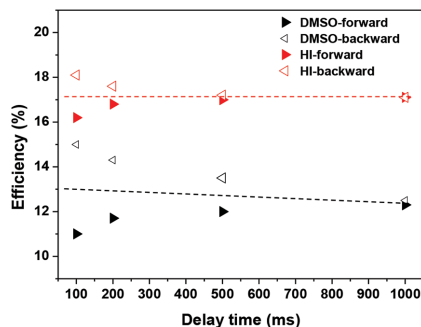


COMMUNICATIONS

Solar Cells

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**Planar $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite
Solar Cells with Constant 17.2%
Average Power Conversion Efficiency
Irrespective of the Scan Rate**



Planar $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite solar cells with constant 17.2% average power conversion efficiency irrespective of the scan rate are described. These properties are attributed to the formation of pure $\text{CH}_3\text{NH}_3\text{PbI}_3$ thin film by introduction of HI solution. Thereby charge injection/separation efficiency, charge collection efficiency, diffusion coefficient, carrier's life time, and traps are improved.

Planar $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Solar Cells with Constant 17.2% Average Power Conversion Efficiency Irrespective of the Scan Rate

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Since Kojima et al.^[1] reported $\text{CH}_3\text{NH}_3\text{PbX}_3$ (MAPbX_3 , $\text{X} = \text{Br}$, I) perovskite-sensitized solar cells, the perovskite hybrid solar cells have been of great interest because of their unique properties such as long charge carrier's diffusion length, strong light absorptivity, ambipolar charge transport, high open circuit voltage, and solution processibility. The perovskite hybrid solar cells can be roughly classified to mesoscopic,^[2] meso-superstructured,^[3] and planar type.^[4] The first uses the mesoscopic TiO_2 electron conductor which can tune the electron flux coming from the hybrid perovskite light absorber. Generally, pure or alloyed perovskite hybrid solar cells adopt this device architecture because the electrons generated in perovskite are injected into mesoscopic TiO_2 . Meanwhile, the second uses the mesoscopic insulator such as Al_2O_3 and as a result, the electrons are transported to electrode through the perovskite itself because the electron injection from perovskite into Al_2O_3 is blocked. The mixed halide perovskites such as $\text{MAPbI}_{3-x}\text{Cl}_x$ ($x = 0.01\text{--}0.03$) are usually chosen for this device structure. The last utilizes the dense thin electron conducting layer such as TiO_2 , ZnO , PCBM ([6,6]-phenyl- C_{61} -butyric acid methyl ester) instead of mesoscopic TiO_2 , of which the electrons generated in planar perovskite thin film are injected into the electron conductor. All of pure, alloyed, and mixed halide perovskites can be used for this planar type of perovskite hybrid solar cell.

Although the record efficiency of perovskite hybrid solar cells reached up to 20.1%,^[5] it was known that the perovskite hybrid solar cells often exhibited significant hysteresis of $J\text{--}V$

(photocurrent density–voltage) curves with respect to the scan direction due to the charge accumulation or dielectric polarization by ferroelectric properties of perovskite materials.^[6,7] It is quite important issue to reduce the $J\text{--}V$ hysteresis with the scan direction in order to determine the real device efficiency. Jeon et al.^[2h] reported that the 200–300-nm thick mesoscopic TiO_2 layer is necessary to reduce $J\text{--}V$ hysteresis with respect to scan direction because the electron–hole diffusion lengths are corresponded to 100–200 nm and the mesoscopic TiO_2 electrode can adjust the flux of electrons (J_e) due to the its controlled interface area.^[2h] In solar cell, the highest device efficiency is obtained when the electron flux (J_e) and the hole flux (J_h) is balanced, of which the flux stands for the number of charge carriers per unit area and time. Otherwise, the unbalanced charge carriers should be recombined by the direct recombination of electrons and holes or the retarded recombination of charge carriers due to the trapping at trap sites. If the material is 100% pure without any traps, the unbalanced charge carriers should be recombined by direct recombination such as radiative or nonradiative decay. Therefore, the traps are closely related to the response time of solar cells and the mesoscopic cells might have advantage to balance the J_e and J_h due to the controllable interface area than the planar cells. This means that the unbalance of J_e and J_h leads charge accumulation to traps and the accumulated charge carriers at traps make $J\text{--}V$ hysteresis with respect to the scan direction. In mesoscopic $\text{TiO}_2/\text{MAPbI}_3$ perovskite hybrid solar cells, the major surface traps might be located at mesoscopic $\text{TiO}_2/\text{MAPbI}_3$ interface due to many junctions between TiO_2 nanocrystals. Therefore, we should consider both interface area and number of surface traps to minimize $J\text{--}V$ hysteresis. So many junctions by thick mesoscopic TiO_2 is good for increasing J_e but is bad for reducing $J\text{--}V$ hysteresis due to increased surface traps.

On the other hand, although the planar perovskite hybrid solar cells have the simplest device architecture like bilayer organic solar cells and the low temperature solution process is possible due to the absent of mesoscopic TiO_2 electrode which generally requires hot processing temperature, it often suffers from the severe $J\text{--}V$ hysteresis with respect to the scan direction. For instance, recently Zhou et al.^[4i] achieved 19.3% planar $\text{MAPbI}_{3-x}\text{Cl}_x$ mixed halide perovskite hybrid solar cells via spin-coating method under controlled humid atmosphere. However, it revealed significant $J\text{--}V$ hysteresis with respect to the forward and reverse scan direction. Accordingly, it is difficult to exactly determine the power conversion efficiency of planar perovskite hybrid solar cells. It is also known that the formation of perovskite hybrid thin film with full surface coverage on

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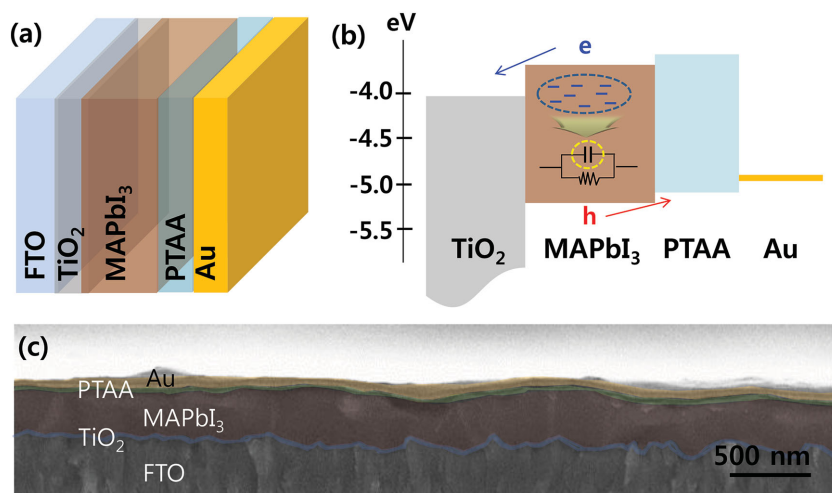


Figure 1. a) Schematic illustration of planar MAPbI₃ perovskite hybrid solar cell, b) its band energy diagram, and c) the SEM cross-sectional image of representative device.

the electron conductor/FTO (F doped SnO₂) substrate is tricky. Here, we report on the straightforward method for the formation of highly pure perovskite thin film with full surface coverage thereby not only reducing significantly the *J*–*V* hysteresis of perovskite hybrid solar cells with respect to the scan direction but also demonstrating the 17.2% planar CH₃NH₃PbI₃ perovskite solar cells with constant average power conversion efficiency irrespective with the scan rate.

Figure 1a depicts the device structure comprised FTO/dense TiO₂ electron conductor (≈50 nm)/MAPbI₃ perovskite (≈300 nm)/PTAA (≈40 nm)/Au. In a typical process for the fabrication of the perovskite hybrid device, a dense TiO₂ electron conductor of ≈50 nm in thickness was deposited on a FTO glass by the spray pyrolysis deposition method. The pinhole-free MAPbI₃ thin films were deposited on the TiO₂/FTO substrate by spin-coating of 40 wt% MAPbI₃/DMF (*N,N*-dimethylformamide: 1 mL) with 100 μL HI or 40 wt% MAPbI₃/DMSO (dimethyl sulfoxide: 1 mL) solutions at 3000 rpm for 200 s. Then, the PTAA solution was spin-coated on MAPbI₃/TiO₂/FTO substrate at 3000 rpm for 30 s. Finally, the Au counter electrode was deposited by thermal evaporation. The representative SEM cross-sectional image of planar MAPbI₃ perovskite hybrid solar cell was shown in **Figure 1c**.

Upon illumination of light, the MAPbI₃ perovskite generates electron–hole pairs and the electrons (holes) are then transported into TiO₂ electron conductor (PTAA hole conductor) as shown in **Figure 1b**. If the MAPbI₃ perovskite layer has some defects, the photocurrent response will be delayed by the internal trap states because the traps act as internal capacitance due to the trap filling and trapping/detrapping process.^[8] Therefore, the impurities in MAPbI₃ perovskite layer will retard the charge injection from MAPbI₃ into TiO₂. In addition, the capacitance element in the impure MAPbI₃ will make severe *J*–*V* hysteresis with respect to scan direction. Especially, the planar MAPbI₃ perovskite hybrid solar cells are expected to reveal more severe *J*–*V* hysteresis than the mesoscopic MAPbI₃ perovskite solar cells^[9,10] because the mesoscopic TiO₂ electron conductor can compensate the electron flux due to the large surface area even though the electron injection is retarded by

the traps whereas the planar TiO₂ electron conductor cannot. The balanced electron and hole flux will not create charge accumulation within MAPbI₃ perovskite layer if the charge transport is not significantly hindered in the electron conductor or the hole conductor. Accordingly, it will be crucial to form pure MAPbI₃ perovskite layer in order to reduce the *J*–*V* hysteresis with respect to scan direction in the planar MAPbI₃ perovskite hybrid solar cells.

As a model system for the formation of pinhole-free MAPbI₃ perovskite thin film on TiO₂/FTO substrate via single step spin-coating process, we used 40 wt% MAPbI₃/DMSO (1 mL) solution and 40 wt% MAPbI₃/DMF (1 mL) solution with 100 μL HI additive solution, respectively, because the DMSO solvent and DMF solvent with HI additive have better solubility to MAPbI₃ perovskite

than the pure DMF solvent thereby facilitating the formation of pinhole-free thin film.^[2h,4d] During a spin-coating process, a MAPbI₃ perovskite solution are spread on the TiO₂/FTO substrate by centrifugal force and the MAPbI₃ perovskite is crystallized on the substrate from the periphery to the center of the substrate by further evaporation of solvent.^[4d] At the moment, more concentrated MAPbI₃ perovskite solution in DMSO and DMF with HI additive can form more dense MAPbI₃ thin film on the whole surface of TiO₂/FTO substrate due to the increased solubility. **Figure 2a,b** shows the SEM surface images of MAPbI₃ perovskite thin film deposited on TiO₂/FTO substrate via simple one-step spin-coating process with MAPbI₃/DMSO (1 mL) solution and MAPbI₃/DMF (1 mL) solution with 100 μL HI additive solution. The SEM images clearly confirm the formation of dense MAPbI₃ thin film without pinholes. To compare the crystalline morphology of whole surface of DMSO- and HI-MAPbI₃ film, we checked SEM surface images of them in detail as shown in **Figure S1**, Supporting Information. We found that the DMSO-MAPbI₃ film has very large crystalline domains, whereas the HI-MAPbI₃ film has not any crystalline domains. Their corresponding SEM cross-sectional images in **Figure 2c,d** indicate that the thickness of both MAPbI₃ layers is ≈300 nm. To check the purity of MAPbI₃ perovskite layer formed by MAPbI₃/DMSO solution (DMSO-MAPbI₃) and MAPbI₃/DMF solution with HI additive solution (HI-MAPbI₃), the XRD patterns were shown in **Figure 2e**. The XRD patterns clearly indicate that the MAPbI₃ perovskite film formed by MAPbI₃/DMSO solution has some impurities such as PbI₂ whereas no impurities are detectable in MAPbI₃ film formed by MAPbI₃/DMF solution with HI additive. Although Jeon et al.^[2h] reported that the DMSO additive does not deteriorate the purity of MAPbI₃ by nonsolvent dripping process, tiny PbI₂ impurity peaks always existed in the closer look of XRD patterns. Similarly, the MAPbI₃ crystals formed by in MAPbI₃/DMF solution (DMF-MAPbI₃) revealed also small amount of PbI₂ impurity peaks in **Figure 2e**. The formation of impurities in MAPbI₃ film formed by the conventional MAPbI₃/DMF and MAPbI₃/DMSO solutions might be associated with the fact that practically, it is very difficult to exactly mix equimolar concentration of MAI and PbI₂ or the MAI can be decomposed or

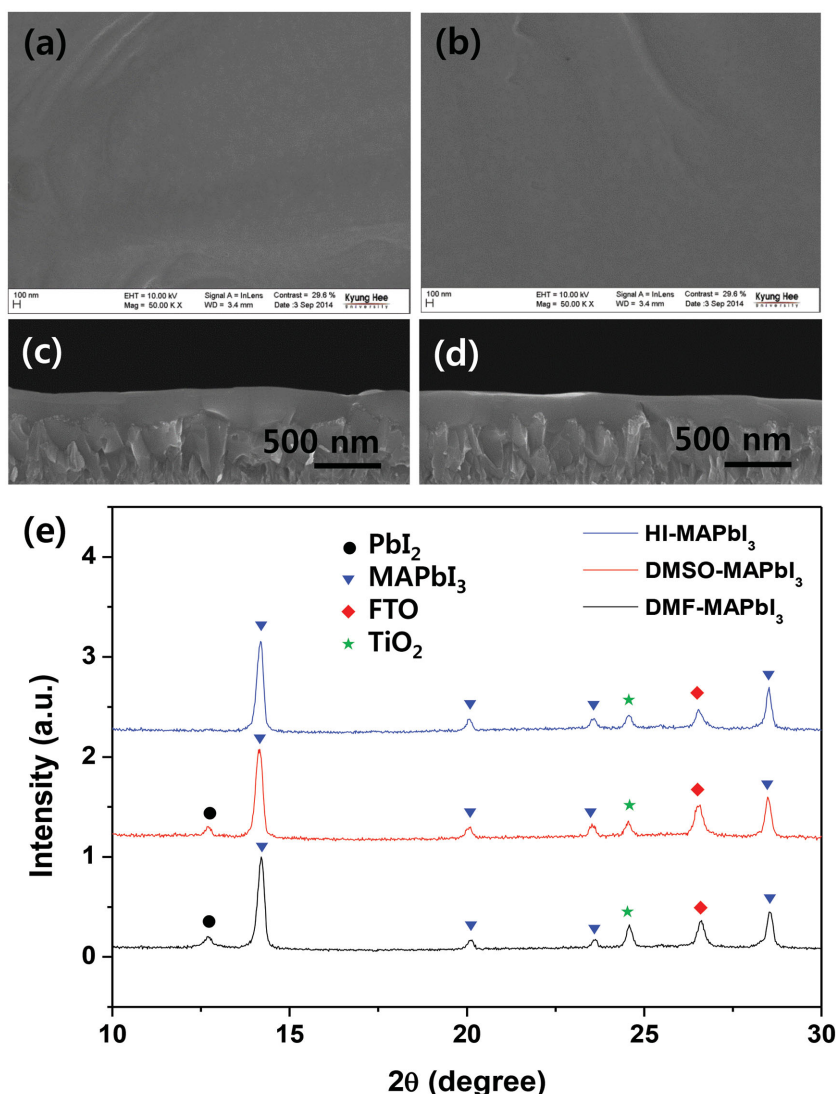


Figure 2. SEM surface a,b) and cross-sectional c,d) images of MAPbI₃ perovskite thin films prepared by one-step spin-coating process using MAPbI₃/DMSO solution (DMSO-MAPbI₃: (a) and (c)) and MAPbI₃/DMF solution with HI additive solution (HI-MAPbI₃: (b) and (d)); and e) XRD patterns of MAPbI₃ perovskite thin films (DMF-MAPbI₃ = MAPbI₃/DMF solution without HI additive solution).

sublimated during the formation of MAPbI₃ crystal film. Therefore, the mesoscopic MAPbI₃ perovskite solar cells exhibited small hysteresis of short circuit current density (J_{sc}), open circuit voltage (V_{oc}), fill factor (F.F.), and efficiency even though the thickness of mesoscopic TiO₂ is optimized.^[2h] On the other hand, the added HI solution can reduce the formation of PbI₂ impurities by decomposition of MAI from MAPbI₃ because the HI solution can recover the methylamine (decomposed product of MAI) into MAI thereby significantly suppressing the decomposition reaction of MAPbI₃ perovskite. Accordingly, it is expected that the planar MAPbI₃ perovskite hybrid solar cells with high purity will exhibit smaller J - V hysteresis with respect to scan direction and scan rate. The effect of PbI₂ impurity on the J - V hysteresis with respect to the scan direction is demonstrated in Figure S2, Supporting Information.

Figure 3a is UV-vis absorption spectra of FTO/TiO₂/MAPbI₃ films prepared from DMSO-MAPbI₃ and HI-MAPbI₃ solutions indicating that both MAPbI₃ films have similar light harvesting efficiency due to the same thickness of MAPbI₃ layer (see Figure 2c,d). Figure 3b exhibits the representative J - V curves of planar MAPbI₃ perovskite hybrid solar cells prepared by DMSO-MAPbI₃ and HI-MAPbI₃ solutions with respect to scan direction under 200 ms of delay time and 10 mV per point (voltage scan step) condition. As expected from the XRD analysis, the planar MAPbI₃ perovskite hybrid solar cells prepared by DMSO-MAPbI₃ had more serious J - V hysteresis with respect to the scan direction than the cell by HI-MAPbI₃ solutions. The photovoltaic properties of DMSO-MAPbI₃ (DMSO) and HI-MAPbI₃ (HI) planar perovskite hybrid solar cells were listed in Table 1. The DMSO-MAPbI₃ device exhibited that 1.06 V of V_{oc} , 18.7 mA cm⁻² of J_{sc} , 59% of F.F., and 11.7% of power conversion efficiency (η) at forward scan direction at 1 sun condition and 1.08 V of V_{oc} , 18.9 mA cm⁻² of J_{sc} , 70% of F.F., and 14.3% of η at backward scan direction thereby yielding to 13% of average power conversion efficiency (η_{avg}). On the other hand, the HI-MAPbI₃ device exhibited 1.1 V of V_{oc} , 20.4 mA cm⁻² of J_{sc} , 75% of F.F., and 16.8% of η at forward scan direction and 1.1 V of V_{oc} , 20.5 mA cm⁻² of J_{sc} , 78% of F.F., and 17.6% of η at backward scan direction, thereby yielding to 17.2% of η_{avg} . These results indicate that the pure MAPbI₃ perovskite can reduce the J - V hysteresis with respect to scan direction and increase the average power conversion efficiency as well. The improved efficiency might be attributed to the enhanced charge injection and/or charge collection efficiency because the HI-MAPbI₃ hybrid solar cells exhibited better EQE (external quantum efficiency) spectrum than the DMSO-MAPbI₃ cells as shown in Figure 3a. The photovoltaic parameters of DMSO-MAPbI₃ and HI-MAPbI₃ planar hybrid solar cells with respect to scan direction under different delay time conditions were summarized in Table S1, Supporting Information. The power conversion efficiencies of DMSO-MAPbI₃ and HI-MAPbI₃ planar hybrid solar cells with respect to scan direction at different delay time condition were plotted in Figure 3c. This clearly shows that the J - V hysteresis of HI-MAPbI₃ planar hybrid solar cells with respect to scan direction is significantly reduced. The HI-MAPbI₃ planar hybrid solar cells had the coincidence of power conversion efficiencies measured by forward and backward scan condition over 500 ms of delay time whereas the DMSO-MAPbI₃ cells had over 1000 ms of delay time. It should be noted that the HI-MAPbI₃ planar hybrid solar cells exhibited constant η_{avg}

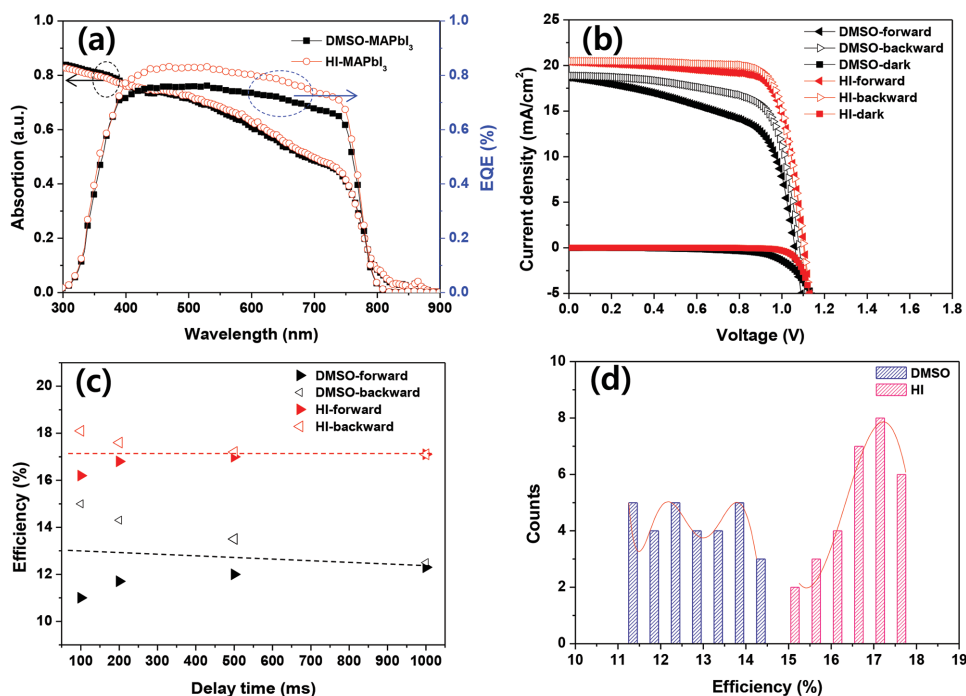


Figure 3. a) Absorption and EQE (external quantum efficiency) spectra of DMSO-MAPbI₃ and HI-MAPbI₃ film and device, respectively and b) J-V curves, c) forward and backward efficiency with delay time, and d) efficiency deviation of DMSO-MAPbI₃ and HI-MAPbI₃ perovskite hybrid solar cells. (DMSO = DMSO-MAPbI₃ device, HI = HI-MAPbI₃ device, forward = forward scan, backward = backward scan.)

irrespective to the delay time whereas the DMSO-MAPbI₃ cells showed slightly declining η_{avg} with the delay time. Figure 3d is the η_{avg} deviation of different 30 DMSO-MAPbI₃ and HI-MAPbI₃ hybrid solar cells, respectively, indicating that the η_{avg} is significantly improved by introduction HI additive which enables to form pure MAPbI₃ perovskite thin film by simple one-step spin-coating process. It is also noted that the existence of J-V hysteresis with respect to the scan direction and scan rate do not make serious problem if we measure correctly measure the efficiency of perovskite hybrid solar cells through sufficiently increasing the delay time (>1000 ms) where the J-V curves of forward and backward scan condition are coincided. Hence, we need to carefully check the J-V curves in perovskite hybrid solar cells to exactly determine the real efficiency. The current density under applied optimal bias voltage at maximum power point with light soaking time shown in Figure S3, Supporting Information, clearly confirms that the HI-MAPbI₃ hybrid solar cell has a constant power conversion efficiency under continuous light illumination of 1 sun, whereas the

DMSO-MAPbI₃ solar cell's efficiency is slightly declined with light soaking time.

To understand the effect of HI additive on the device efficiency and J-V hysteresis due to the higher impurities which might be associated with the traps, the trap density of completed solar cell was investigated by using admittance spectroscopy (AS). AS can probe trap energy level and trap density of the absorber layer.^[11] The trap energy level is derived by the

relation, $\omega_0 = \beta T^2 \exp\left(\frac{-E_a}{k_B T}\right)$, where ω_0 is characteristic transi-

tion frequency, β is temperature independent parameter, E_a is depth of trap energy level, k_B is the Boltzmann constant, and T is the temperature. Using this equation, Arrhenius plot of characteristic frequency is plotted, and E_a is the slope of the Arrhenius plot line. The trap density can be derived by the equation,

$$N_t = -\frac{V_{bi}}{qw} \frac{dC}{d\omega} \frac{\omega}{k_B T}, \text{ where } C \text{ is the capacitance, } \omega \text{ is the applied}$$

frequency, q is the elementary charge, k_B is the Boltzmann constant, T is the temperature, V_{bi} is the built-in potential, and w is the depletion width, respectively. The values of V_{bi} and w are obtained from Mott-Schottky analysis.

Figure 4a-f shows the results of AS measurements. DMSO solar cell shows trap energy level of 0.27 eV and trap energy density of $\approx 10^{17} \text{ cm}^{-3}$, whereas HI solar cell exhibits trap energy level of 0.28 eV and trap energy density of $\approx 10^{16} \text{ cm}^{-3}$. The trap energy of 0.27–0.28 eV is shallower than that reported by Shao et al.^[12] and deeper than the result by Duan et al.^[13] It should be noted that trap density of DMSO cell is 10 times larger than that of HI cell. The higher defect density induces larger electrical element of capacitance in the

Table 1. Photovoltaic properties of DMSO-MAPbI₃ (DMSO) and HI-MAPbI₃ (HI) planar perovskite hybrid solar cells (100 mW cm⁻² AM 1.5G, delay time = 200 ms, voltage scan step = 10 mV).

Device	Scan direction	V_{oc} [V]	J_{sc} [mA cm ⁻²]	F.F. [%]	η [%]	Avg. η [%]
DMSO	Forward	1.06	18.7	59	11.7	13.0
	Backward	1.08	18.9	70	14.3	
HI	Forward	1.1	20.4	75	16.8	17.2
	Backward	1.1	20.5	78	17.6	

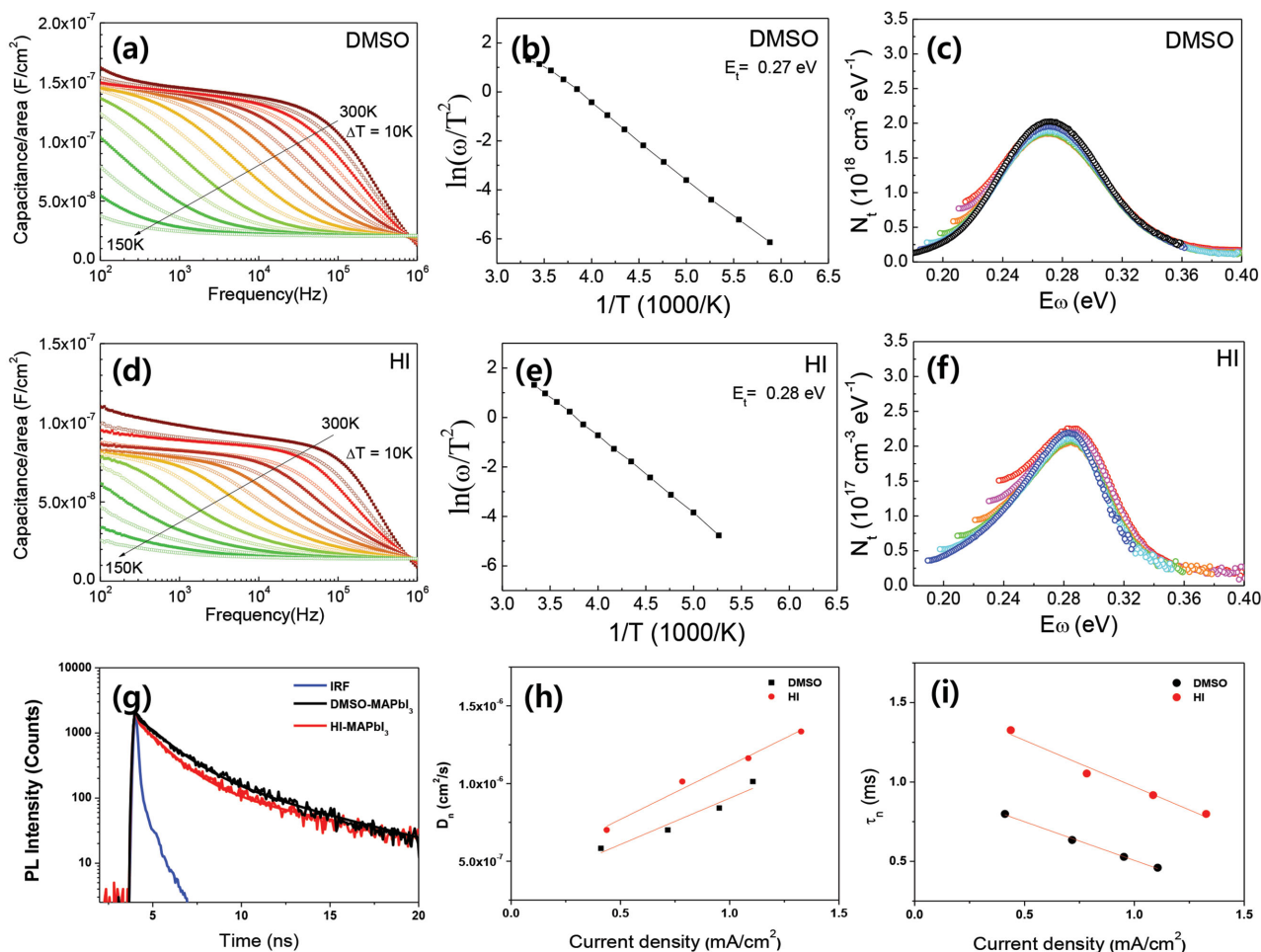


Figure 4. Temperature dependent capacitance spectra (a) for DMSO, d) for HI, Arrhenius plots of characteristic frequencies (b) for DMSO, e) for HI, and trap density profiles (c) for DMSO, f) for HI of DMSO (a–c) and HI (d–f) cells, respectively; g) time-resolved photoluminescent (PL) decay curves of DMSO and HI; and h,i) charge carrier's diffusion coefficient from (h) IMPS and decay time from (i) IMVS of DMSO and HI device. (DMSO = DMSO-MAPbI₃ planar hybrid solar cell, HI = HI-MAPbI₃ planar hybrid solar cell.)

complete solar cell, which may result in hysteresis of solar cell. It should be noted that the capacitance elements are attributed to the impurities in MAPbI₃ perovskite thin film within itself because the charges can be accumulated at the trap sites. Therefore, the traps are gradually filled at forward scan condition, whereas the traps are fully filled at backward scan condition. Under fast scan rate (short delay time) condition of J - V curves, the photocurrent is measured before reaching the saturation value so that the J_{sc} is increased with the delay time at forward scan condition, whereas the J_{sc} is decreased with the delay time due to the recombination through the trap sites at backward scan condition. As a result, the η of DMSO-MAPbI₃ device reveals significant hysteresis with respect to the scan direction, whereas the J_{sc} of HI-MAPbI₃ device is less sensitive with the scan rate than the DMSO-MAPbI₃ device. Consequently, the HI-MAPbI₃ perovskite hybrid solar cells exhibited constant η_{avg} irrespective to the scan rate meanwhile the η_{avg} of DMSO-MAPbI₃ device was slightly decreasing with the delay time. In addition, we need to consider the change of ferroelectric properties with different perovskite

thin films of DMSO-MAPbI₃ and HI-MAPbI₃. If the change of dielectric polarization by ferroelectric properties is dominant factor to make J - V hysteresis, the J - V hysteresis were greatly dependent on the perovskite crystalline domain size but here the morphologies of perovskite thin films were similar so that the traps might be the major factor to make J - V hysteresis (see the more detailed explanation for AS analysis in the Supporting Information).

To compare the charge carrier dynamics (charge transfer or charge injection/separation behavior), we measured the time-resolved photoluminescent (PL) decay curves of DMSO-MAPbI₃ and HI-MAPbI₃ planar hybrid solar cells as shown in Figure 4g.^[14] The shortened PL decay in HI-MAPbI₃ solar cells confirmed the faster transfer of the charge carriers into TiO₂ electron conductor and PTAA hole conductor than that in the DMSO-MAPbI₃ solar cells, which means that HI-MAPbI₃ perovskite hybrid solar cells can inject the charge carriers from MAPbI₃ perovskite into TiO₂ electron conductor more efficiently. From the convolution of the time-resolved PL decays with a biexponential function, the average

PL lifetime (τ_{avg}) of HI-MAPbI₃ (2.058 ns) is shorter than that of DMSO-MAPbI₃ (2.278 ns), as listed in Table S2, Supporting Information.

To check what the purity of MAPbI₃ perovskite can affect the device operation, we measured diffusion coefficient (D_n) and charge carrier's life time (τ_n) from IMPS (intensity modulated photocurrent spectroscopy) and IMVS (intensity modulated photovoltage spectroscopy) analysis as shown in Figure 4h,i. The original Nyquist plots of IMPS and IMVS were shown in Figure S4, Supporting Information. From the plots of D_n and τ_n with current density (J), we could recognize that the D_n and τ_n of HI-MAPbI₃ planar hybrid solar cells are increased to ≈ 1.3 and ≈ 1.6 -fold, respectively, than the DMSO-MAPbI₃ devices. Accordingly, the diffusion length ($L_n = (D_n \cdot \tau_n)^{0.5}$) of MAPbI₃ planar hybrid solar cells was increased from ≈ 230 to ≈ 350 nm by using pure MAPbI₃ perovskite (HI-MAPbI₃). From the analysis of transient PL decay, IMPS, and IMVS, we could conclude that i) the EQE of HI-MAPbI₃ planar hybrid solar cell is improved by the enhanced charge injection/separation efficiency and charge collection efficiency thereby improving J_{sc} ; ii) the F.F. and V_{oc} of HI-MAPbI₃ planar hybrid solar cell is enhanced by the improved D_n and τ_n thereby reducing the backward recombination of electrons and holes; and iii) the J - V hysteresis of HI-MAPbI₃ device with respect to the scan direction and rate is greatly reduced by the formation of highly pure MAPbI₃ perovskite by addition of HI additive solvent thereby eliminating number of traps which may create the internal capacitance elements within MAPbI₃ perovskite layer.

In summary, the pinhole-free MAPbI₃ perovskite hybrid thin-films were formed by the simple one-step spin-coating process by using MAPbI₃/DMSO solution and MAPbI₃/DMF with HI additive solvent. The XRD analysis confirmed that the pure MAPbI₃ perovskite hybrid thin film could be formed by the contribution of HI additive solvent because HI can prohibit the decomposition of MAPbI₃ to MAI and PbI₂ whereas conventional MAPbI₃ in DMF or DMSO solution made some impurity such as PbI₂. Through the formation of pure MAPbI₃ perovskite hybrid thin films by introduction of HI additive solvent, we could enhance 1.3-fold of the η_{avg} under illumination of 1 sun (100 mW cm⁻² AM 1.5G) light and consequently obtained 17.2% of η_{avg} irrespective with the scan direction and rate because the HI-MAPbI₃ planar perovskite hybrid solar cells exhibited ≈ 1.4 -fold longer diffusion length than the DMSO-MAPbI₃ planar solar cells owing to ≈ 1.3 and ≈ 1.6 -fold of the improved D_n and τ_n , respectively, than DMSO-MAPbI₃ planar solar cells. In addition, the charge injection/separation efficiency and trap sites are also improved by the formation of pure MAPbI₃ perovskite hybrid thin films. From the AS results, we found that both DMSO- and HI-cells have similar trap energy level of 0.27–0.28 eV but the HI cell has ≈ 10 -fold lower trap density than the DMSO cell. Therefore, the HI cell reveals lower J - V hysteresis with respect to the scan direction due to the smaller number of capacitance element. Therefore, we believe that if we balance the electron (J_e) and hole flux (J_h) and eliminate the trap sites in MAPbI₃ planar perovskite hybrid solar cells, the highly efficient planar perovskite hybrid solar cells without J - V hysteresis with respect to scan direction could be fabricated.

Experimental Section

Preparation of MAPbI₃ Perovskite Solution: To synthesize CH₃NH₃I₃, 50 mL hydriodic acid (48% in water, Aldrich) and 30 mL methylamine (40% in methanol, Junsei Chemical Co. Ltd.) were reacted in a 250-mL round-bottom flask at 0 °C for 2 h with vigorous stirring. The products were recovered by evaporation and then were dissolved in ethanol, recrystallized from diethyl ether. Finally, the products were dried at the room temperature in a vacuum oven for 24 h. To form the CH₃NH₃PbI₃ thin film, two kinds of solutions such as 40 wt% of CH₃NH₃PbI₃ in dimethyl sulfoxide and *N,N*-dimethylformamide with added 100 μ L hydriodic acid were prepared by reacting the synthesized CH₃NH₃I and PbI₂ (Aldrich) at 1:1 mole ratio at 60 °C for 30 min.

Device Fabrication: To fabricate the planar CH₃NH₃PbI₃ perovskite hybrid solar cell, dense TiO₂ blocking layer (bl-TiO₂) of ≈ 50 nm thickness was deposited on cleaned F-doped SnO₂ (FTO, Pilkington, TEC8) glass substrate by spray pyrolysis deposition (SPD) method with 20×10^{-3} M of titanium diisopropoxide bis(acetylacetonate) (Aldrich) solution at 450 °C. To form the CH₃NH₃PbI₃ layer on bl-TiO₂/FTO substrate, the 40 wt% CH₃NH₃PbI₃ in dimethyl sulfoxide and *N,N*-dimethylformamide solution with added 100 μ L HI was then coated by spin-coating and dried on a hot plate at 100 °C for 2 min. In each solvent, the spin-coating conditions are at 2000 rpm for 60 s then 4000 rpm for 120 s and at 3000 rpm for 200 s. Poly[bis(4-phenyl)-(2,4,6-trimethylphenyl)amine] (PTAA; EM index) hole transporting materials (HTM) were spin-coated on CH₃NH₃PbI₃/bl-TiO₂/FTO substrate at 2000 rpm for 30 s by using HTM/toluene (15 mg/1 mL) with 7.5 μ L Li-bis(trifluoromethanesulfonyl) imide (Li-TFSI)/acetonitrile (170 mg/1 mL) and 7.5 μ L t-BP/acetonitrile (1 mL/1 mL) additives and without additives. Finally, Au counter electrode was deposited by thermal evaporation. The active area was fixed to 0.16 cm². All device fabrications were conducted below 50% of relative humidity.

Device Characterization: The current density–voltage (J - V) curves were measured by a solar simulator (Pecell, PEC-L01) with a potentiostat (IVIUM, IviumStat) at 100 mA cm⁻² illumination AM 1.5G and a calibrated Si-reference cell certificated by JIS (Japanese Industrial Standards). For the measurement hysteresis of J - V curves, the forward and reverse scan rate was set to 200 ms/10 mV as a standard condition and was varied from 100 ms/10 mV to 1000 ms/10 mV. The J - V curves of all devices were measured by masking the active area with metal mask of 0.096 cm². The external quantum efficiency (EQE) was measured by a power source (ABET 150W Xenon lamp, 13014) with a monochromator (DONGWOO OPTORN Co., Ltd., MonoRa-500i) and a potentiostat (IVIUM, IviumStat). AS measurements were carried out by using precision LCR meter (Agilent, E4980A) under dark condition at frequencies between 0.1 and 1000 kHz. Sample was located in home-made cryostat using liquid nitrogen, and the range of measurement temperature was 150–300 K. As temperature was cooled down with cooling rate of ≈ 2 K min⁻¹, capacitance spectra were measured at every 10 K, and all measurements were done at corresponding temperature with error bar of ± 0.05 K or less.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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