Charge Accumulation, Recombination, and Their Associated Time Scale in Efficient (GUA)$_x$(MA)$_{1-x}$PbI$_3$-Based Perovskite Solar Cells

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Supporting Information

ABSTRACT: Here, we study the influence of guanidinium (GUA) ions on the open-circuit voltage ($V_{oc}$) in the (GUA)$_x$(MA)$_{1-x}$PbI$_3$ based perovskite solar cells. We demonstrate that incorporation of GUA forms electronic and ionic accumulation regions at the interface of the electron transporting layer and perovskite absorber layer. Our electrochemical impedance spectroscopy results prove that the formed accumulation region is associated with the enhanced surface charge capacitance and photovoltage. Furthermore, we also demonstrate the influence of the GUA ions on the enhanced interfacial and bulk electronic properties due to more efficient charge transfer between the bulk and interfaces and the reduced electronic defect energy levels.

INTRODUCTION

Over the last decade, organometal halide perovskites have attracted significant attention as promising materials for next-generation thin film photovoltaic (PV) technology. The appealing physicochemical properties of these compounds such as high carrier mobility and diffusivity, low exciton binding energy, tunable bandgap, long charge-carrier diffusion length, and tolerance to defects provide a broad application horizon from perovskite solar cells (PSCs) to light emitting diodes or lasers. Despite the great achievements in the efficiency of the PSCs, the optoelectronic properties of these devices are mostly influenced by the phenomena occurring at the interfaces between the perovskite layer and either the electron transporting layer (ETL) or the hole transporting layer (HTL). A recent report on the surface recombination and collection efficiency in PSCs has demonstrated that the nonradiative recombination at the interface (ETL/perovskite) plays a crucial role in the $V_{oc}$ and charge transfer phenomenon. The surface and bulk recombinations in the framework of Shockley Read Hall can occur in two fractions: (i) a doped semiconductor, in which the doped material undergoes rapid recombination due to the presence of excess carriers and (ii) an intrinsic semiconductor, in which the recombination is delayed, and this could be certainly beneficial for achieving higher photovoltage. Small perturbation techniques, such as intensity-modulated photocurrent and photovoltage spectroscopy (IMPS and IMVS), and frequency domain measurements are able to efficiently extract the dynamic operating parameters of solar cells. These characterization tools have been widely employed for evaluation of...
However, incorporation of 25 mol % GUA reduces the PCE to 16.0 ± 0.5% for MAPbI₃ and (GUA)₀.₁₀(MA)₀.₉₀PbI₃ devices. (b) Capacitance–frequency (C–f) measurements at zero bias under dark conditions for MAPbI₃ and (GUA)₀.₁₀(MA)₀.₉₀PbI₃ devices.

Figure 1. (a) Current–voltage characteristics measured under 1 Sun illumination Air Mass 1.5G in the backward direction for MAPbI₃, (GUA)₀.₁₀(MA)₀.₉₀PbI₃ and (GUA)₀.₂₅(MA)₀.₇₅PbI₃ devices. (b) Capacitance–frequency (C–f) measurements at zero bias under dark conditions for MAPbI₃ and (GUA)₀.₁₀(MA)₀.₉₀PbI₃ devices.

The IMPS response permits the quantization of the charge carrier lifetime and $V_{oc}$ of the PSCs compared to the pristine MAPbI₃ based devices. However, the origin of such improvements and the charge dynamic mechanism have not been widely investigated.

In this work, we investigate the role of GUA in charge carrier and recombination dynamics in fully working (GUA)$_x$(MA)$_{1−x}$PbI$_3$-type PSCs. Our analysis using small perturbation techniques reveals that the incorporation of GUA causes electrode polarization at the interface, which could be responsible for the prominent hysteresis in GUA-based PSCs. The IMPS response permits the quantization of the charge transport phenomena, which affects the photogenerated charge collection. Furthermore, we demonstrate that the incorporation of GUA causes excess electronic charge accumulation at the interface, which is responsible for the observed enhancement in photovoltage. These results provide a pathway to achieve efficient solar cells along with an in-depth working mechanism.

**RESULTS AND DISCUSSION**

To study the effect of GUA on the photovoltaic (PV) properties of the PSCs as also reported in the literature, we fabricated a batch of solar cells with the following architecture: FTO/compact TiO₂/mesoporous TiO₂/perovskite/SpiromOMeTAD/Au (more details can be found in the Experimental Section). Figure 1a shows the current–voltage (J–V) characteristics of the best performing (GUA)$_x$(MA)$_{1−x}$PbI$_3$ PSCs (where $x = 0, 0.10$, and 0.25) measured under reverse bias and Air Mass 1.5G (AM1.5G) (the statistic histogram of PV parameters are shown in Figure S1). We found that the replacement of 10 mol % MA with GUA increases the $V_{oc}$ and $J_{sc}$ over 30 mV and 1.2 mA cm$^{-2}$, respectively. As a result, the PCE of the prepared devices increases from 17.5 ± 0.5% for MAPbI₃ to 18.0 ± 0.5% for (GUA)$_{0.10}$(MA)$_{0.90}$PbI₃ PSCs. However, incorporation of 25 mol % GUA reduces the PCE to 16.0 ± 0.5% due to a decrease in the FF and $V_{oc}$. These data are consistent with our previous work, where the introduction of a small amount of GUA into the perovskite composition increased the $V_{oc}$ and PCE. The MAPbI₃ and (GUA)$_{0.10}$(MA)$_{0.90}$PbI₃ PSCs with a PCE of 17.5 ± 0.5% were employed to study the role of GUA in the hysteresis effect and charge carrier and recombination dynamics.

**Hysteresis Effect.** Figure S2 shows the hysteresis curves of the MAPbI₃ (reference) and (GUA)$_{0.10}$(MA)$_{0.90}$PbI₃ PSCs. We used the following formula to calculate hysteresis indices (HIs) of the PSCs:

$$HI(\%) = \left(\frac{PCE_{backward} - PCE_{forward}}{PCE_{backward}}\right) \times 100$$

From the J–V result, the HI was calculated to be 18.5% for the reference device and 16.8% for the (GUA)$_{0.10}$(MA)$_{0.90}$PbI₃ PSC. Despite the favorable properties of GUA cations such as zero dipole moment and hydrogen bonding capability, the hysteresis is more prominent in GUA-based devices. To rationalize the observed hysteresis feature, we measured the capacitance–frequency (C–f) responses at zero bias under dark conditions (Figure 1b). The distinct features in the low and high frequencies of the C–f response are clearly distinguishable. A constant capacitance element in frequency $>10^3$ Hz for the reference and (GUA)$_{0.10}$(MA)$_{0.90}$PbI₃ is associated with the dielectric response of the absorber material, while the capacitance in the low-frequency region has originated from the ionic characteristics. It is clear that due to the presence of GUA cations in the perovskite, which have a larger size (278 pm) and weaker bonding ability than MA cations, GUA cations can pile up near the interfaces and distribute the local electric field, leading to a higher capacitance in the low-frequency range. By assuming only the electrostatic interaction at room temperature, the space charge densities of $6.04 \times 10^{17}$ and $1.1 \times 10^{18}$ and were obtained for the reference and (GUA)$_{0.10}$(MA)$_{0.90}$PbI₃, respectively. The accumulation of excess GUA ions in the (GUA)$_{0.10}$(MA)$_{0.90}$PbI₃ PSCs increases the capacitance in the low-frequency region and leads to the current hysteresis. Moreover, the ion movement under the applied bias amplifies the hysteresis by screening the internal electric field at the interface between TiO₂ and perovskite.

**Charge Transport and Time Responses.** To elucidate the influence of GUA on the transport properties of the PSCs, the intensity-modulated photocurrent spectroscopy (IMPS) under constant light intensity was performed (Figure 2). The IMPS response for both PSCs shows distinguishable characteristics in the low and high frequency regions and exhibits...
different time constants. We analyzed the frequency arcs according to the established transport mechanism for the TiO2/perovskite interface, TiO2 ETL, and the perovskite layer.35,36 The slow response time in the low-frequency region is dominated by the transport process in the TiO2 or TiO2/perovskite interface, while the higher frequency of the arc from 1 to 10 Hz (faster transport) is ascribed to the perovskite layer.

The low-frequency component (800 mHz to 1 Hz) of MAPbI3 is dominated by the transport process in the TiO2 or TiO2/perovskite interface, while the higher frequency of the arc from 1 to 10 Hz (faster transport) is ascribed to the perovskite layer. The low-frequency component (800 mHz to 1 Hz) of MAPbI3 correspond to the time constant of 0.031±1 s. However, the low-frequency component of the (GUA)0.10(MA)0.90PbI3 device slightly shifts toward a higher frequency, which corresponds to the lower time constant, suggesting the modification in the interfacial electrical response. To have a better understanding of this phenomenon, we further examined the device with a higher amount of GUA (25%). As expected, the low-frequency component in the (GUA)0.25(MA)0.75PbI3 device shifts toward a higher frequency as compared to the (GUA)0.10(MA)0.90PbI3 device. In contrast, the high frequency responses (shorter time constant) centered at 7 Hz are almost similar in all of the investigated PSCs. The diffusion coefficient $D_n = d^2/2.35 \tau_m$, where $D_n$ is the diffusion parameter, $d$ is the thickness of the perovskite absorber layer, and $\tau_m$ represents the time constant, is calculated to be $1.23 \times 10^{-6}$ and $2.83 \times 10^{-6}$ cm$^2$ s$^{-1}$ for the reference and (GUA)0.10(MA)0.90PbI3 PSCs, respectively. The charge transport at the TiO2/perovskite interface can also be visualized by the current transient measurements near the short circuit condition as shown in Figure S3. The shorter decay time in the (GUA)0.10(MA)0.90PbI3 device confirms the faster charge transport at the TiO2/perovskite interface as compared to the reference device. From the IMPS and transient responses, we conclude that the GUA cations improve the charge transport and diffusion coefficient.

The pXRD patterns of (GUA)$_x$(MA)$_{1-x}$PbI$_3$ films (where $x = 0, 0.10$, and 0.25) are shown in Figure S4, which are in good agreement with previous reports.35,36 Figure S5a shows the UV-visible spectra of the perovskite films with different amounts of GUA cations. As seen, the perovskite film with 10% mol GUA has better absorption than the reference sample. Also, the photoluminescence (PL) emission of this sample is much stronger than the others (see Figure S5b). The observed better optical properties of (GUA)$_0.10$(MA)$_{0.90}$PbI3 perovskite together with the improved charge transfer properties could be the main reasons for the improved current density in these PSCs. Additionally, we study the morphology of the corresponding perovskite films using scanning electron microscopy (SEM) and atomic force microscopy (AFM) techniques, as shown in Figures S6 and S7. From the SEM images, the GUA-based perovskite films have different morphology with slightly lower grain sizes compared to pure MAPbI3. As mentioned in the literature,25 the GUA-based perovskites have large crystal domains containing small grain sizes, which can affect the optoelectronic properties of the perovskite films. In fact, the AFM results show similar morphology and grain size to the SEM images. We found that the surface roughness of the (GUA)$_0.10$(MA)$_{0.90}$PbI3 perovskite film (21 ± 6 nm) is lower than that of the pure MAPbI3 sample (34 ± 9 nm). This result indicates that the GUA-based perovskite has a smoother contact than the reference sample with the HTL, suggesting better charge transport at this interface with possibly lower recombination.37,38

To gain insight into the band diagram of the GUA-based perovskite, ultraviolet photoelectron spectroscopy (UPS) measurement was performed (Figure S8). The extracted data from the UPS curves are summarized in Table S2. Based on these values, we draw the band diagram of the perovskite films, as shown in Figure S8c. We found that by introduction of GUA cations into the perovskite composition, the energy levels of both valence and conduction bands become deeper and upon increasing the amount of GUA, the energy levels are further enhanced. We observed this enhancement for the Fermi level as well. Interestingly, these results indicate that addition of the GUA cations makes the perovskite film more p-type. This could help for a better charge transfer between the perovskite and TiO2 ETL, due to the presence of a stronger p-type.
electrical field at the interface and also a closer conduction band of GUA-based perovskites to that of the TiO2 ETL.38 However, if we look at the interface between the perovskite and spiro HTL, it is clear that pure MAPbI3 perovskite shows better charge transfer (hole) with respect to the spiro HTL, due to its closer valence band to that of the HTL. Notably, by increasing the amount of GUA to 25 mol %, the valence band of the perovskite film increases to 5.5 eV, which is much deeper than that of the spiro HTL, resulting in more difficult hole transfer and thus more interfacial recombination.

Charge Accumulation and Time Responses. The effect of GUA on the interfacial electronic charge accumulation properties were further studied by measuring the capacitance versus frequency response under illumination at different applied biases from knee voltages to the Voc of the PSCs. The C–f plot, shown in Figure 3, demonstrates that the capacitive element due to the surface charge accumulation (Cg) dominates at low frequency (∼1 Hz) and the capacitance due to the dielectric response of the perovskite thin film (Cf) predominates at high frequency (∼103 Hz). The low-frequency C–f plot (Figure 1b), assigned to the accumulation of ions and ionic space charge capacitance, exhibits values in the order of microfarad, which substantially increases to millifarad under illumination conditions, indicating that the interfacial capacitance is changed by the electronic phenomena (Figure 3).6,16,17 However, as the ionic capacitance under open-circuit conditions is limited by the Helmholtz capacitance, a higher value of Cg is obtained for (GUA)0.10(MA)0.90PbI3 as compared to that of the MAPbI3 device. On the contrary, the Cf value remains unchanged under illumination for both PSCs and is attributed to the dielectric characteristics of the perovskite film. This mechanism shows that the electronic accumulation is kinetically controlled by GUA ionic species. The buildup of electronic accumulation capacitance at the TiO2/perovskite interface follows the exponential voltage dependence by $C_i = \varepsilon\varepsilon_0/(2L_D) \exp(qV/2k_BT)$, where $(L_D = (\varepsilon_0\varepsilon_rk_BT/q^2P_0)$ is the Debye length and $q$ and $k_BT$ are the elementary charge and thermal energy, respectively.31,32,39

Recently, it was reported that a part of Voc in the PSCs has originated from the charge accumulation, while the other part of Voc has originated from band bending.40,41 In the case of the (GUA)0.10(MA)0.90PbI3 PSC, ion accumulation causes the formation of an accumulation zone, where upon illumination and under open-circuit conditions, photogenerated charges get accommodated and forms the photovoltage. To investigate the time response associated with the charge accumulation and dielectric phenomenon of the corresponding PSCs, the intensity-modulated photovoltage spectroscopy (IMVS)–derived time constant as a function of Voc was recorded for both PSCs and is shown in Figure 4a. One can easily calculate the time response by the inverse of frequency in the low and high frequency spectra of IMVS. The high frequency peak, assigned to the dielectric capacitance of the absorber layer, provides information about the carrier lifetime. The reference device exhibits a carrier lifetime of ∼4–5 μs, whereas the (GUA)0.10(MA)0.90PbI3 sample shows an enhanced charge-carrier lifetime of ∼6–7.5 μs, attributing to the lower charge recombination, which is in good agreement with the previous report.24 In line with a similar effect observed by the other authors,24,25 where the GUA enhanced the carrier lifetime and Voc of the PSCs24,25 the present study indicates that along with the enhanced carrier lifetime, the higher electronic accumulation at the interface also significantly contributes to the Voc.

To further understand the influence of GUA on the defect-state energy level of the perovskite films, the defect energy level and defect density of MAPbI3 and (GUA)0.10(MA)0.90PbI3 PSCs were investigated using thermal admittance spectroscopy (TAS), as shown in Figure 4b. TAS is a well-established technique to probe both shallow and deep defect energy levels with defect density on thin films.42–44 The defect energy level is calculated by using the expression, $\omega_0 = \beta T^2 \exp(-E_a/k_BT)$, where $E_a$ is the defect activation energy level and $\omega_0$ is the characteristic transition frequency related to the rate of carrier emission and capture in the defect states. The $E_a$ of the reference device is calculated as 0.40 eV, while a significantly lower $E_a$ of 0.22 eV was obtained for the (GUA)0.10(MA)0.90PbI3 PSC. The obtained defect energy levels are in accordance with the commonly quoted values in the literature and are potentially ascribed to iodine interstitials.43,44 The trap densities corresponding to the obtained $E_a$ can be calculated by using the expression of $N_t = (V_{th}/qW)(dC/d\omega)/(\omega/k_BT)$, where $V_{th}$ is built in potential, $W$ is the depletion width, $dC/d\omega$ is the derivative of capacitance with respect to the angular frequency. By considering the Gaussian distribution, the defect states are centered at 0.40 eV for the reference and at 0.22 eV for the (GUA)0.10(MA)0.90PbI3 PSCs. Moreover, an integrated defect density of $\sim10^{16}$ cm$^{-3}$ was obtained for both PSCs.
CONCLUSIONS

In conclusion, we have investigated the role of GUA in the charge carrier and recombination dynamics and their associated time responses in the (GUA)\(_x\)(MA)\(_{1-x}\)PbI\(_3\) PSCs. From the IMPS analysis and transient responses, we demonstrated that the addition of GUA improves the charge transport and diffusion coefficient. Lower charge recombination times of \(\sim 4\)–5 and \(\sim 6\)–7.5 \(\mu\)s for MAPbI\(_3\) and (GUA)\(_{0.10}\)(MA)\(_{0.90}\)PbI\(_3\) PSCs, respectively, were observed. We found that along with the enhanced carrier lifetime, the higher electronic accumulation at the interfaces also significantly contributes to the \(V_{oc}\) enhancement. In fact, the incorporation of GUA into the perovskite leads to an improved interfacial and bulk electronic properties due to better charge transport across the bulk and interface and lower electronic defect at energy levels.

EXPERIMENTAL SECTION

Materials. Guanidinium hydroiodide (TCI, 99.95%), methylammonium iodide (DyeSol), PbI\(_2\) (TCI, 99.99%), dimethyl sulfoxide (DMSO, 99.9%), chlorobenzene (95%), titanium(IV) isopropoxide (99.9%), 4-tert-butylpyridine (Sigma-Aldrich, 96%), and lithium bis(trifluoromethylsulphonyl)imide (Sigma-Aldrich, Li-TFSI, 95%) were used. The TiO\(_2\) paste (18 NRD) was purchased from Dyesol.

Solar Cell Device Fabrication. PSCs were fabricated according to our previously published paper. Briefly, GUAHI, MA-HI, and PbI\(_2\) precursors were dissolved in anhydrous DMSO (in corresponding molar ratios) at 60 °C together with vigorous stirring overnight to achieve GUA\(_x\)MA\(_{1-x}\)PbI\(_3\) solutions (\(x = 0, 0.10,\) and 0.25) with 1.4 M. Then, a two-step program was employed to deposit perovskite solutions, i.e., spin coating at 1000 and 6000 rpm for 10 and 20 s, respectively. To form perovskite, the antisolvent technique was used, and the substrates were annealed at 100 °C for 30 min in a dry air box. For the HTL, a solution of spiro-MeOTAD was prepared by dissolving lithium bis(trifluoromethylsulphonyl)imide (Li-TFSI) dissolved in acetonitrile (520 mg in 5 mL of a solution of tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)cobalt(III) bis(trifluoromethylsulphonyl)imide (FK 209) dissolved in acetonitrile (300 mg mL\(^{-1}\)), and 28.8 \(\mu\)L of tert-butylpyridine. Afterward, the HTL solution was spin-coated on the perovskite films at 4000 rpm for 20 s. Finally, the fabrication of the devices was completed by thermal evaporation of 80 nm-thick gold under high vacuum.

Film Characterization. PXRD diffractograms were recorded on an X Pert MPD PRO (Panalytical) diffractometer (Cu anode, \(\lambda = 1.54 \) 060 A\(_{0}\)) in an angle range of \(2\theta = 5\)–40° with a step of 0.02 degree. UV–vis spectra were recorded by a Varian Cary S and PL spectra using Fluorolog 322 (Horiba Jobin Yvon Ltd.). The morphology and smoothness of the films were studied using high-resolution scanning electron microscopy (ZEISS Merlin) and atomic force microscopy (AFM, NanoScope IIIa/Dimension 3100), respectively. UPS was employed to record the valence and Fermi levels of perovskite films using He I (21.2 eV) by AXIS NOVA (Kratos Analytical Ltd., U.K.).

Device Characterization. To measure the \(J–V\) curves, a light source (a 450 W Xenon lamp, Oriel) with an intensity of 100 mW cm\(^{-2}\) and a sunlight filter (Schott K113 Tempax, Praezisions Glas & Optik GmbH) were employed. The purpose of using a filter was to adjust the measurement according to the AM1.5G standard condition. \(J–V\) measurements were obtained by a Keithley (Model 2400) digital source meter upon applying external bias to the devices. A shadow mask with a black color was used to define the active area, which was 0.16 cm\(^2\) in our cases. To perform the electrochemical impedance spectroscopy characterization, a Bio-Logic SP-300 potentiostat together with a frequency response analyzer was used. For impedance measurement, the direct current (DC) bias range was varied from 0 to 0 to open-circuit voltage and the alternating current perturbation signal was set to 10 mV. The frequency was changed from 1 Hz to 100 kHz to monitor the device behavior. For IMVS and IMPS measurements, a Bio-Logic SP-300 potentiostat together with a frequency response analyzer was employed and 10% of the DC background illumination intensity was set for modulation current. The galvanostatic mode of Bio-Logic SP-300 with a cool white-light-emitting diode array (12 V, 10 W) as the light source was employed here.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01701.

- Statistic histogram; \(J–V\) hysteresis; current transient measurement; pXRD patterns; UV–vis and PL spectra; SEM images; AFM images; and UPS graphs (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

1) Jena, A. K.; Kulkarni, A.; Miyasaka, T. Halide Perovskite Photovoltaics: Background, Status, and Future Prospects. Chem. Rev. 2019, 119, 3036–3103.
2) Tavakoli, M. M.; Tress, W.; Milić, J. V.; Kubicki, D.; Emsley, L.; Grätzel, M. Addition of Adamantylammonium Iodide to Hole Transport Layers Enables Highly Efficient and Electroluminescent Perovskite Solar Cells. Energy Environ. Sci. 2018, 11, 3310–3320.
(3) Wehrenfennig, C.; Eperon, G. E.; Johnston, M. B.; Snaith, H. J.; Herz, L. M. High Charge Carrier Mobilities and Lifetimes in Organolead Trihalide Perovskites. Adv. Mater. 2014, 26, 1584−1589.

(4) Shi, D.; Adinolfi, V.; Comin, R.; Yuan, M.; Alarousu, E.; Buin, A.; Chen, Y.; Hoogland, S.; Rothenberger, A.; Katsiev, K.; Losovyj, Y.; Zhang, X.; Dowben, P. A.; Mohammed, F. F.; Sargent, E. H.; Bakr, O. M. Low Trap-State Density and Long Carrier Diffusion in Organolead Trihalide Perovskite Single Crystals. Science 2015, 347, 519−522.

(5) Sutton, R. J.; Eperon, G. E.; Miranda, J.; Parrott, E. S.; Kamino, B. A.; Patel, J. B.; Hörnenter, M. T.; Johnston, M. B.; Haghighirad, A. A.; Moore, D. T.; Snaith, H. J. Bandgap-Tunable Cesium Lead Halide Perovskites with High Thermal Stability for Efficient Solar Cells. Adv. Energy Mater. 2016, 6, No. 1502458.

(6) Stranks, S. D.; Eperon, G. E.; Grancini, G.; Menelau, C.; Alcocer, M. J. P.; Leijtens, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J. Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an Organometal Trihalide Perovskite Absorber. Science 2013, 342, 341−344.

(7) Veldhuis, S. A.; Boix, P. P.; Yantara, N.; Li, M.; Sum, T. C.; Mathews, N.; Mhaisalkar, S. G. Perovskite Materials for Light-Emitting Diodes and Lasers. Adv. Mater. 2016, 28, 6804−6834.

(8) Wang, X.; Li, M.; Zhang, B.; Wang, H.; Zhao, Y.; Wang, B. Recent Progress in Organometal Halide Perovskite Photodetectors. Org. Electron. 2018, 52, 172−183.

(9) Zhao, Z.; Gu, F.; Rao, H.; Ye, S.; Liu, Z.; Bian, Z.; Huang, C. Metal Halide Perovskite Materials for Solar Cells with Long-Term Stability. Adv. Energy Mater. 2019, 9, No. 1802671.

(10) Yang, W. S.; Park, B.-W.; Jung, E. H.; Jeon, N. J.; Kim, Y. C.; Lee, D. U.; Shin, S. S.; Seo, J.; Kim, E. K.; Noh, J. H.; Seok, S. I. Iodide Management in Formamidinium-Lead-Halide-Based Perovskite Layers for Efficient Solar Cells. Science 2017, 356, 1376−1379.

(11) Jeon, N. J.; Na, H.; Jung, E. H.; Yang, T.-Y.; Lee, Y. G.; Kim, G.; Shin, H.-W.; Seok, S.; Lee, J. E. A Fluorene-Terminated Hole-Transporting Material for Highly Efficient and Stable Perovskite Solar Cells. Nat. Energy 2018, 3, 682−689.

(12) Prochowicz, D.; Runjhung, R.; Takavoli, M. M.; Yadav, P.; Sasaki, M.; Alnazi, A. Q.; Kubicki, D. J.; Kaszkur, Z.; Zakeeruddin, S. M.; Lewinski, J.; Grätzel, M. Engineering of TiO2 ETL for Highly Efficient and Hysteresis-Less Perovskite Solar Cells. Adv. Energy Mater. 2019, 9, No. 1802646.

(13) Takavoli, M. M.; Yadav, P.; Prochowicz, D.; Sponseller, M.; O’Regan, B.; Martowicz, M.; Kong, J. Carrier Trapping and Recombination: The Role of Defect Physics in Enhancing the Open Circuit Voltage of Metal Halide Perovskite Solar Cells. Nat. Photonics 2020, 13, 460−466.

(14) Jiang, Q.; Zhao, Y.; Zhang, X.; Yang, X.; Chen, Y.; Chu, Z.; Ye, Q.; Li, X.; Yin, Z.; You, J. Surface Passivation of Perovskite Film for Efficient Solar Cells. Nat. Photonics 2019, 13, 460−466.

(15) Takavoli, M. M.; Saliba, M.; Yadav, P.; Holzhouy, P.; Hagfeldt, A.; Zakeeruddin, S. M.; Grätzel, M. Synergistic Crystal and Interface Engineering for Efficient and Stable Perovskite Photovoltaics. Adv. Energy Mater. 2019, 9, No. 1802646.

(16) Giordano, F.; Abate, A.; Correa Baena, J. P.; Saliba, M.; Matsui, T.; Lim, S. H.; Pandey, K.; Zakeeruddin, S. M.; Grätzel, M. Reduction in the Interfacial Trap Density of Mechanochemically Synthesized MAPbI3. ACS Appl. Mater. Interfaces 2017, 9, 28418−28425.

(17) Leijtens, T.; Eperon, G. E.; Barker, A. J.; Grancini, G.; Zhang, W.; Xiong, J.; Li, J.; Zhu, Z.; Jen, A. K.-Y. Efficient Large Guanidinium Mixed Perovskite Solar Cells with Enhanced Photovoltage and Low Energy Losses. Chem. Commun. 2019, 55, 4315−4318.

(18) Alharbi, E. A.; Dar, M. I.; Arora, N.; Alotaibi, M. H.; Alzhrairi, Y. A.; Yadav, P.; Tress, W.; Alyamani, A.; Albadri, A.; Zakeeruddin, S. M.; Grätzel, M. Perovskite Solar Cells Yielding Reproducible Photovoltage of 1.20 V. Research 2019, 2019, 1−9.

(19) Kubicki, D. J.; Prochowicz, D.; Hofstetter, A.; Sasaki, M.; Yadav, P.; Bi, D.; Pellet, N.; Lewinski, J.; Zakeeruddin, S. M.; Grätzel, M.; Emsley, L. Formation of Stable Mixed Guanidinium–Methylvammonium Phases with Exceptionally Long Carrier Lifetimes for High-Efficiency Lead Iodide-Based Perovskite Photovoltaics. J. Am. Chem. Soc. 2018, 140, 3345−3351.

(20) Kim, H.-S.; Jang, I.-H.; Ahn, N.; Choi, M.; Guerrero, A.; Bisquet, I.; Park, N.-G. Control of I− V Hysteresis in CH3NH3PbI3 Perovskite Solar Cells. J. Phys. Chem. Lett. 2015, 6, 4633−4639.

(21) Almora, O.; Zarazua, I.; Mas-Marza, E.; Mora-Sero, I.; Bisquet, J.; García-Belmonte, G. Capacitive Dark Currents, Hysteresis, and Electrode Polarization in Lead Halide Perovskite Solar Cells. J. Phys. Chem. Lett. 2015, 6, 1645−1652.

(22) Zarazua, I.; Bisquet, J.; García-Belmonte, G. Light-Induced Space-Charge Accumulation Zone as Photovoltaic Mechanism in Perovskite Solar Cells. J. Phys. Chem. Lett. 2016, 7, 525−528.

(23) Yadav, P.; Turren Cruz, S. H.; Prochowicz, D.; Takavoli, M. M.; Pandey, K.; Zakeeruddin, S. M.; Grätzel, M.; Hagfeldt, A.; Saliba, M. Elucidation of Charge Recombination and Accumulation Mechanism in Mixed Perovskite Solar Cells. J. Phys. Chem. C 2018, 122, 15149−15154.

(24) Prochowicz, D.; Takavoli, M. M.; Solanki, A.; Goh, T. W.; Sum, T. C.; Yadav, P.; Recognition of Correlation between Open Circuit Voltage in Planar Heterojunction Perovskite Solar Cells. J. Mater. Chem. C 2019, 7, 1273−1279.

(25) Guillén, E.; Ramos, F. J.; Anta, J. A.; Ahmad, S. Elucidating Transport-Recombination Mechanisms in Perovskite Solar Cells by Small-Perturbation Techniques. J. Phys. Chem. C 2014, 118, 22913−22922.
Lithium Doping for High-Efficiency Perovskite Solar Cells. Nat. Commun. 2016, 7, No. 10379.

(37) Salado, M.; Idigoras, J.; Calio, L.; Kazim, S.; Nazeeruddin, M. K.; Anta, J. A.; Ahmad, S. Interface Play between Perovskite and Hole Selective Layer on the Performance and Stability of Perovskite Solar Cells. ACS Appl. Mater. Interfaces 2016, 8, 34414−34421.

(38) Prochowicz, D.; Tavakoli, M. M.; Kalam, A.; Chavan, R. D.; Trivedi, S.; Kumar, M.; Yadav, P. Influence of A-Site Cations on the Open-Circuit Voltage of Efficient Perovskite Solar Cells: A Case of Rubidium and Guanidinium Additives. J. Mater. Chem. A 2019, 7, 8218−8225.

(39) Zarazua, I.; Han, G.; Boix, P. P.; Mhaisalkar, S.; Fabregat-Santiago, F.; Mora-Seró, I.; Bisquert, J.; García-Belmonte, G. Surface Recombination and Collection Efficiency in Perovskite Solar Cells from Impedance Analysis. J. Phys. Chem. Lett. 2016, 7, 5105−5113.

(40) Gottesman, R.; Lopez-Varo, P.; Gouda, L.; Jimenez-Tejada, J. A.; Hu, J.; Tirosh, S.; Zaban, A.; Bisquert, J. Dynamic Phenomena at Perovskite/Electron-Selective Contact Interface as Interpreted from Photovoltage Decays. Chem. 2016, 1, 776−789.

(41) Almora, O.; Aranda, C.; Mas-Marzá, E.; Garcia-Belmonte, G. On Mott-Schottky Analysis Interpretation of Capacitance Measurements in Organometal Perovskite Solar Cells. Appl. Phys. Lett. 2016, 109, No. 173903.

(42) Prochowicz, D.; Tavakoli, M. M.; Solanki, A.; Goh, T. W.; Pandey, K.; Sum, T. C.; Saliba, M.; Yadav, P. Understanding the Effect of Chlorobenzene and Isopropanol Anti-solvent Treatments on the Recombination and Interfacial Charge Accumulation in Efficient Planar Perovskite Solar Cells. J. Mater. Chem. A 2018, 6, 14307−14314.

(43) Jiang, M.; Lan, F.; Zhao, B.; Tao, Q.; Wu, J.; Gao, D.; Li, G. Observation of Lower Defect Density in CH₃NH₃Pb(I,Cl)₃ Solar Cells by Admittance Spectroscopy. Appl. Phys. Lett. 2016, 108, No. 243501.

(44) Liu, J.; Gao, C.; He, X.; Ye, Q.; Ouyang, L.; Zhuang, D.; Liao, C.; Mei, J.; Lau, W. Improved Crystallization of Perovskite Films by Optimized Solvent Annealing for High Efficiency Solar Cell. ACS Appl. Mater. Interfaces 2015, 7, 24008−24015.

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