Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting information

Cooperative kinetics of depolarization in $CH_3NH_3PbI_3$ perovskite solar cells

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Device fabrication

Sing-MA/I-Cl: The Fluorine-doped tin oxide substrates, FTO, (Pilkington TEC15, ≈15 Ω/sq resistance) were etched with Zn powder and HCl to obtain the desired electrode design. The substrates were thoroughly cleaned with soap (Hellmanex), deionized water and ethanol, followed by sonication in a mixture acetone: water (v/v = 1:1) and ozone cleaning. A ≈50 nm-thick TiO_2 compact layer was deposited onto FTO by aerosol spray pyrolysis at 450 ºC using a solution of titanium diisopropoxide bis(acetylacetonate) (75% in 2-propanol) diluted in ethanol (1:39, v/v) and oxygen as carrier gas. For the TiO_2 mesoporous electrodes a solution of 20-nm-sized paste (Dyesol, 90-T) diluted in terpineol (1:3, v/v) was spin-cast for 30 s at 4000 rpm and sintered at 450 ºC in air for 30 min, yielding a 200 nm-thick nanostructured film. The $MAPbI_{3-x}Cl_x$ films grown by one step methodology were prepared as reported by Snaith and co-workers.[1] In this procedure, the precursor solution was a 3:1 molar ratio mixture of MAI and $PbCl_2$ dissolved in DMF at 40%. PS films were deposited onto the mesoporous electrode by spin coating at 2000 r.p.m for 30s. The films were annealed at 100 ºC for 10 min. The deposition was carried out in the glovebox. Finally the substrates were placed in a furnace at 100 ºC under air stream, where the color of the film changed from yellow to dark brown. The hole transport solution was deposited by spin-coating of a Spiro-MeOTAD solution prepared by dissolving 72.3 mg of Spiro-MeOTAD (Merk), 28.8 μL of 4-*tert*-butylpyridine (Aldrich, 96%) and 17.5 μL of lithium bis(trifluoromethanesulfonyl)imide (LITFSI, Aldrich, 99.95%) solution (520 mg

LITSFI in 1 mL acetonitrile (Sigma-Aldrich, 99.8%)) in 1 mL of chlorobenzene (Sigma- Adrich, 99.8%). The HTM was deposited on top of perovskite substrates, by spin coating at 4000 r.p.m. for 30 s outside of the glovebox. Finally, a 60 nm-thick gold counter electrode was deposited by thermal evaporation.

Seq-MA/I: CH_3NH_3I was synthesized by reacting 0.273 mol of CH_3NH_2 with 0.223 mol of aqueous HI. The reactions were carried out in a round bottom flask for 2 h. The resulting CH_3NH_3I was collected by evaporating the solvent using a rotary evaporator at 50 ºC. The collected powder was washed with diethyl ether five times and dried in a vacuum oven for more than 12 h. FTO glasses (Pilkington, TEC-8, ≈8 Ω/sq) were cleaned by UV-ozone treatment for 15 min. The FTO substrates were further cleaned by detergent and sonication in ethanol bath for 15 min. The TiO_2 compact layer was deposited by spin-coating a solution of 0.15 M titanium diisopropoxidebis(acetylacetonate) (Aldrich, 75 wt.% in isopropanol) in 1-butanol (Aldrich, 99.8%) at 2000 r.p.m for 40 s, and dried on a hot plate at 125 ºC for 5 min. A 150 nm-thick mesoporous TiO_2 layer was formed by spin-coating the 40 nm average sized TiO_2 paste diluted with ethanol (1.4g TiO_2 paste in 10 mL ethanol) at 2000 r.p.m, and annealed at 550 ºC for 1 h. The mesoporous TiO_2 layer was further treated with 20 mM aqueous $TiCl_4$ (Aldrich, >98%) solution at 70 ºC for 10 min, which was annealed at 500 ºC for 30 min. 30 µL of 1 M PbI_2 (Aldrich, 99%) in dimethylformamide (DMF) (Sigma-Aldrich, 99.8%) solution was spin-coated on the mesoporous TiO_2 layer at 500 rpm for 5 s and 6000 rpm for 20 s, and immediately placed on hot plate at 40 ºC for 3 min and at 100 ºC for 10 min. The PbI_2 coated film was immersed in a 51.1 mM solution of CH_3NH_3I in 2-propanol (Sigma-Aldrich, 99.5%). The dipping time was 1 min. The films were spun at 500 rpm for 5s, 1500 rpm for 10s and 3000 rpm for 20 s for drying. After completion of the spin-coating cycle, the $CH_3NH_3PbI_3$ coated film was heated at 40 ºC for 3 min and 100 ºC for 10 min. To remove the excess of reagents, the films were washed with 2-propanol and dried on a hot plate for 5 min at 100 ºC. On the top of the perovskite, the hole transport layer was deposited by spin-coating a Spiro-MeOTAD solution prepared by dissolving 72.3 mg of Spiro-MeOTAD (Merk), 28.8 µL of 4-*tert*-butylpyridine (Aldrich, 96%) and 17.5 µL of lithium bis(trifluoromethanesulfonyl)imide (LITFSI, Aldrich, 99.95%) solution (520 mg LITSFI in 1 mL acetonitrile (Sigma-Aldrich, 99.8%)) in 1 mL of chlorobenzene (Sigma- Adrich, 99.8%). The Spiro-MeOTAD solution was spin-coated at 4000 r.p.m for 20 s. Finally, the gold contact was deposited by thermal evaporation at rate of 1 A/s.

MA/I-Carbon:. Mesoscopic $CH_3NH_3PbI_3/TiO_2$ solar cells were fabricated by the following process.[2, 3] FTO glass substrates (CSG Holding Co. Ltd) with high transparency in the visible range were patterned using Zn and 2M HCl aqueous solution. After cleaning the glass substrate with deionized water, ethanol and acetone using an ultrasonic bath for 15 min, successively, a compact TiO_2 layer was prepared by aerosol spray pyrolysis deposition of titanium di-isopropoxide bis(acetyl acetonate) solution in ethanol on the glass substrate. Then a 0.8 μm porous TiO_2 layer, a 0.8 μm ZrO_2 spacer layer, and a 10 μm carbon CE were screen printed on the substrate layer by layer (the slurries were prepared following previous report).[4] The TiO_2 layer was sintered at 500 °C for 30 min, and the ZrO_2 and carbon layer were sintered at 400 °C for 30 min. The synthesis of $CH_3NH_3PbI_3$ and deposition on the monolithic device was carried out by drop-coating of a 40 wt% precursor solution onto the carbon black/graphite layer. Upon drying at 100 °C for 10 min, the films darkened in color, indicating the formation of $CH_3NH_3PbI_3$ in the solid state.

Device characterization.

The efficiencies were obtained through the *J/V* curves, which were recorded under AM 1.5 G (100 $mW \cdot cm^{-2}$) using a solar simulator (ABET Technologies Sun 2000) coupled with a Keithley 2400, previously calibrated with an NREL-certified Si solar cell. All the *J/V* measurements were performed by using a shadow mask of 0.1 cm^2.

Small perturbation transient photovoltage (TPD) experiments were performed by using a Nd:YAG pulsed laser (pulse duration 4-6 ns), model Brilliant (Quantel), coupled to an optical parametric oscillator (OPO), model Vibrant (Opotek), as excitation light source (650 nm). The power intensity of the laser was adjusted by using neutral density filters to afford a small perturbation of the cell photovoltage (≈ 20 mV). A white light halogen lamp and neutral density filters were employed to vary the back illumination level. The photovoltage decays were monitored by using a digital oscilloscope, model TDS5000B (Tektronix).

Results

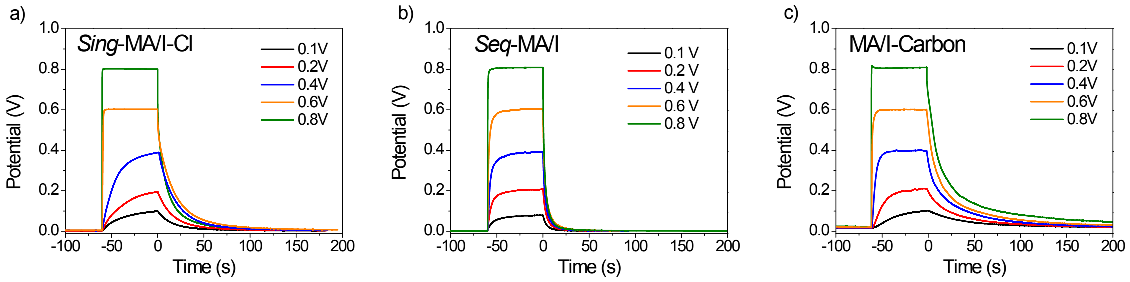

Fig. SI 1. Large perturbation V_{oc} decays at different illumination levels for the three different perovskite devices.

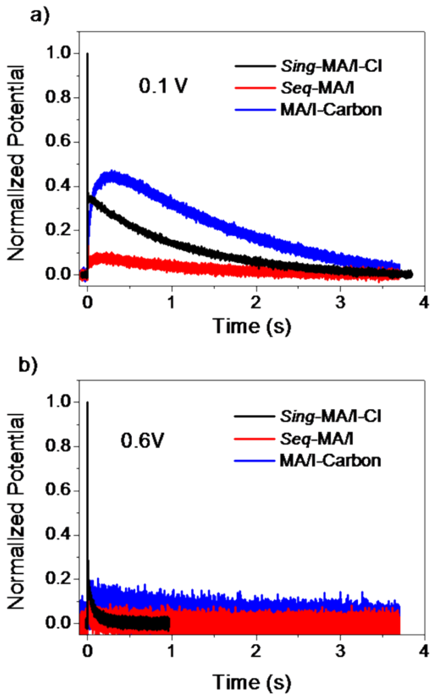

Fig. SI 2. View of second timescale of normalized small perturbation transient photovoltage decays (TPD) of three different perovskite based devices (*Sing*-MA/I-Cl, *Seq*-MA/I and MA/I-Carbon) at two different bias illumination levels; 0.1 V and 0.6 V respectively.

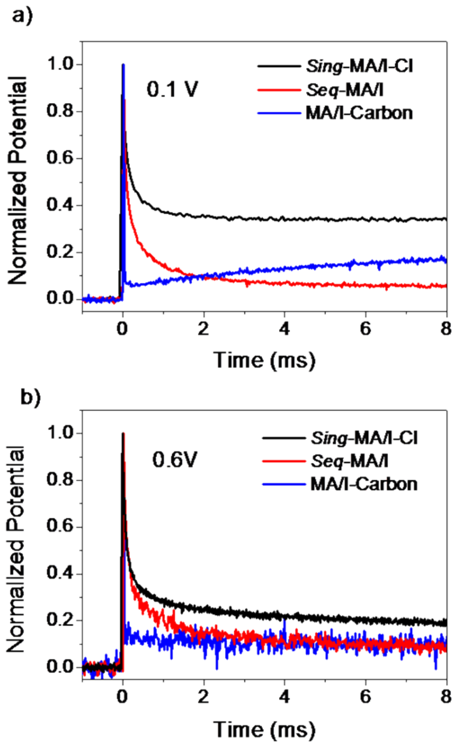

Fig. SI 3. View of ms timescale of the normalized small perturbation transient photovoltage decays (TPD) of three different perovskite based devices (*Sing*-MA/I-Cl, *Seq*-MA/I and MA/I-Carbon) at two different bias illumination levels; 0.1 V and 0.6 V respectively.

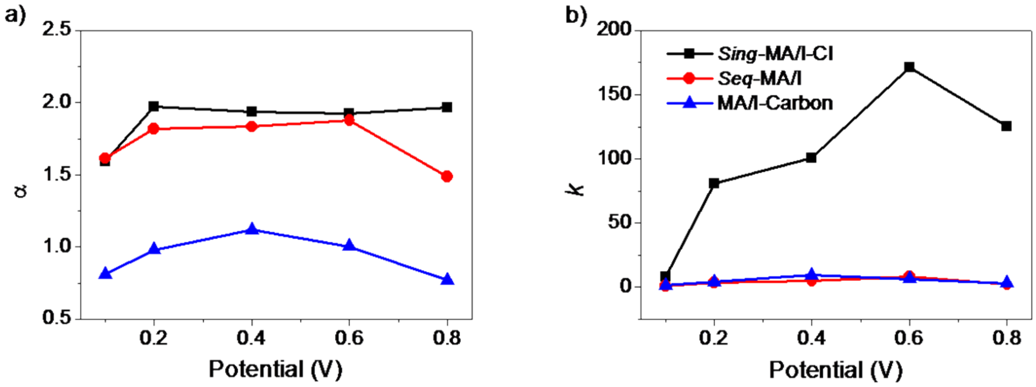

Fig. SI 4: Parameters of the power law domain in the instantaneous relaxation time τ_{ir} of Fig. 2, according to $\tau_{ir} = k^{1/\alpha} V^{-1/\alpha} / \alpha$. (a) Exponent and (b) prefactor.

References.

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