Direct Insight into Crystallization and Stability of Hybrid Perovskite CH$_3$NH$_3$PbI$_3$ via Solvothermal Synthesis

Electronic Supplementary Information:

**Experimental Section**

In a typical experimental process, 15 mg lead(II) of acetatetrihydrate (Pb(OAc)$_2$•3H$_2$O) (99.8%, Aldrich) was completely dissolved in 1 mL of hydriodic acid (45% in water, J&K Scientific) with the help of continuous magnetic stirring, then 30 mL of isopropanol (99.9%, J&K Scientific) was added and stirred violently. The solution was stirred for 15 min, then it turned into yellow. 300 μL of methylamine solution (33 wt. % in absolute ethanol, Aldrich) was added dropwise. The mixture was further stirred for 15 min and then transferred into Teflon-lined autoclave, sealed and kept at 120 °C for 12 h in a furnace, and cooled to room temperature. The black precipitates were collected and washed with isopropanol, and then dried in a vacuum oven at 55 °C for 12 h. The equipment with the total volume of isopropanol was kept constant.

**Material Characterization**

Crystallographic information on CH$_3$NH$_3$PbI$_3$ crystals was investigated by powder X-ray diffraction (XRD, Bruker D8 Advanced Diffractometer, Cu Kα radiation, 40 kV). The morphology and structure of the samples were characterized by field emission scanning electron microscopy (FESEM, HITACHI S4800) and transmission electron microscopy (TEM, JEOL JEM-2100, 100 kV). Perovskite samples were dispersed in isopropanol, and then dropped on a conductive SEM sample holder, or a carbon-coated copper grid with irregular holes, for electron microscopy (SEM/TEM) analysis. The optical absorption spectra were measured by using a Cary 500 Spectrophotometer. The photofluorescence spectra were obtained from a Fluorolog-3-P molecular fluorescence spectrometer with excitation wavelength of 460 nm.

![Figure S1. PXRD patterns of the CH$_3$NH$_3$PbI$_3$ crystals synthesized with different time of reaction. From top to bottom are 36 h, 24 h, 12 h, 6 h and 1 h respectively.](image-url)
Figure S2. SEM image of the remaining tetrahedrons after collapsed at 120 °C for 60 h.

Figure S3. SEM image of the excessive etched crystals obtained 120 °C for 36 h.

Figure S4. The SEM image of the crystals preserved in the humidity of sixty percent for 3 h.
Figure S5. (A) UV–vis absorption and (B) photoluminescence spectrum of the CH$_3$NH$_3$PbI$_3$ products prepared with different reaction time.