Enhanced Carrier Lifetimes of Pure Iodide Hybrid Perovskite via Vapor Equilibrated Re-Growth (VERG)

B. Selin Tosun, Hugh W. Hillhouse*
Department of Chemical Engineering and Molecular Engineering and Sciences Institute
University of Washington, Box 351750, Seattle, WA 98195–1750, USA.

Supporting Information

Materials and Methods:

Fabrication of Scanning Electron Microscope and X-Ray Diffraction samples: Both scanning electron microscope (SEM) and x-ray diffraction samples are deposited on F-doped SnO_2 (FTO, purchased from Sigma-Aldrich TEC 15) coated glass substrates. The FTO coated substrates are cleaned by ultra-sonication in acetone, de-ionized water, and isopropanol; then by 1 hour of oxygen plasma to remove the remaining contaminations prior to the TiO_2 sputtering. TiO_2 film is deposited using a Lesker Sputterer Model Lab18 under 1 x 10^{-6} Torr with Ar^+ plasma. A continuous, columnar grained, 50 nm thick TiO_2 film is formed after 1 hour of deposition. These TiO_2 coated FTO-glass substrates are also cleaned by ultra-sonication in acetone, de-ionized water, and isopropanol; then by 1 hour of oxygen plasma prior to the perovskite depositions.

Fabrication of Time-Resolved Photoluminescence Samples: The time resolved photoluminescence samples are prepared on 2 mm thick fused silica substrates. The silica substrates are cleaned by ultra-sonication in acetone, de-ionized water, and isopropanol; then by 1 hour of oxygen plasma to remove the residual organic contaminations similar to the other characterization samples prior to the perovskite depositions.

Methyl Ammonium Iodide Preparation: The methyl ammonium iodide has been prepared according to the previous recipes published in the literature.[18] CH_3NH_3I (MAI) is synthesized by

adding ~28 mL of CH_3NH_2 (MA) to 30 mL of HI in a round-bottom flask at room temperature and mixed at room temperature for 4 hours. The MAI powder is achieved by evaporation at 60 °C using a rotary-evaporator. This first batch of MAI powder is mixed thoroughly to dissolve in ethanol, precipitated by adding diethyl ether to the solution, and then the MAI powder is dried in a vacuum oven kept at 60 °C overnight.

$MAPbI_3$ and $MAPbCl_xI_{3-x}$ Film Formation: We used two deposition methods: (1) the conventional two-step solution based deposition and a new method that is based on thermal evaporation of the PbI_2 or $PbCl_2$ followed by spin coating of a MAI solution to form the hybrid perovskite layer. PbI_2 powder is purchased from Alfa Aesar, 99.9985 % metal basis; and $PbCl_2$ anhydrous beads are purchased from Sigma Aldrich, 99.999 % metal basis. The conventional two-step deposition recipe is taken from Burschka et.al.[18] The 462 mg/mL of PbI_2 (~ 1 M) is prepared in *N,N-dimethylformamide* by stirring on a hot plate (70 °C) over-night. The PbI_2 solution is deposited on the substrates by spin coating at 1500 rpm for 30 sec, followed by a short hot plate (at 70 °C) treatment to evaporate the residual solvent in a glove box using N_2 inert atmosphere. For the thermal evaporation method, the cleaned substrates are coated with approximately ~100 nm PbI_2 and $PbCl_2$ (in equal moles of Pb ions). The film evaporation is conducted at pressures as high as 1×10^{-4} mbar with high rate of reproducibility, which indicates that the thermal evaporation method followed by a solution based spin coating is highly tolerant which does not require the expensive high vacuum levels and does not impede the cost-effectiveness. Electron micrograph of the deposition PbI_2 films are given in supporting information, figure SI-1. Later, for both perovskite deposition methods, an approximately 30 μL of MAI in IPA is dropped on the PbI_2 or $PbCl_2$ film, soaked for 3 minutes, and spinned at 1500 rpm for 30 seconds. This is followed by an annealing step at 90 °C on hot plate for 30 minutes.

This MAI soaking and annealing step is repeated three times. One observation was, while the PbI_2 films turns very dark even during the soaking, the $PbCl_2$ samples changed their color to darker shades after annealing on the hot plate. This agrees with the slow reaction and formation of the intermediate $CH_3NH_3PbCl_3$ phase as indicated in references 13 and 15. Half of the same batch samples are inserted in an autoclave for VERG treatment, and the other half is rinsed with clean IPA three times, and immediately encapsulated by spin coating 40 mg/mL PMMA dissolved in chlorobenzene at 1000 rpm for 30 seconds to eliminate the sample degradation during characterization. The scanning electron micrographs of the respective $MAPbCl_xI_{3-x}$ are given in figure SI-2.

Vapor Equilibrated Re-growth (VERG): $MAPbI_3$ and $MAPbCl_xI_{3-x}$ perovskite samples are placed in ~100 mL autoclave (Model # 302AC-T304-060501) purchased from Parr Instrument Company (Moline, Illinois U.S.A.) using PTFE (tetrafluoroethylene) liner (Model # 762HC7HA) and rapture disc (Model # T304-080201) with 140 mg MAI, and sealed tightly in a glove box that is kept under N_2 inert atmosphere. The autoclaves are placed in a preheated (~110 °C) furnace, and kept there for approximately 48 hours. After 48 hours, the autoclaves are transferred back into glove box, left for cooling overnight. Prior to opening the autoclaves, the spin coater is rinsed with DMSO and IPA thoroughly, and the ambient atmosphere in the glove box is recycled and refreshed for approximately 15 minutes to eliminate any cross contamination problems and decomposition of the perovskite film. We observed that when DMSO containing atmosphere is not recycled in the glove box, the perovskite samples immediately decompose with spinning. Immediately after opening the autoclaves, the perovskite films are rinsed with clean IPA three times and coated with PMMA as described before.

All samples are stored in glove box under N_2 inert atmosphere and wrapped with aluminum foil to eliminate any degradation or changes in the material by light soaking and ambient atmosphere.

Characterization: The XRD spectra of the prepared films is measured using a Bruker AXS D8-Discover diffractometer (Cu K_α, λ=1.5406 Å) and GADDS software to angle-integrate the acquired diffraction pattern in the 2D detector. The micrographs are obtained using a FEI Sirion XL30 scanning electron microscope. The time-resolved photoluminescence measurements are conducted using the time-correlated single photon counting method. Room temperature samples are photo-excited using a 481 nm (250 kHz repetition rate) pulsed diode laser at 1.2 nJ/cm^2/pulse fluence. A reflecting material, Spectrolon, is used for the prompt calibrations in the time-resolved photoluminescence measurements. Samples and calibrations are conducted at a 60° incoming excitation angle to the sample normal. The emission spectrum is filtered using a long pass filter for 532 nm and below. The peak point of the photoluminescence from the samples, ~765 nm (1.62 eV), is used for the decay acquisitions.

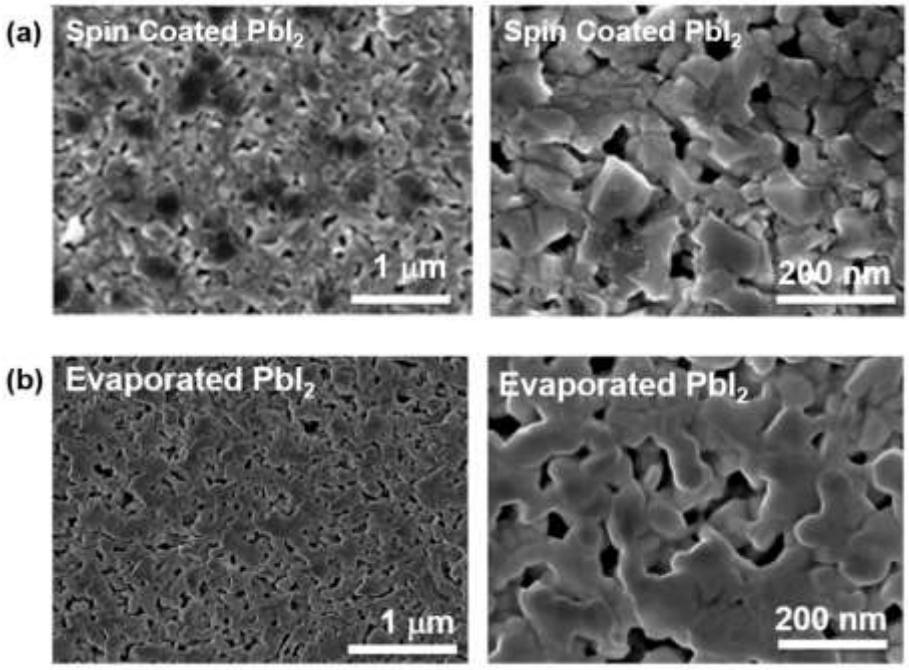

Figure SI-1: The top-view electron micrographs of **(a)** spin coated solution deposited PbI_2, **(b)** thermally evaporated PbI_2 films.

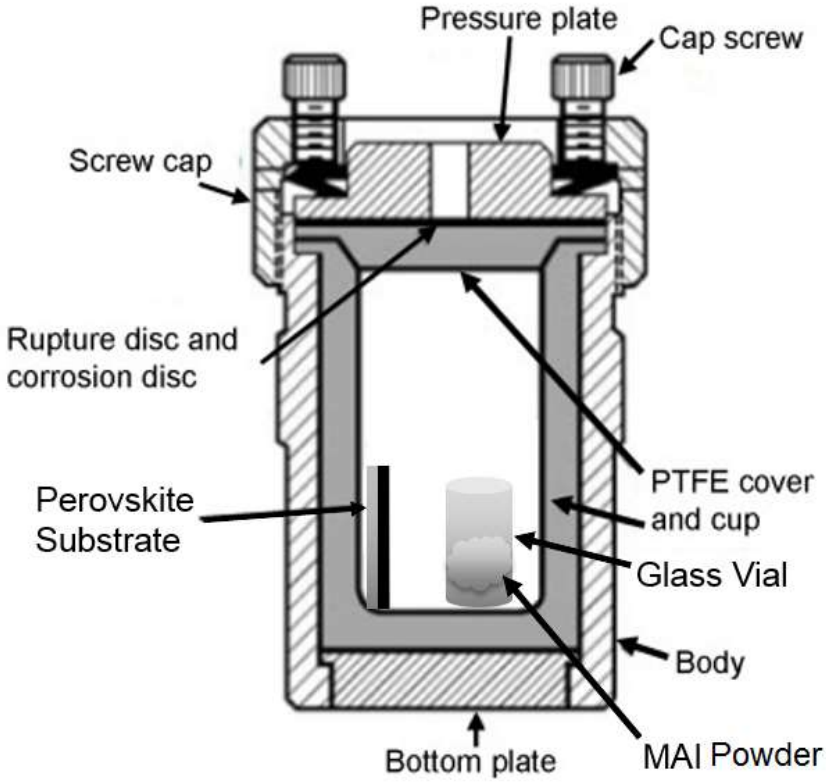

Figure SI-2: Detailed cross sectional schematic of the autoclaves used during VERG treatment.

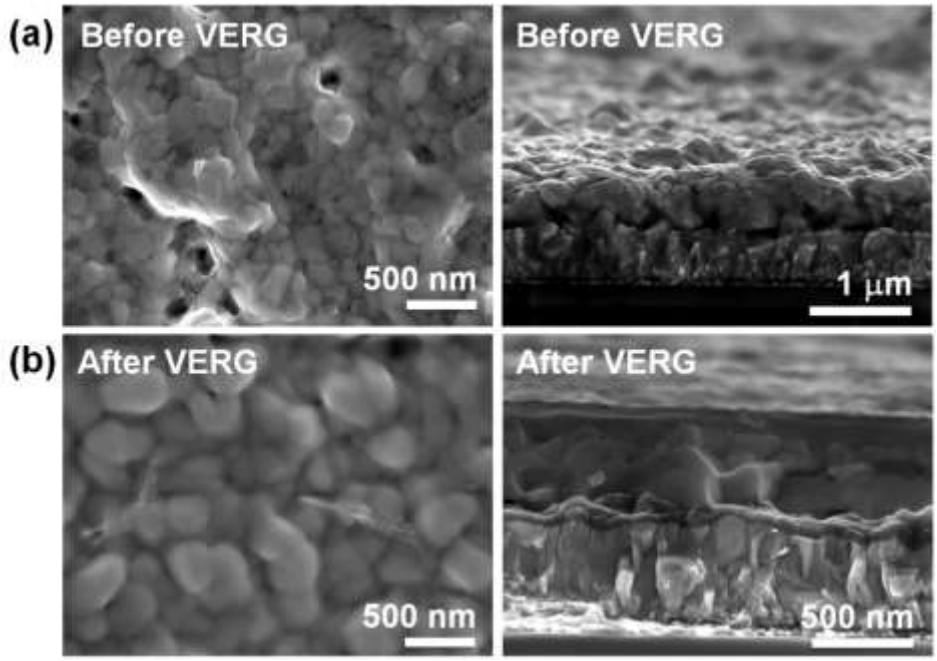

Figure SI-3: Top and cross-sectional electron micrographs of $MAPbCl_xI_{3-x}$ **(a)** before VERG treatment and, **(b)** after VERG treatment.