Electronic Supplementary Information for

Formic Acid: An Accelerator and Quality Promoter for Nonseeded Growth of $CH_3NH_3PbI_3$ Single Crystal

Qianrui Lv, Zhipeng Lian, Qiang Li, Jia-Lin Sun and Qingfeng Yan[*]

S1. Experimental section

$CH_3NH_3PbI_3$ single crystal growth. All chemicals were used as received without further purification. $Pb(CH_3COOH)_2•3H_2O$ of analytical grade and carbon tetrachloride (99%) was from Sinopharm Chemical Reagent Co., Ltd., China. 57% HI aqueous solution with 0.75% H_3PO_2 as stabilizer was from Acros and 40% CH_3NH_2 aqueous solution was from Alfa. Formic acid (98%) was from J&K Scientific Ltd.. To grow $CH_3NH_3PbI_3$ single crystals by STL method with formic acid, briefly, 22.5 g of $Pb(CH_3COOH)_2•3H_2O$ was dissolved in 90 ml of a 57% HI aqueous solution contained in a borosilicate glass bottle (purchased from Cleman Chemical Ltd.) followed by heating and stirring at 110 ºC for 10 min. An additional 18 ml of 57% HI solution with 6 ml of CH_3NH_2 40% aqueous solution was added to the solution drop by drop at 110 ℃ to ensure no black solid appear. Then 5.4 ml of formic acid was added to the homogeneous bright yellow solution. The glass bottle was sealed and put into an oven after sealing. The temperature was kept 110 ºC for 1h then dropped to 97 ℃ by a cooling rate of 0.5 ℃/h, then 1 ºC/h to 65 ℃, and whereafter 2 ℃/h to 40 ºC. The cooling rate at the beginning was relatively slow, which made the nucleation process more stable and the subsequent crystal growth was carried out at fewer sites. The cooling accelerated in two steps because the effect of temperature on the crystallization quality at low temperatures was much lower than that at high temperatures. Black single crystals were grown at the bottom of the glass bottle. The growth of $CH_3NH_3PbI_3$ single crystals by STL method without formic acid and ITC method were described in our previous work (Ref. 23 in the manuscript).

Materials characterization. Several as-grown single crystals were ground to powder and the powder XRD data were collected in by X-ray crystal diffraction (XRD) instrument (Brüker P4) using Cu K_α radiation at a scan rate of 12 degree/min under operation condition of 40 kV and 40 mA. The transmission spectrum of the $CH_3NH_3PbI_3$ [100]-cut single crystal plate were collected using a UV–vis–NIR spectrophotometer (Perkin Elmer Lambda 950). Steady-state PL spectrum was acquired with an optical spectrometer (FLS920, Edinburgh Instruments, Livingston, UK). The sample was illuminated by a monochromatic light (λ_{exc}=460 nm, Xenon lamp). High resolution X-ray rocking curves were characterized using high resolution X-ray diffractometry (D8 Discover, Brüker). Photographs of as-grown crystals were taken by a digital camera (EOS 600D, Canon). Optical microscopic images were taken by an optical microscope (BX51TRF Olympus) that was connected to a CCD camera (Pixelink-B742) and a computer for image.

Extraction of I_2 from the growth mother liquor. As to the growth mother liquor with and without addition of formic acid, the extraction process was exactly the same. After the single crystal growth, 2 ml of the growth mother liquor was taken out and moved into 40 ml of deionized water, and then a yellow turbid solution was obtained. The turbid solution was added to 40 ml CCl_4 to extract the I_2 in it. After extraction for 10 h, the concentration of iodine element in the carbon tetrachloride layer was determined by inorganic mass spectrometry (Thermo ICP－MS iCAPQ).

Device fabrication and characterization. For dark *I-V* measurement to investigate the trap-state density n_{trap} and estimate the carrier mobility μ, [100]-cut and [112]-cut single crystal plates were prepared via mechanical polishing, thickness of which was about 2 mm. 60 nm-thick Au electrodes were deposited on the top and bottom surfaces of single crystal plates. Dark *I-V* curves were collected by a Keithley 2400 sourcemeter. In the evaluation of n_{trap} and μ, 32 is chosen as the relative dielectric constant (ε) of $CH_3NH_3PbI_3$, which is consistent with the standards of Huang's group (Ref. 8 in the manuscript) and our perivous report (Ref. 23 in the manuscript).

Single crystals grown by STL method with formic acid, by STL method without formic acid and by ITC method were selected. Au strips of 50 nm in thickness were deposited on the surface of (100) facets of them by a conventional thermal evaporation method through a stainless steel mask. The channel width (W) was 2 mm, and the channel length (L) was 0.5 mm. We tested response of the current at 3 V bias under the dark condition and under the solar simulator condition (The power density was 100 mw cm^{-2}).

Moisture erosion to $CH_3NH_3PbI_3$ single crystals. Single crystals grown by STL method with formic acid, by STL method without formic acid and by ITC method were placed in a sealed plastic box containing saturated NaCl solution. Under 25 ℃, the relative humidity inside the box was 75%. Single crystals suffered from the moisture erosion for three days. To eliminate the effect of other factors affecting the photocurrent measurement, the samples were exposed in the moisture for a same period and the photocurrent characterizations were conducted in a similar manner for different samples.

S2. A comparison of μ and n_{trap} of $CH_3NH_3PbI_3$ single crystals grown by different methods along different axes

Table S1. A comparison of μ and n_{trap} of $CH_3NH_3PbI_3$ single crystals grown by different methods along different axes.

	STL with Formic Acid		**STL without Formic Acid**		**ITC**	
	(100) Axis	**(112) Axis**	**(100) Axis**	**(112) Axis**	**(100) Axis**	**(112) Axis**
μ / cm^2 V^{-1} s^{-1}	162	158	129	111	82	75
n_{trap} / cm^{-3}	3.1×10^9	4.3×10^9	5.2×10^9	6.1×10^9	7.7×10^9	9.1×10^9

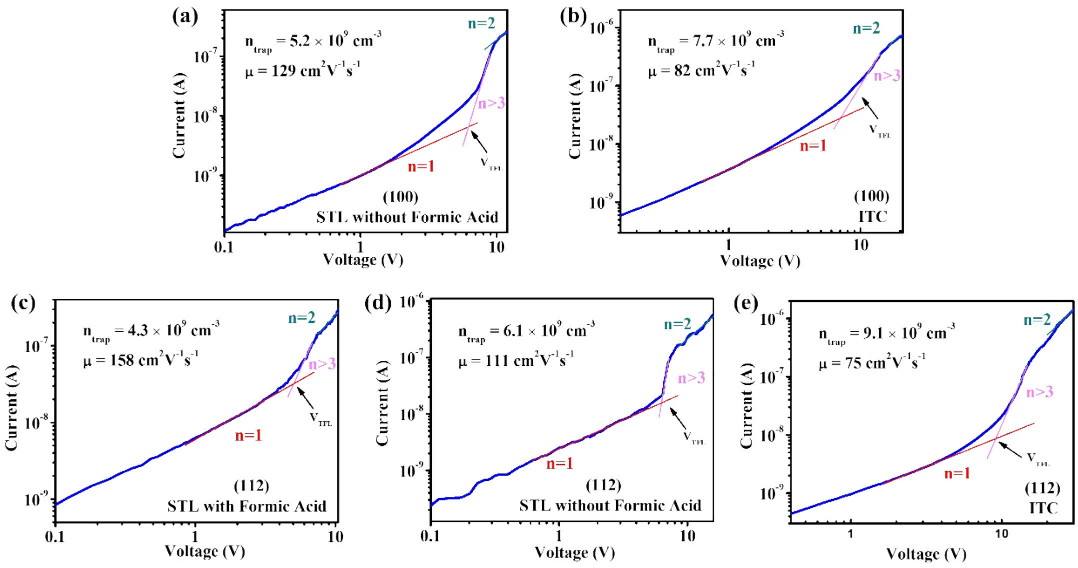

Figure S1. Dark current−voltage measurement according to the SCLC model of $CH_3NH_3PbI_3$ single crystals grown by STL method without formic along (100) axis (a), ITC method along (100) axis (b), STL method with formic along (112) axis (c), STL method without formic along (112) axis (d), and ITC method along (112) axis (e).

S3. Photograph of oxidized growth solution

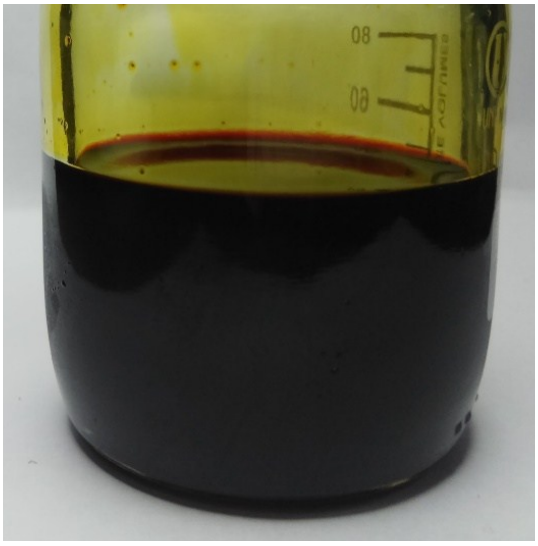

Figure S2. Photograph of the mother liquor after the single crystal growth by the conventional STL method when the glass bottle was not completely sealed.

S4. Reduction of I_2 by formic acid in an aqueous solution

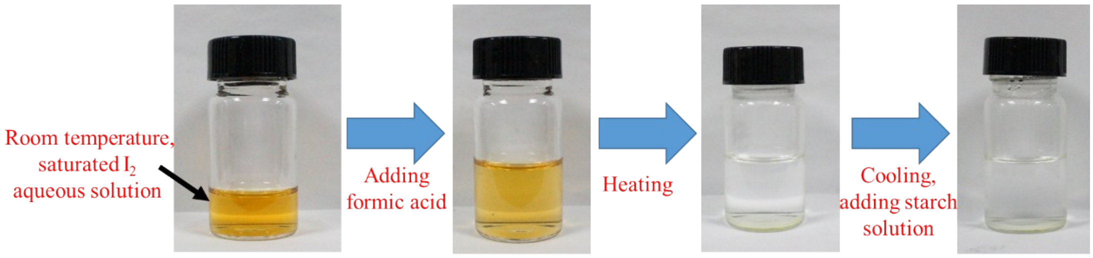

Figure S3. Photographs of the process of formic acid reacting with iodine in an aqueous solution.

To confirm the formic acid did be able to reduce the iodine in aqueous solution, a simple experiment was conducted. When formic acid was added to the brown saturated iodine aqueous solution, after slightly heated, the solution became colorless. After cooling, a starch solution was added. The solution remained colorless rather than turned blue, indicating iodine was completely reduced by the formic acid added.

S5. The effect of water on extraction of I_2 from the growth mother liquor

To make a sufficient extraction, we found that addition of same amount of water into the growth mother liquor before extraction was needed. In the presence of a large number of iodide ions, Pb^{2+} and I^- will form $[PbI_4]^{2-}$ in the growth mother liquor. In addition, I^- and I_2 produced by oxidation will form polyiodide ions (here taking I_3^- as an example). There is a balance in the solution:

$$PbI_2\ (s) + 3I^-\ (aq) + I_2\ (aq) \leftrightharpoons [PbI_4]^{2-}\ (aq) + I_3^-\ (aq)$$

After adding water, the balance moves to the left, causing the oxidized iodine element to be present in the form of I_2 in the aqueous solution, and facilitating the next extraction step. Therefore, after the subsequent extraction, the upper layer is the turbid liquid containing solid PbI_2 and soluble ions, while the lower layer is carbon tetrachloride solution of I_2.

S6. The effect of formic acid amount on the quality of $CH_3NH_3PbI_3$ single crystal

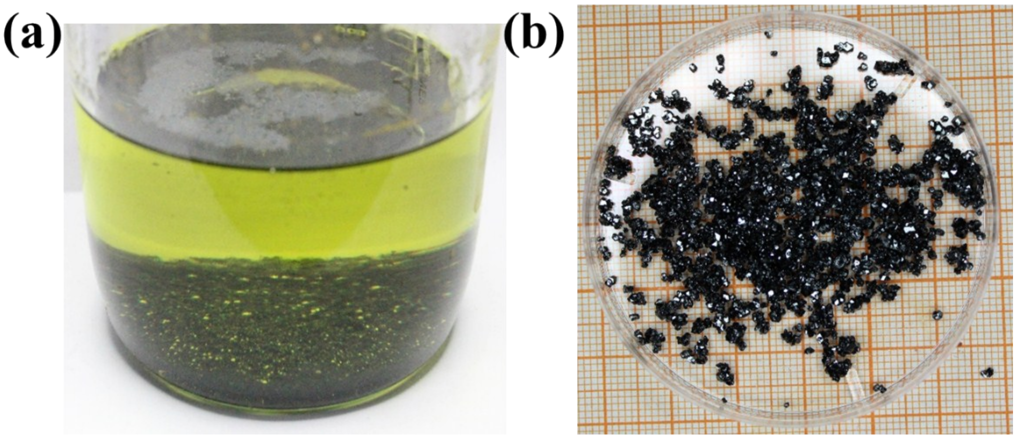

Figure S4. Photographs of $CH_3NH_3PbI_3$ single crystals grown with excessive formic acid (10% of the volume of hydroiodic acid) in the solution (a) and after filtration (b).

To obtain high-quality $CH_3NH_3PbI_3$ single crystals, the amount of formic acid added to the growth solution has an important. The optimal volume of formic acid was 5% of that of hydroiodic acid. If the amount of formic acid was too large (Figures S3), the bubble of CO_2 produced from the redox reaction would disturb the growth process and made a negative influence to the quality of the $CH_3NH_3PbI_3$ single crystal.

S7. The moisture stability of $CH_3NH_3PbI_3$ single crystal grown by different methods

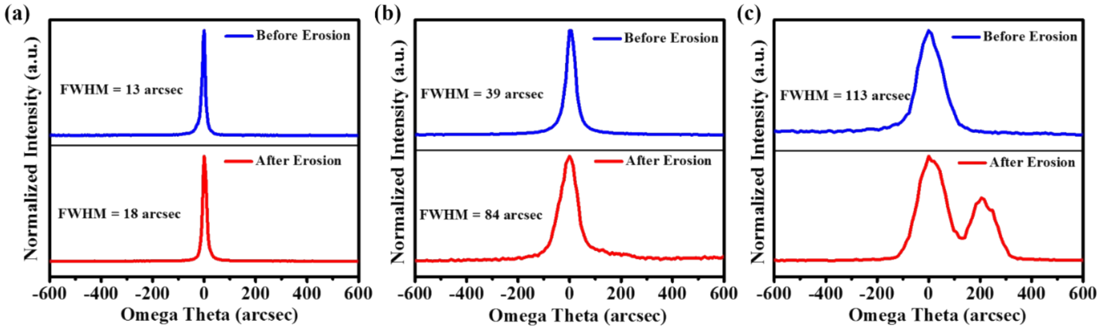

Figure S5. FWHMs of HR-XRCs of the (400) diffraction of $CH_3NH_3PbI_3$ single crystals grown by STL method with formic acid (a), STL method without formic acid (b) and by ITC method (c) before and after same moisture erosion.

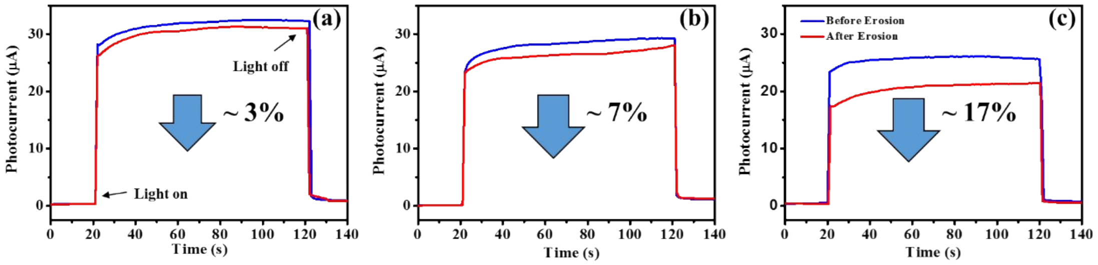

Figure S6. Photocurrent stability of the $CH_3NH_3PbI_3$ single crystals grown by STL method with formic acid (a), STL method without formic acid (b) and by ITC method (c) before and after same moisture erosion. After the moisture erosion for 3 days, the photocurrent of the crystal grown by ITC method decreased more than that of others.

$CH_3NH_3PbI_3$ single crystals grown by STL method with formic acid, by STL method without formic acid and by ITC method were selected respectively to test their FWHMs of HR-XRCs of the (400) diffraction and their photoelectric property before and after same moisture erosion. As shown in Figures S5a and S5b, the FWHMs of the $CH_3NH_3PbI_3$ single crystals grown by STL method are only a certain degree of broadening after the moisture erosion. And the FWHM of the single crystal grown without the addition of formic acid broadened more obviously than that of the single crystal grown with formic acid. While, the HR-XRC of the $CH_3NH_3PbI_3$ single crystals grown by ITC method shows peak split (Figure S5c), which means that the crystal structure appears more obvious collapse after the moisture erosion. The comparison of their photoelectric property is shown in Figure S6. According to our recent research (Ref. 10 in the manuscript), it seems to result from the reduction of iodide ion vacancies because iodide ions act as barriers against water molecules attacking methylammonium ions and impede the moisture erosion to $CH_3NH_3PbI_3$ single crystals.