## **Supporting Information**

## Decisive Influence of Amorphous PbI<sub>2-x</sub> on Photodegradation of Halide Perovskite

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## **Experimental section**

**Materials.** Unless otherwise stated, all materials were purchased from Sigma Aldrich and all chemicals were used as purchased without further purification.

**Sample Preparation.** For the *Quasi-in situ* TEM observations, the polycrystalline  $CH_3NH_3PbI_3$  film was deposited directly on thin carbon-coated TEM grid substrate. Firstly, the TEM grids were fixed on a small piece of glass and then cleaned with a plasma cleaner for about 3 minutes to improve the surface hydrophilicity. Precursor solutions were prepared by combining lead iodide (PbI<sub>2</sub>, Sigma Aldrich) and methylammonium iodide (CH<sub>3</sub>NH<sub>3</sub>I, MAI, Sigma Aldrich) with 1:1 stoichiometry in dimethylformamide (DMF), obtaining a solution with the optimal concentration at 1 M. The CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film was then deposited by spin coating the precursor solution at 4000 rpm (the optimal speed) for 30 s, and then annealed on heating plate at 100 °C for 10 min. For XRD, SEM and the optical performance investigation, the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> film samples were directly deposited on an indium tin oxide (ITO) glass (surface area of 2

 $cm \times 2$  cm) rather than TEM grids using the same process and conditions. In order to minimize degradation due to environmental factors, the perovskite film samples were placed in a sealed, argon-filled container immediately, especially during their transportation.

For the synthesis of  $PbI_2$  single crystal nanoplate: 1g  $PbI_2$  powder was dissolved into 200 mL deionized water, which was then heated up to 100 °C and stirred for 12 h under 1000 r/min, finally the supersaturated precursor solution was formed. However, due to

a variable solubility of PbI<sub>2</sub> in water at different temperatures (0.124 g at 40 °C, 0.193 g at 60 °C, 0.294 g at 80 °C, and 0.42 g at 100 °C per 100 mL water), the precursor solution couldn't completely dissolve into the supersaturated PbI<sub>2</sub>-water solution especially after putting it into an ice water bath, then the crystallized PbI<sub>2</sub> nanoplates precipitated from the solution.

Light illuminating treatment. The as-prepared CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> films were illuminated by 50 W/cm<sup>2</sup> white light LED (400~780 nm) in a glove box with argon protection, then the samples were used for the XRD, XPS, SEM and other experiments. During the light illumination treatment of the MAPbI<sub>3</sub> film, all the samples were put into the Arprotected glove box and illuminated with a 5 and 50 W/cm<sup>2</sup> white light soaking. For Quasi-in situ TEM observations, the photo-illuminated samples were removed into the TEM holder quickly (less than 5 min, in dark), and the transition process was protected by a self-made equipment of Ar-protection environment. It should point out that the gas pressure in glove box is about 2 atm, such a high gas pressure may be helpful for the adsorption of volatilizable I2 and CH3NH3I on the TEM carbon grids, and this is why we could detect the existence of the photodegraded products of I<sub>2</sub> and CH<sub>3</sub>NH<sub>3</sub>I even in the high vacuum TEM observation (Fig. S1 and Fig. 4). In addition, the oxygen concentration is extremely low in the glove box (less than 0.01 ppm), so the effect of oxygen on the photodegradation of MAPbI<sub>3</sub> film can be ignored. In order to characterize the light illumination effect on the degradation of PbI<sub>2</sub>, the as-prepared precursor solution with PbI<sub>2</sub> single crystal nanoplates was dropped and dried on the Cu microgrids, then they were illuminated by the 50 W LED light for different times (in a glove box with Ar gas protection). After that, the samples were put into the TEM for observation.

Film Characterization. The optical absorption spectrum was measured by an ultraviolet-visible near-infrared spectrophotometer (UV-Vis) (Hitachi, UH-4150). The crystallographic properties of the perovskite film were characterized by using an X-ray diffractometer (BRUKER, D8 ADVANCE) at room temperature with monochromatic Cu K<sub>a</sub> radiation ( $\lambda = 0.154$  nm). A scanning electron microscope (FEI Quanta 200) operated at 5 kV was used to characterize changes in surface morphology of the film. An X-ray photoelectron spectroscope (Thermo Fisher, ESCALAB 250Xi) was used to characterize the chemical and electronic states of elements using Al K<sub>a</sub> radiation generated from a monochromated X-ray source, the beam diameter is about 360 µm.

**TEM Observation.** A FEI Tecnai-T20 transmission electron microscope (TEM) with an accelerating voltage of 200 kV was used for *Quasi-in situ* TEM observation and selected area electron diffraction analysis. The *in situ* TEM observation for the heating effect on the MAPbI<sub>3</sub> film is operated on a Gatan heating holder. A FEI Titan-G2 60-300 Cs-corrected transmission electron microscope with an accelerating voltage of 300 kV was used to take the scanning transmission electron microscopy-high angle angular dark field (STEM-HAADF) images. As an attachment of the FEI Titan-G2 TEM, an Xray energy dispersive spectrometer with four silicon drift windowless detectors (Super-EDX) was used to take element mapping images. The energy resolution of the Super-EDX was at 137 eV. The excited characteristic  $M_{\alpha}$  X-ray from Pb (2.342 keV) and  $L_{\alpha}$ X-ray from I (3.937 keV) were detected for element mapping, respectively.



**Figure S1.** HAADF images and the corresponding EDS detection of the different elements on the light-soaked MAPbI<sub>3</sub> film, showing two different I-rich lumps adhered on the surface of perovskite film.



**Figure S2**. Effects of the spin coating speed and precursor solution concentration on the morphology and thickness of perovskite films. (a-c) TEM images of the as-prepared perovskite films with different spin coating speed of 3000, 4000, 5000 rpm, while the concentration of the precursor solution keeps to be 1 M. (d-f) TEM images of the as-prepared perovskite films with different precursor solution concentration of 0.6, 1.0, 1.6 M, but the spin coating speed is same of 4000 rpm. Obviously, the TEM images (b) and (e) are with suitable film thickness and quality for TEM observation. So, the optimal spin coating speed and precursor solution concentration to prepare perovskite film should be operated at 4000 rpm and 1 M.



**Figure S3.** Atomic-resolution HAADF images of the  $Pb@PbI_{2-x}$  nanoparticles, from which we can see that the shell of the nanoparticles is mostly with an amorphous structure. (a) HAADF image of the  $Pb@PbI_{2-x}$  nanoparticle. (b, c) The corresponding Fourier Transform (FT) patterns of image (a) from the core (area I) and the shell (area II), respectively. (c) HAADF image of another  $Pb@PbI_{2-x}$  nanoparticle, and (e, f) are the corresponding FT patterns from the core (area III) and the shell (area IV), respectively.



**Figure S4.** TEM characterization of a single crystal  $PbI_2$  nanoplate. (a) HAADF image and EDS mappings of the pristine  $PbI_2$  nanoplate, which is with the uniformly elementary distribution of Pb and I. (b, c). Atomic-resolution HAADF images of the single crystalline  $PbI_2$  nanoplate, the selected area electron diffraction (SAED) pattern (inset in b) and the fast Fourier transform (FFT) image (inset in c) show the projection direction along [001].



**Figure S5.** (a) HAADF image and EDS mappings of the crystalline PbI<sub>2</sub> nanoplate after photodegradation for 48 h, which clearly show the Pb<sup>0</sup>-enriched cores to be surrounded by the Pb-I mixed shells (as the form of Pb<sup>0</sup>@Pb-I core-shell nanostructure). (b) SAED pattern corresponding to (a), showing the coexistence of metallic Pb<sup>0</sup> and crystalline PbI<sub>2</sub>, moreover there is an epitaxial orientation relationship between the metallic Pb core and the crystalline PbI<sub>2</sub> shell ([111]<sub>Pb</sub> // [001]<sub>PbI2</sub>; (-220)<sub>Pb</sub> // (110)<sub>PbI2</sub>). (c) The HAADF image selected from the purple square area of (a). Insets show the NBD patterns from the red (top image) and blue (bottom image) cycle areas in (c). (d) Atomic-resolution HAADF image of the Pb<sup>0</sup>@PbI<sub>2</sub> core-shell nanoparticles, showing the shell is with the hexagonal PbI<sub>2</sub> crystal structure, and the core is with cubic Pb<sup>0</sup> phase. After storage the sample in dark for 48 hours, such a Pb<sup>0</sup>@PbI<sub>2</sub> core-shell nanostructure still exists.