Electronic Supplementary Information:

Solution-Precipitation Synthesis of Perovskite Polyhedron and its Lasing Applications

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Experimental Section

In a typical experimental process, 20µL 25mM PbBr₂ (99.99%, Aladdin) in DMF (99.9%, Aladdin) was dropped into isopropanol (99.9%, Aladdin) together with 1mM CH₃NH₃Br (99%, Shanghai MaterWin New Materials Co., Ltd). The solution was mixed by an ultrasonic machine. The color of mixture turned into orange after 30 minutes. After mixing for about 60 minutes, solution of orange precipitates was drop-casted on a glass substrate and dried at room temperature for subsequent experiments. For powder X-ray diffraction measurements, the orange precipitates were collected and washed with isopropanol, and dried in a vacuum oven at 60 °C for 6 hours.

For sonic bath fabrications, starting temperature was 20°C, and rose to 65°C at the end of the one-hour reaction. To exclude possible influence of this temperature rise upon final products, we kept reaction time and sonic strength the same for all reactions, to ensure same amount of temperature rise therein. Furthermore, we have performed fabrications of $CH_3NH_3PbBr_3$ crystals by using a water bath, where temperature could be kept constant at different temperatures during the reactions. Experimentally, 1 mM of CH_3NH_3Br solution was magnetically stirred (1000r/min) with 25mM PbBr₂ in a water bath at constant temperatures of 45 °C, 55 °C and 65 °C, respectively. It was found that precipitation of $CH_3NH_3PbBr_3$ could be clearly observed at about 5 min, 3 min and 2 min, which gradually accelerated with increasing water bath temperatures. With corresponding SEM images of the samples in Figure S3, all products show cubic morphologies, with size gradually decreasing for increasing water bath temperatures. This is clear evidence that higher temperature could accelerate the reaction and produce smaller crystals. To be noted that, there was no polyhedral $CH_3NH_3PbBr_3$ observed in the final products, indicating a key point that slow reaction rate (i.e., in sonic bath) was feasible for polyhedral $CH_3NH_3PbBr_3$ formation.

It is also noted that the concentration of PbBr₂ would have an impact on crystal morphology. However, it is noted that PbBr₂ is insoluble in isopropanol. And white precipitate of PbBr₂ would appear when PbBr₂/DMF solution was dropped into the isopropanol solution. Therefore, it was more convenient to change concentration of CH₃NH₃Br rather than PbBr₂ from experimental view of point. And CH₃NH₃Br was set to be excessive so as to ensure complete reaction of PbBr₂ experimentally. It is believed to change concentration of either PbBr₂ or CH₃NH₃Br would have same yielding results once appropriate solution used.

Material Characterization

Crystallographic information of fabricated CH₃NH₃PbBr₃ crystals was investigated by powder X-ray diffraction (XRD, X'Pert Pro, PANalytical, Netherlands). Morphologies and structures of the samples were characterized by a field emission scanning electron microscopy (FESEM, Merlin, Zeiss, Germany) and transmission electron microscopy (TEM, 2100F, JEOL, Japan). Optical spectra were measured by using a spectrometer (Princeton Instruments, Acton SP-2300) with a 1200mm⁻¹grating.



Figure S1. Schematic diagram of the fabrication process of the as-grown perovskite microcrystals.



Figure S2. PXRD patterns of the $CH_3NH_3PbBr_3$ crystals synthesized with different concentration of CH_3NH_3Br . From top to bottom are 3.0mM, 2.0mM, 1.5mM, 1.2mM, 1.0mM and 0.8mM respectively.



Figure S3. $CH_3NH_3PbBr_3$ products prepared by dropping $PbBr_2$ solution (25 μ L) into 1.0mM CH_3NH_3Br solution (3 mL) and mixing by magnetic mixer (1000 r/min) for 10 minutes at 45°C(a), 55°C(b), 65°C(c).



Figure S4. The size distribution of CH₃NH₃PbBr₃ products prepared with different CH₃NH₃Br concentration: a, b, c, d, e and f for 3.0 mM, 2.0 mM, 1.5 mM, 1.2 mM, 1.0 mM and 0.8 mM, respectively.



Figure S5. The shape distribution of CH₃NH₃PbBr₃ products prepared with different CH₃NH₃Br concentration: a, b, c, d, e and f for 3.0 mM, 2.0 mM, 1.5 mM, 1.2 mM, 1.0 mM and 0.8 mM, respectively. The particle shape distribution is evaluated by counting 50 individual particles in each SEM micrograph.



Figure S6. CH₃NH₃PbBr₃ products prepared by dropping PbBr₂ solution into 2.0mM CH₃NH₃Br solution and keeping stand for 24 hours. The red circle regions indicated etching by DMF, while blue square regions represented unreacted PbBr₂. Inset: SEM image of unreacted PbBr₂ in IPA.



Figure S7. Home-made experiment setup for optical measurement. Samples were pumped by a frequency doubled Ti: Sapphire laser (TOPAS Prime, 400 nm, 1 kHz, ~120 fs) with beam diameter of 100 μm.