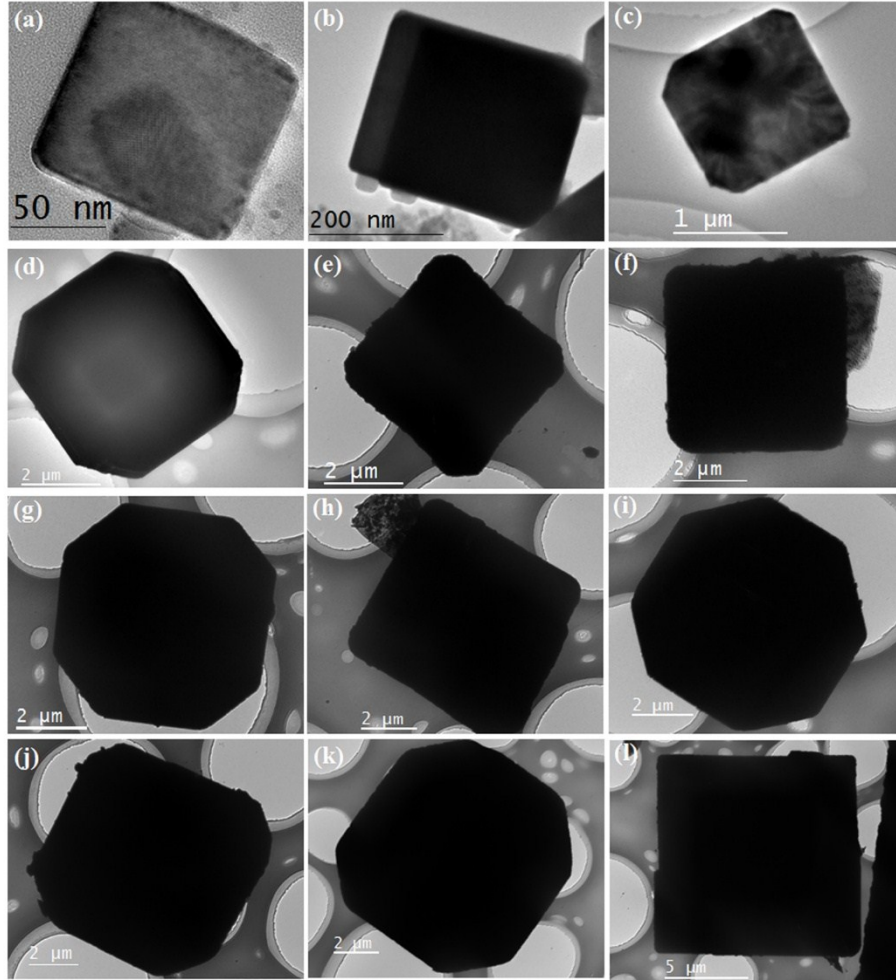


Figure S2: A series of TEM images of pure inorganic lead halide perovskite cube with size increasing from nano-cube to micro-cube. The cube sizes are 100 nm, 300 nm, 1.4 μm , 3 μm , 4 μm , 5 μm , 6 μm , 6.5 μm , 7 μm , 8 μm , 9 μm , and 11.6 μm in (a)-(l), respectively.

There are twelve different size samples, 100 nm, 300 nm, 1.4 μm , 3 μm , 4 μm , 5 μm , 6 μm , 6.5 μm , 7 μm , 8 μm , 9 μm , and 11.6 μm in (a)-(l), respectively. The size of cubes increases with reaction duration from nano-cube to micro-cube. The cubes have two different shapes, octagon and square. The (100) facet is exposed for the square shape, while the (100) and (110) facets are exposed with the octagonal shape. It indicates that the cube had two different growth directions of (100) and (110).¹⁻²

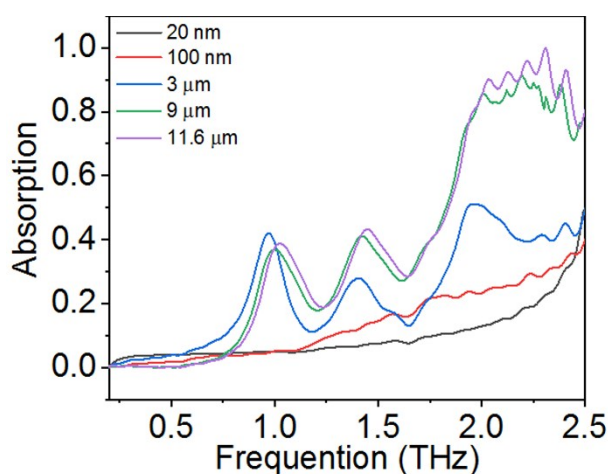


Figure S3: Terahertz absorption of pure inorganic lead halide perovskite (20 nm, 100 nm, 3 μm , 9 μm , and 11.6 μm)

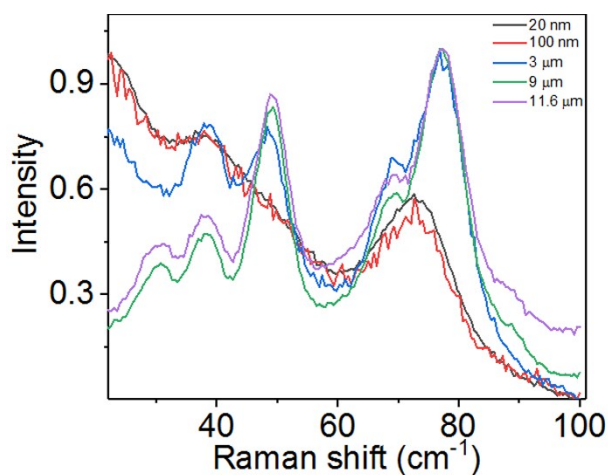


Figure S4: Raman shift of pure inorganic lead halide perovskite (20 nm, 100 nm, 3 μm , 9 μm , and 11.6 μm)

Nano-cube samples (20 nm and 100 nm; black and red curve) have similar results of THz and Raman measurement, which could evidence they are mainly composed by cubic phase of perovskite CsPbBr_3 . Micro-cube samples (3 μm , 9 μm , and 11.6 μm ; blue, green, and purple) have similar results of THz and Raman measurement, which could evidence they are mainly composed by tetragonal phase of perovskite CsPb_2Br_5 .

Reference:

1. Li, G.; Wang, H.; Zhu, Z.; Chang, Y.; Zhang, T.; Song, Z.; Jiang, Y., Shape and phase evolution from CsPbBr_3 perovskite nanocubes to tetragonal CsPb_2Br_5 nanosheets with an indirect bandgap. *Chem Commun (Camb)* **2016**, 52 (75), 11296-11299.
2. Xia, Y.; Xiong, Y.; Lim, B.; Skrabalak, S. E., Shape-controlled synthesis of metal nanocrystals: simple chemistry meets complex physics? *Angew Chem Int Ed Engl* **2009**, 48 (1), 60-103.