Large-size $CH_3NH_3PbBr_3$ Single Crystal: Growth and In Situ Characterization of the Photophysics Properties

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EXPERIMENTAL SECTION

Reagents

All raw materials were of analytical grade from commercial sources. Hydroiodic acid (HI), methylamine (MA), dimethyl formamide (DMF) solution, and lead dibromide ($PbBr_2$) were purchased from Aladdin-reagent, without further treatment.

Materials Preparation

Excessive amounts of methylamine alcohol solution (47 wt%) reacted with HI (47%, water solution) in ice bath in ambient atmosphere for 2 hours. The crystallization of methyl-ammonium bromide (CH_3NH_3Br) was achieved using a rotary evaporator at 50 ^oC. After that, a white microcrystal CH_3NH_3Br powder was washed with absolute diethyl ether several times. Finally, the products were dried at 60 °C in a vacuum oven overnight.

The growth of large-scale $MAPbBr_3$ single crystal was processed through a two step method from single solution. Equimolar CH_3NH_3Br and $PbBr_2$ were dissolved in

DMF, with the total mass concentration of 50%. Homogeneous orange-yellow solution was obtained after continuously stirred 15 min at 60 ^{o}C. The mixed solution was kept at 70 ^{o}C, when small single crystal with the dimension of 2 × 2 cm dissolved out. After picked up a well crystallized single crystal, the rest solution and crystals were reheated to form a homogenous solution. After cooled to room temperature, the selected small single crystal was put in to the vessel. The crystal $MAPbBr_3$ sample could be obtained after several days.

Single crystal characterization

Single crystal diffraction data were collected on a Bruker SMART APEX II CCD diffractometer using monochromatic Mo Ka radiation at 293 K and integrated with the SAINT program. The numerical absorption corrections were carried out using the SADABS program for area detector. All calculations were performed with programs from the SHELXTL crystallographic software package. The crystallographic structure was solved by direct methods, and all of the atoms were refined using full-matrix least-squares techniques with anisotropic thermal parameters and final converged for I > 2s. Powder X-ray diffraction data was collected using a Bruker D8 Advance diffractometer in Bragg-Brentano geometry and operating with Cu Kα radiation.

Asylum Research MFP-3D Scanning Probe Microscopy (SPM, Oxford Instruments) was utilized to carry out the photophysics measurements. To inspect the properties under irradiation, an optical fiber is equipped on xenon lamp to transform the visible light to the crystal's surface.

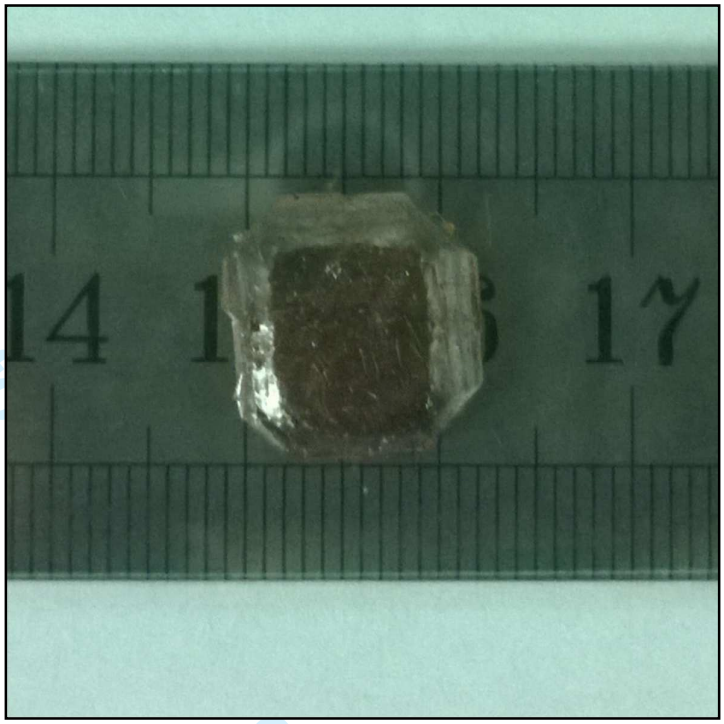

Figure S1 The digital photograph of as-prepared $CH_3NH_3PbBr_3$ single crystal, the scale in the ruler was 1 millimeter

Table S1 Crystallographic Parameters Obtained from single crystal X-ray diffraction

Empirical formula	$CH_3NH_3PbBr_3$
Formula weight	478.977 g/mol
Crystal system	cubic
Space-group	P-43m(215)
Cell parameters	
a	5.9361(11) Å
b	5.9361(11)Å
c	5.9361(11)Å
α	90°
β	90°
γ	90°
Cell volume	209.17(12) $Å^3$
Z	1
Calc. density	4.92134g/cm^3
RAll	0.0159

Table S2 Bond lengths for $MAPbBr_3$

Atom 1	Atom 2	Count	d (1,2) [Å]
Br2	H1	8x	2.2791
C1	H1	8x	0.9294
	H2	2x	2.2504
N2	H2	6x	0.7177
H2	N2	1x	0.7177
	H2	4x	1.0149
	H2	1x	1.4353
	H1	4x	1.8671
	C1	1x	2.2504
	H1	4x	2.4258
H1	C1	1x	0.9294
	H1	1x	1.0519
	H1	1x	1.0821
	H1	1x	1.0853
	H1	1x	1.5091
	H1	2x	1.5219
	H1	1x	1.8586
	H2	1x	1.8671
	Br2	1x	2.2791
	H1	1x	2.3632
	H2	1x	2.4258