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# Defect-passivation of organometal trihalide perovskite with functionalized organic small molecule for enhanced device performance and stability

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# ABSTRACT

Defects in solution-processed organic and inorganic halide perovskite thin films deteriorate their photovoltaic performance and stability. Here, a bisimidazole-based organic small molecular hole transport material (HTM) that can suppress interfacial defects of the perovskite with its functional groups working as Lewis bases is newly introduced. Surface passivation of perovskite film leads to the reduction in non-radiative recombination trap density as well as the improvement of its crystallinity, consequently enhancing the efficiency of perovskite solar cell (PSC) from 16.3% to 18.3% with superior stability, preserving 92% of its initial efficiency for 500 h in an atmosphere.

# 1. Introduction

Organic-inorganic halide perovskite solar cells (PSCs) have shown tremendous potentials during the last decade for conversion of solar energy to electrical energy. Correspondingly, the PSCs have gained their power conversion efficiency (PCE) from 3.8% in 2009 to 25.2% now. These incredible progresses in PSCs are due to their exceptional optoelectronic properties such as high absorption coefficient, high defect tolerable limit, high carrier mobility, and long carrier diffusion length [1-5]. The PSC devices are generally sandwiched by interfacial electron transport layer (ETL) and hole transport layer (HTL), and those are classified as n-i-p and p-i-n, depending on the order of interfacial layers. The PSCs having n-i-p configuration, of which a ETL has been firstly deposited on a transparent conducting oxide (TCO) layer, have shown higher PCE than that of PSCs having p-i-n configuration, but they had limitations such as high process temperature (>400 °C), required for the annealing of ETL (e.g. TiO<sub>2</sub>), and hysteretic behaviors, often observed in this configuration without a mesoporous structure. In comparison, the p-i-n configuration PSCs, of which a HTL is formed on a TCO, have

shown various advantages like low processing temperature, negligible hysteresis, etc. [6–9].

The performances of PSCs are largely dependent on the interfacial characteristics between the charge transport layer (ETL and HTL) and perovskite photoactive layer. Especially for the hole transport material (HTM), a superior hole-extracting and electron-blocking capability along with a low carrier recombination property at the interface with the perovskite layer are required. Moreover, for the layer to be efficiently utilized as a HTL in the p-i-n configuration PSC, a chemical robustness that can help to form a stable perovskite layer on top of the HTL is also necessary [9-12]. In these aspects, a variety of inorganic HTMs such as CuO<sub>x</sub>, MoO<sub>3</sub>, graphene oxide, CuSCN, CuI, CuS, CuGaO<sub>2</sub>, V<sub>2</sub>O<sub>5</sub>, and NiOx have been intensively investigated due to their suitable band alignment, hole mobility, stability, and cost effectiveness [10-12]. Among those, NiOx is one of the widely explored HTMs because of its high band gap, high transmittance in visible range and deep valance band edge [13-17]. However, NiOx-based PSCs have often suffered from a poor interfacial property between NiO<sub>x</sub> and perovskite layer, because low temperature solution processed-NiOx usually had high defect

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density, which reduced its hole extraction ability [18–22]. This incurred the accumulation of hole near the interface with the perovskite and increased the trap-assisted non-radiative recombination losses, consequently decreasing the efficiency of devices. Moreover, a rough surface of NiO<sub>x</sub> layer deteriorates the surface morphology and crystallinity of the following perovskite layer, also degrading their performances. Therefore, a strategy that can enhance the interfacial properties between NiO<sub>x</sub> and perovskite can be an effective approach to achieve high efficiency PSCs.

Among various heterocyclic aromatic organic materials, imidazole derivatives have attracted significant attention because of their exclusive optical, thermal, and electronic properties [23,24]. Combination of electron donating (D) groups and electron accepting (A) moieties are frequently used to generate dipolar push-pull systems that feature low bandgap energy as well as intense charge transfer absorption [25,26]. The substitution of various electron D/A groups to initial imidazole moiety increased polarizability, stability, and thermal or chemical robustness [27]. Charge transport and balance are key factors for obtaining high device performances, and bisimidazole derivatives with proper D/A moieties have showed promising hole transport characteristics for organic light-emitting diodes (OLEDs), dve-sensitized solar cells, and PSCs [28-30]. In this work, a bisimidazole-based organic HTM molecule is newly designed and introduced between NiOx and perovskite layer of p-i-n structure PSC devices for improving their interfacial properties. Especially, methoxy functional groups, attached to the organic molecule, are shown to passivate non-radiative recombination trap sites of perovskite as well as to improve its crystallinity, consequently enhancing the performances and stability of PSC devices.

#### 2. Results and discussion

# 2.1. Organic HTM with defect-passivating functional groups

Recently, lophine (2,4,5-triphenyl-1H-imidazole) derivatives showed attractive emitting characteristics for OLEDs [31–36], lasing materials [37–39], and chemosensors [40], and transporting properties for HTMs [17,41,42]. Especially, the molecular structure of lophine can

be tailored with diverse D and A groups on the phenyl ring that present in the C2, C4 and C5 positions, together with N1 position of the imidazole ring (Fig. S1) [17,31,32,41]. These structural modifications can also be used to modulate the bandgap of imidazole derivatives, which are suitable for HTMs of PSCs [17,41,43].

Here, aiming at development of robust and facile imidazole-based HTMs for PSCs, we have introduced D-A-D structures with extended  $\pi$ -conjugation. By simple alteration of benzaldehyde into terephthaldehyde, a bisimidazole-based HTMs (1,4-bis(4,5-bis(4-methoxyphenyl)-1-phenyl-1H-imidazol-2-yl)benzene) was designed and synthesized through the one-pot condensation of Debus-Radziszewski imidazole synthetic route [44] with cost-effective high reaction yield (molecular structure in Fig. 1a, synthetic procedure in Fig. S2, and cost evaluation chart in Table S1). Compared to asymmetric D-A-structured monoimidazole HTMs or conventional spiro-OMeTAD molecules, the  $\pi$ -conjugated system of planar bisimidazole makes high density packing possible in solid state, which is helpful in obtaining higher hole mobility [45]. Also, the two imidazole rings, which are linked by central phenyl spacer, effectively lower highest occupied molecular orbital (HOMO, -5.23 eV) and lowest unoccupied molecular orbital (LUMO, -2.12 eV) energy levels, and minimize the energy offset between the valence band maximum of perovskite and the HOMO of the HTMs (Table S2). Additionally, its low absorbance in visible wavelength region (Fig. S3a) is beneficial to increase the amount of photon into the perovskite photo-absorber in p-i-n structure PSC devices. For reference, cyclic voltammetry results for energy level calculation are in Fig. S4, and material characterization data such as photoluminescence (PL) (Fig. S3b), TGA results along with DSC (Fig. S5), <sup>1</sup>H NMR (Fig. S6), and HR-MS (Fig. S7) are in Supplementary data.

Furthermore, four methoxy groups, introduced to the organic molecule, are expected to work as Lewis bases due to their excess electron lone pairs, which can passivate unsaturated bonds such as under-coordinated  $Pb^{2+}$  ions in the perovskite [46]. The reduced deep level defects at the interface by the passivation are advantageous to decrease non-radiative recombination losses [47,48]. Raman spectrum of the perovskite film, cast on top of the organic HTM, shows a peak at 350 cm<sup>-1</sup> that can be assigned to Pb–O bond stretching (Fig. 1b), and



**Fig. 1.** (a) Molecular structure of designed bisimidazole derivative organic HTM. (b) Raman spectra of perovskite films (bare perovskite and perovskite cast on organic HTM thin film). (c) SEM image of perovskite cast on organic HTM. (d) X-ray diffraction (XRD) patterns of the perovskite films (NiO<sub>x</sub>/perovskite and NiO<sub>x</sub>/ organic/perovskite). (e) Variation of XRD patterns of perovskite films depending on UV illumination time.

this validates the formation of Lewis adduct between O atom of the organic HTM and unsaturated  $Pb^{2+}$  ions of the perovskite [49,50]. To rule out the possibility of oxidation of perovskite, we immediately characterized the samples, and no peak was observed from the perovskite-only layer even after its exposure to air for several hours.

X-ray diffraction (XRD) patterns in Fig. 1d, referenced to ITO signals, show that the crystallinity of perovskite is enhanced on the underlying organic HTL. The passivation of defect at the interface is believed to assist the growth of perovskite crystal in the preferred orientation. Moreover, under UV-irradiation (from perovskite-side), while a diffraction peak at 12.6°, related to (001) plane of PbI<sub>2</sub> impurity, is newly generated from the pristine perovskite, demonstrating the decomposition of the perovskite, no PbI<sub>2</sub>-related peak is observed from the perovskite, grown on the organic HTM, proving its enhanced UV-stability after passivation (Fig. 1e) [51,52]. The variation of intensity and full width at half maximum (FWHM) of main XRD peak of perovskite at  $\sim 14^{\circ}$  is summarized in Table S3, for reference. Additionally, the perovskite grains with and without organic HTM are shown in scanning electron microscope (SEM) images in Fig. 1c and Fig. S8.

Fig. 2a shows that photoluminescence (PL) intensity of perovskite is 30% and 54% reduced in NiO<sub>v</sub>/perovskite and NiO<sub>v</sub>/organic HTM/ perovskite films, respectively, compared to that of pristine perovskite film. These reduced PL spectra represent that the recombination loss in the perovskite photo-absorber is suppressed by the passivation of its defects with the organic HTM [53-56]. Additionally, charge transfer dynamics at the interface was further examined by time-resolved photoluminescence (TRPL) measurement (Fig. 2b and Table S4), and it was confirmed that the carrier lifetime of 202 ns, observed from the perovskite-only thin film, decreased to 165 ns with NiOx and it was further reduced to 157 ns with the additional organic HTM on NiO<sub>x</sub>. The shortened lifetime could be a proof of improved carrier extraction at the interface with the passivation. For calculating those lifetimes, the samples were excited using a picosecond diode laser (510 nm wavelength) from the perovskite-side, and their carrier lifetimes ( $\tau_{avg}$ ) were calculated by fitting their decay curves to a bi-exponential equation:  $\tau_{avg} = A_1$  $\exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ , where  $\tau_1$ ,  $\tau_2$ ,  $A_1$ , and  $A_2$  were lifetimes for slow and fast decay, and their relative amplitudes, respectively (Table S4) [57].

#### 2.2. Perovskite solar cell performances

The enhanced interfacial properties between perovskite and HTL with the addition of organic HTM are expected to improve the performances and stability of PV devices. To confirm this, we prepared p-i-n architecture PSC devices with the following structure, ITO/NiO<sub>x</sub>/ organic HTM/perovskite[Cs<sub>0.04</sub>(FA<sub>0.92</sub>MA<sub>0.08</sub>)<sub>0.96</sub>Pb(I<sub>0.92</sub>Br<sub>0.08</sub>)<sub>3</sub>]/ fullerene(C<sub>60</sub>)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline(BCP)/ silver(Ag) (inset of Fig. 3a), and their current density-voltage (*J-V*)

characteristics, which were measured under 100 mW cm<sup>-2</sup> AM 1.5G illumination, at a scan rate of 0.05 V  $s^{-1}$  for forward scan, in an atmosphere without encapsulation, and with an aperture area of  $0.096 \text{ cm}^2$ , are represented in Fig. 3a. J-V curves of PSCs show that the efficiency of the PSC without organic HTM is largely improved from 16.28% [short circuit current density ( $J_{sc}$ ): 21.95 mA cm<sup>-2</sup>, open circuit voltage ( $V_{oc}$ ): 1.04 V, fill factor (FF): 71.44%] to 18.29% ( $J_{sc}$ : 22.41 mA cm<sup>-2</sup>,  $V_{oc}$ : 1.04 V, and FF: 78.47%) with the addition of organic HTL. For reference, the average values of PV cell parameters, obtained by J-V characteristics, are summarized in Table 1. The enhancement of photocurrent could be further confirmed by external quantum efficiency (EQE) spectra (Fig. 3b), and the  $J_{sc}$  values, obtained by integrating the EQE spectra, were well-matched to those from the J-V plots. Meanwhile, the PSCs with organic HTM did not show any hysteretic behaviors, as shown in Fig. 4a, and the performances of devices, measured at the maximum power point, were comparable to those from *J-V* scanning (Fig. 4b), representing the stable operation of the devices. As mentioned, the improved interfacial properties along with the superior quality of defectpassivated perovskite are also expected to enhance the stability of PSC devices [58], and we confirmed that the PSCs with organic HTM showed excellent stability (Fig. 4c), preserving 92% of its initial efficiency for 500 h in ambient air (Al<sub>2</sub>O<sub>3</sub>-encapsulation, room temperature, and the relative humidity between 30% and 50%).

#### 2.3. Reduced trap-density at the interface between perovskite and HTL

The trap-density of the perovskite can be calculated by estimating the trap-filled limited voltages ( $V_{TFL}$ ) of dark *J*-V curves of hole-only devices (ITO/NiO<sub>x</sub>/organic HTM/perovskite/*spiro*-OMeTAD/Au) with the following equation (1) [59,60].

$$N_{\rm trap} = 2\varepsilon\varepsilon_0 V_{\rm TFL} (eL^2)^{-1} \tag{1}$$

where *e* is elementary charge,  $\varepsilon \varepsilon_0$  is semiconductor permittivity, and *L* is the layer thickness. Fig. 5a and Table S5 confirmed that the calculated static trap-density of the perovskite film was reduced after passivation from  $1.18 \times 10^{16}$  to  $0.88 \times 10^{16}$  cm<sup>-3</sup>. The hole-mobility ( $\mu$ ) was also obtained by fitting the curves in space-charge-limited-current (SCLC) regime with the Mott-Gurney law (2) [61].

$$I = 9\varepsilon\varepsilon_0 \mu V^2 (8L^3)^{-1} \tag{2}$$

The calculated hole-mobility was enhanced from  $1.2 \times 10^{-3}$  to  $3.0 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> with the organic passivation layer (Table S5), indicating that the reduced trap density was beneficial to the efficient charge transport.

The decreased trap-states are also advantageous to suppress the nonradiative recombination of photo-generated carrier in the photoabsorbing layer, consequently increasing its quasi-Fermi level



Fig. 2. (a) Steady-state photoluminescence (PL) spectra of perovskite films (perovskite, NiO<sub>x</sub>/perovskite, and NiO<sub>x</sub>/organic/perovskite). (b) Time-resolved PL (TRPL) decay curves of perovskite films (perovskite, NiO<sub>x</sub>/perovskite, and NiO<sub>x</sub>/organic/perovskite).



Fig. 3. Performances of perovskite solar cell (PSC) devices: (a) J-V curves and (b) External quantum efficiency (EQE) spectra.

 Table 1

 Perovskite solar cell performances with and without organic HTM.

	$V_{\rm oc}$ (V)	J <sub>sc</sub> (mA cm <sup>-2</sup> )	FF (%)	PCE (%)
Without org.	1.04	21.95	71.44	16.28
HTM	(1.03)	(21.62)	(69.85)	(15.52)
With org. HTM	1.04	22.41	78.47	18.29
	(1.05)	(22.35)	(75.83)	(17.64)

Numbers in and out of the parenthesis are average and best values, respectively.

splitting, and thus improving the built-in potential ( $V_{bi}$ ) of devices. From the Mott-Schottky plots of the devices (Fig. 5b), obtained by the reciprocal of the square of capacitance-voltage ( $C^{-2}$ -V) curves,  $V_{bi}$  of PSCs with and without organic HTM could be estimated using equation (3) [62,63].

$$C^{-2} = 2(V_{\rm bi} - V)(A^2 e \varepsilon_0 N_{\rm A})^{-1}$$
(3)

where A and  $N_{\rm A}$  are device area and doping concentration, respectively. The calculated  $V_{\rm bi}$  of the device with the organic HTM (1.06V) is higher than that without the HTM (1.01V), advantageous to better charge extraction.

Admittance spectroscopy could be further utilized to prove the



Fig. 4. (a) *J*-V curves of organic HTM-introduced PSC device depending on the scanning direction. (b) Power conversion efficiencies (PCEs) of PSC devices at maximum power point (0.84 V). (c) Normalized PCEs of PSC devices (Al<sub>2</sub>O<sub>3</sub>-added) depending on the time in an atmosphere.



**Fig. 5.** (a) *J-V* curves of hole-only devices with and without the organic HTM at dark condition. (b) Mott-Schottky plots of PSCs with and without the organic HTM. (c) Trap density of state of PSCs with and without the organic HTM with respect to the energetic demarcation ( $E_{trap} - E_{band edge}$ ).

reduced trap-density with the organic passivation layer. The trap density of states ( $N_t$ ) can be estimated from the capacitance-angular frequency (C- $\omega$ ) curves using the following equation (4) [64,65].

$$N_{\rm t} = -V_{\rm bi} \left( ek_{\rm B}TW \right)^{-1} \left( \omega dC/d\omega \right) \tag{4}$$

where  $k_{\rm B}$  is Boltzmann constant and *T* is temperature. Fig. 5c represents the trap density of states according to the energetic demarcation ( $E_{\omega}$ ), the difference between  $E_{\rm trap}$  and  $E_{\rm band\ edge}$  ( $E_{\omega} = E_{\rm trap} - E_{\rm band\ edge}$ ), defined by  $E_{\omega} = k_{\rm B}T\ln(\omega_0/\omega)$ , where  $\omega_0$  is the attempt-to-escape frequency, and it is confirmed that the density of deep-level traps, which generally exist at the interface, is significantly reduced by the passivation of the organic HTM [66].

#### 2.4. Recombination kinetics in PSCs

Recombination kinetics of the PSC devices can be estimated by investigating their light intensity(*I*)-dependent  $J_{sc}$  and  $V_{oc}$  characteristics (Fig. 6a and b). The  $J_{sc}$  of PSC generally has a power law dependence according to the light intensity ( $J_{sc} \propto I^{\alpha}$ ), and its exponential parameter  $\alpha$ , obtained by fitting its data in a double log scale to a linear curve, approaches 1, when a bimolecular recombination in the PSC device at short-circuit condition is not noticeable. The logarithmic dependence in Fig. 6a shows that the slope  $\alpha$  of the defect-passivated PSC device with the organic HTM is much closer to 1, representing a reduced bimolecular

recombination in that device (with and without organic HTM are 0.992 and 0.959, respectively) [67–70]. Meanwhile, the  $V_{\rm oc}$  of the PV device has the following relation with the light-intensity:  $V_{\rm oc} \approx n k_{\rm B} T/e \ln (J_{\rm sc}/J_{\rm o}) \approx \alpha (n k_{\rm B} T/e) \ln(I) + c$ , where *n* is the diode ideality factor,  $J_{\rm o}$  is the reverse saturation current density at dark condition, and *c* is a fitting parameter, as far as it has high shunt resistance. The estimated diode ideality factors of PSC devices with and without organic HTM are 1.15 and 1.63, respectively, which represents that Shockley–Read–Hall (SRH) trap-assisted recombination is significantly reduced after passivation with organic HTM [71].

Additionally, an electrochemical impedance spectroscopy (EIS) was further utilized to understand the charge transport and recombination behaviors in PSC devices. Fig. 6c shows that recombination resistance ( $R_{rec}$ ) of the PV device, measured at low frequency, significantly increases with the organic HTM from 518 to 1451  $\Omega$ , and its series resistance ( $R_s$ ), calculated at high frequency, slightly decreases from 20 to 18  $\Omega$ , indicating the enhanced interfacial property of the PV device with the organic HTM layer [72,73].

#### 3. Conclusion

In this work, we represent that the performances of PSC devices can be enhanced by passivating the defects of perovskite at the interface with the HTL. For this purpose, a lophine-based bisimidazole derivative



**Fig. 6.** (a) Light intensity dependent  $J_{sc}$  characteristics of the PSCs with and without the organic HTM. (b) Light intensity dependent  $V_{oc}$  characteristics of the PSCs with and without the organic HTM. (c) Nyquist plots of the PSCs with and without the organic HTM.

organic molecule is newly prepared, and the Lewis-base type functional groups of this organic HTM are proved to interact with undercoordinated  $Pb^{2+}$  ions of perovskite. The designed organic molecule is inserted to the interface between  $NiO_x$  and perovskite, and it is confirmed that this modification can not only elaborate the rough surface of  $NiO_x$  but also passivate the defects existing at the interface with polycrystalline perovskite, improving its crystallinity and reducing nonradiative recombination in the devices. Consequently, the performances and stability of PSCs are significantly enhanced. We believe that our approach through a molecular design of organic HTM can be an effective way to complement structural defects of the perovskite for realizing high performance PSC devices having long-term stability.

# 4. Experimental section

# 4.1. Synthesis of organic HTM

The mixture of terephthalaldehyde (1 eq), corresponding aniline (2.1 eq), *p*-anisil (2.1 eq) and ammonium acetate (7 eq) in glacial acetic acid were refluxed for 12 h and cooled to room temperature. The resulting precipitates were filtered and washed with small amount of acetic acid, sodium carbonate solution followed by copious amount of water and dried. Then, the crude product was purified by silica gel column chromatography (DCM:EtOAc = 90:10) and recrystallized from CHCl<sub>3</sub>: EtOAc (70:30) solvent mixture. Pure white spongy solid. Yield: 1.5 g (51%). <sup>1</sup>H NMR (400 MHz, Chloroform-d)  $\delta$  7.50 (d, *J* = 8.9 Hz, 4H), 7.27 (s,4H), 7.25–7.21 (m, 6H), 7.00 (dd, *J* = 12.6, 7.8 Hz, 8H), 6.79 (d, *J* = 8.9 Hz, 4H), 6.74 (d, *J* = 8.8 Hz, 4H), 3.77 (d, *J* = 9.8 Hz, 12H). HRMS-TOF [M+H]<sup>+</sup>: *m*/*z* calcd for [C<sub>52</sub>H<sub>42</sub>N<sub>4</sub>O<sub>4</sub>+H]<sup>+</sup> 787.3284; found 787.3379.

#### 4.2. Materials

Foramidinium iodie (FAI) and Methyl ammonium bromide (MABr) were purchased from the Great Cell Solar Company and Xi'an Polymer Light Technology Corp, respectively. Cesium iodide (CsI, 99.9%), lead bromide (PbBr<sub>2</sub>, 98%), bathocuproine (BCP, sublimed grade, 99.99%), Octylamine (OA, >99.5%) dimethyl sulfoxide (DMSO, anhydrous), chlorobenzene (CB, anhydrous), N,N-dimethylmethanamide (DMF, anhydrous), N-methyl-2-pyrrolidone (NMP, anhydrous) were purchased from Sigma Aldrich. Lead iodide (PbI2 10-mesh beads, ultra-dry, 99.999%) and Fullerene (C60) were purchased from Alfa Aesar and Nano C, respectively. All chemicals were used for experiments without any further purification. NiOx nanoparticles (NPs) synthesis method, used in this work, was optimized from the previous studies [74-77]. To prepare the NiOx NPs, Ni(NO3)2.6H2O (0.04 mol) was dispersed in deionized water to obtain a dark green solution. NaOH (0.08 mol) was dispersed in deionized water under the cold condition to prevent precipitation through reverse reactions. Then, NaOH solution was added slowly to Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O solution drop by drop until the pH value reaches 10. During the dropping process, the colloidal precipitate was produced. The whole reaction process was carried out under stirring condition. After the reaction, the colloidal precipitate was washed with deionized water more than three times to remove impurities. And the washed colloidal precipitation was dried at 80 °C for overnight. After drying, green powder was produced, and then calcined at 285 °C for 2 h inside the furnace to get black powder. Finally, the black powder was pulverized to be small sized particles through a grinder. The NiOx NPs solution was used by dispersing the black powder in deionized water at an appropriate concentration.

# 4.3. Preparation of perovskite precursor

The perovskite solution of  $Cs_{0.04}(FA_{0.92}MA_{0.08})_{0.96}Pb(I_{0.92}Br_{0.08})_3$  composition was prepared by dissolving 1.35 M mixed metal lead salts (0.883 PbI<sub>2</sub>: 0.077 PbBr<sub>2</sub>) and 1.35 M mixed organic cation (0.883 FAI: 0.077 MABr) into mixed solvent of DMF/DMSO (4:1 vol ratio). Other precursor CsI of 0.05 M and alkylammonium ligands (OA) of 0.1 wt% were added into the prepared solution. The perovskite composition was well-optimized by tuning the previous work [78].

# 4.4. Device fabrication

We prepared a p-i-n architecture PSC device with the following structure, ITO/NiO<sub>x</sub>/organic HTM/perovskite[Cs<sub>0.04</sub>(FA<sub>0.92-</sub> MA<sub>0.08</sub>)<sub>0.96</sub>Pb(I<sub>0.92</sub>Br<sub>0.08</sub>)<sub>3</sub>]/fullerene(C<sub>60</sub>)/2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline(BCP)/silver(Ag). Initially, we patterned the ITO glass substrate and followed the etching process using HCl (35%) and zinc powder. Further patterned substrates were cleaned sequentially in deionized water, isopropyl alcohol, and acetone with ultra-sonication. The substrates were dried with N<sub>2</sub> blowing and further treated with oxygen plasma for 20 min at 60 W. A NiO<sub>x</sub> hole transport layer of 30 nm was deposited on the plasma-treated substrate by spin-casting of nanoparticle solution (20 mg NiOx nanoparticles dissolved into 1 mL deionized water) at 2000 r.p.m for the 30s and further annealed at 150 °C for 10 min. The process followed for the synthesis of NiO<sub>x</sub> is reported in our previous work [74]. Next, organic HTL was deposited on NiO<sub>x</sub> film by spin-casting of organic HTL solution (1.5 mg of organic material dissolved into 1 mL of NMP) at 2000 r.p.m for 25s and further annealed in a vacuum oven (1 kPa) at 100 °C for 10 min. Perovskite solution was prepared in N<sub>2</sub> filled glove box and filtered using PTFE filter of 0.2  $\mu$ m. The filtered solution was spin-coated with two-step process (2000 r.p.m for 10s and then 4500 r.p.m for the 50s) to prepare the perovskite film. Anti-solvent CB of 160  $\mu$ L was drop-cast on the substrate during the second step of spinning at 45 s. Further, the perovskite film was annealed at 100 °C for 30 min. Moreover, C<sub>60</sub> (19 nm), BCP (4 nm) and Ag (120 nm) were deposited sequentially using the high vacuum thermal evaporator. The hole-only devices were prepared by replacing the C<sub>60</sub>/BCP and Ag to spiro-OMeTAD, spin-coated on the perovskite layer at 4000 r.p.m for the 30s, and Au, respectively. The device area of 0.096 cm<sup>2</sup> defined using the metal mask.

#### 4.5. Device characterization

A solar simulator with AM 1.5G 100 mW cm<sup>-2</sup> of illumination was utilized for *J-V* curves. The intensity was calibrated by an infrared cutoff filter (KG5)-equipped NREL certified Si photodiode, reducing spectral mismatch. An ABET technology 10,500 solar simulator and a SPECTRO Mmac-200 were used as light source and light solution. The EQE was measured at a short-circuit condition. Mott-Schottky plots, Nyquist plots, and trap density of states were plotted at room temperature using a potentiostat (SP-300, BioLogic). A Mott-Schottky analysis was performed at fixed frequency (100 kHz). Electrochemical impedance spectroscopy data was measured at 0.3 V DC bias and 30 mV amplitude with a frequency ranging from 1 MHz to 1 mHz. For trap density of state variation, *C-w* curves were measured at 0 V DC bias and 30 mV amplitude from frequency range of 1 MHz–1 mHz in logarithmic steps.

#### 4.6. Thin film characterization

Raman spectra were measured with visible-NIR 532 nm laser by NRS-3100 (JASCO), having 1 cm<sup>-1</sup> of resolution. Raman sample configuration: glass/ITO/perovskite, glass/ITO/organic/perovskite. SmartLab (Rigaku) was used to collect X-ray diffraction signals. XRD patterns were collected by measuring from  $2\theta = 10^{\circ}$  to  $2\theta = 50^{\circ}$  after optical and sample alignment. XRD sample configuration: glass/ITO/

 $NiO_x/perovskite$  and glass/ITO/NiO<sub>x</sub>/organic/perovskite. Steady-state and time-resolved PL (TRPL) curves were depicted via FlouTime 300 (PicoQuant). For steady-state PL, the excitation source was from a monochromated lamp, and, for time-resolved PL, a green laser diode was used for the excitation. Steady-state PL and TRPL sample configuration: glass/ITO/perovskite, glass/ITO/NiO<sub>x</sub>/perovskite, and glass/ ITO/NiO<sub>x</sub>/organic/perovskite. PL decay curves were fitted with biexponential components to obtain a slow and a fast decay lifetime. SEM images were taken from Nova Nano SEM 450 (FEI).

# CRediT authorship contribution statement

Joonhyuk Choi: Validation, Formal analysis, Investigation, Data curation, Writing – original draft. Eswaran Kamaraj: Validation, Formal analysis, Investigation, Data curation, Writing – original draft. Hansol Park: Formal analysis, Investigation, Data curation. Bum Ho Jeong: Formal analysis, Investigation. Hyoung Won Baac: Software, Validation, Formal analysis, Supervision. Sanghyuk Park: Conceptualization, Methodology, Validation, Formal analysis, Writing – original draft, Writing – review & editing, Supervision, Project administration. Hui Joon Park: Conceptualization, Methodology, Validation, Formal analysis, Writing – original draft, Writing – review & editing, Visualization, Supervision, Project administration, Funding acquisition.

# Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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# Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2021.109255.

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