Supplementary information

Suppression of hydrogen bonds and control of surface dipole: effective passivation for hydrophobic perovskite photoabsorber layers in solar cells

Naoyuki Nishimura*, Siby Mathew and Takuro N. Murakami

National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba,

Ibaraki 305-8565, Japan.

1. Experimental methods

1-1. Materials

All materials were reagent grade and used as purchased. 2-methoxyethanol, ethanol and n-hexadecane were purchased from WAKO-Chemicals Co. Ltd.. Formamidine hydroiodide (FAI), lead iodide (PbI_2), methylammonium chloride, n-octyl ammonium iodide (OAI), phenylethyl ammonium iodide (PEAI), 4-tert-butylpyridine (tBP), tetrabromoethane were purchased from Tokyo Chemical Industry Co. Ltd.. Mesoporous titanium oxide (m-TiO_2; 18NR-T) precursor was from Great Cell Solar. 2,2',7,7'-tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (Spiro-OMeTAD) was from Nippon Fine Chemical Co. The used water for the wettability measurements was Milli-Q grade. Other reagents were from Sigma Aldrich. Fluorine-doped tin oxide (FTO) coated transparent glass (thickness: 1.6 mm, sheet resistance ≤ 10 Ω cm^{-2}) was purchased from Nippon Sheet Glass.

1-2. Synthesis of FAPbI₃ powder

$FAPbI_3$ powder was synthesized as the precursor of the thin film along the previously reported method.[1] 0.8 M of FAI and PbI_2 were dissolved into 2-methoxyethanol, and the solution was heated at 393 K for 1 h under stirring. The precipitated black particles were collected by filtration, and subsequently heated at 423 K for 30 min. Finally, the resulting powder was dried under evacuation at room temperature for 30 min.

1-3. Solar cell fabrication

TiO_2 compact layer (~50 nm) was coated over fluorine-doped tin oxide (FTO) glass substrate, which was placed on a hotplate at 673 K, by spray pyrolysis using 7.5 vol% of titanium diisopropoxide bis(acetylacetate) diluted with ethanol. After that, m-TiO_2 layer was deposited by spin coating of TiO_2 paste diluted with ethanol onto the substrate at 2000 rpm for 30 s, followed by calcinating the substrate at 723 K for 30 min.

$FAPbI_3$ perovskite layer was deposited on the as-prepared TiO_2/FTO by spin coating in a dry room (temperature: 291 K, dew point: <243 K). 1.8 M of $FAPbI_3$ precursor solution was prepared by dissolving the synthesized $FAPbI_3$ powder and 40 mol% of methylammonium chloride into a mixed solution of N,N-dimethylformamide and dimethyl sulfoxide and (4:1 vol ratio).[2] The TiO_2/FTO substrate was spin-coated with the precursor solution at 6000 rpm for 50 s. During the spin-coating, 1 mL of chlorobenzene was dropped after spinning for 10 s. After the spin-coating, the sample was immediately heated at 423 K for 10 min. The passivation was employed with 15 mM of OAI or PEAI/ isopropyl alcohol solution in the dry room.[1,3,4] This solution was spin-coated over the $FAPbI_3$ layer at 3000 rpm for 30 s, followed by drying in the dry room for 1 h. The hole transport material (HTM) was deposited by spin-coating of its precursor solution at 3000 rpm for 30 s in the dry room. The HTM solution was prepared by dissolving 70 mM Spiro-OMeTAD into chlorobenzene and mixing the CB solution with 0.27 mM tBP and the stock solutions of bis(trifluoromethane) sulfonamide lithium salt/acetonitrile and tris(2-(1H-pyrazol-1-yl)-4-tertbutylpyridine)-

cobalt(III)tris(bis(trifluoromethylsulfonyl)imide (FK209)/acetonitrile to be 35 mM and 4.2 mM, respectively. It is noteworthy here that the dropped amount of the HTL precursor solution for the OAI-passivated was twice (200 μL) than that for the pristine and PEAI-passivated perovskite layer (100 μL) as the HTM solution possesses low wettability for the OAI-passivated layer as shown in Fig. 1d. Finally, gold (Au) conductor layer (~200 nm) was deposited via thermal evaporation.

1-4.   Preparation of perovskite thin film samples for the wettability measurement

The samples of wettability measurement were prepared as follows: m-TiO$_2$ layer was deposited by spin-coating with the TiO$_2$ paste at 2000 rpm for 30 min, followed by heating at 723 K for 30 min. Subsequently, FAPbI$_3$ layer was deposited by the same procedure as the solar cell fabrication. Also, some samples were employed by the passivation procedure.

1-5.   Current-voltage curve measurement

Current-voltage curves were measured with a source meter (R6243, ADVANTEST) and solar simulator (XIL-05B100KP, Seric Co.) calibrated using a Si-reference cell to generate AM1.5G (100 mW cm^{-2}). The current-voltage scan was conducted under a constant speed of 100 mV s^{-1} f under irradiation of the simulated sunlight. Over 15 samples were measured for each condition, then the best samples were chosen among them for Fig. 2a. Also, averages of the solar cell properties were calculated with the over 15 samples, and these error bars were estimated by their standard deviation.

The external quantum efficiency (EQE) action spectra were measured by carried out with an action spectrum measurement setup (CEP-99W, Bunkou Keiki).

1-6. Wettability measurement

The wettability of each solution over the perovskite layer was measured with a contact angle meter (Kyowa Interface Science Co.; DMo-401), equipped with a syringe whose needle was made of pristine SUS (Φ0.47 mm) for water or of SUS coated with Teflon (Φ0.40 mm) for other liquids, in nitrogen atmosphere. 0.6 μL of a liquid droplet contacted to perovskite layers with or without passivation, then CA between the liquid and the solid layer (i.e., perovskite layer) after 1 s was measured. The CA values of each condition were determined by an average of 4−6 points, and these error bars were estimated by the standard deviation.

1-7. Photoluminescence measurement

Photoluminescence (PL) measurements were measured for perovskite layer on quartz substrate, which was deposited by the procedure same as the cell fabrication. The steady state PL measurements were conducted by wavelength-calibrated fluorescence spectrometer (FP8600, JASCO Co.) with excitation at 532 nm. The PL lifetimes were measured by a TCSPC system (C12132, Hamamatsu Photonics) with excitation at 532 nm with pulse power of 0.3 nW, and estimated with single exponential fitting at the emission peak by the Origin software.

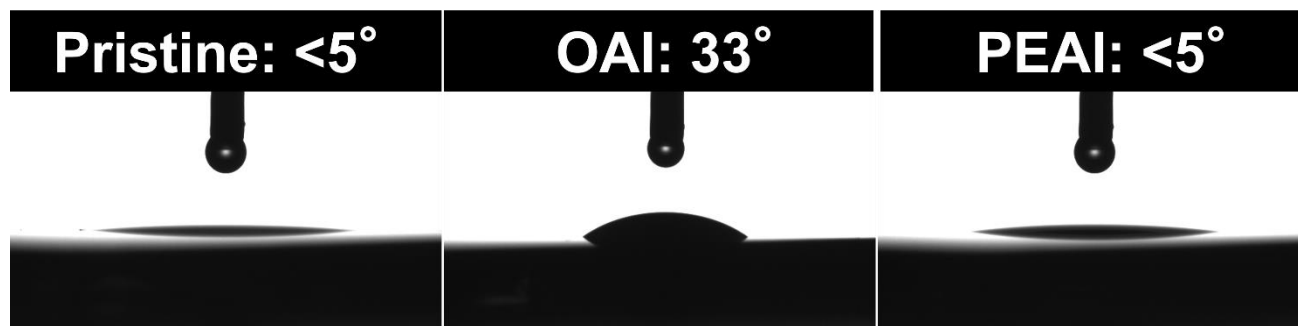## 2. CA of HTM solution for FAPbI₃ perovskite

Fig.S1 CA of HTM solutions over perovskite layer, corresponding to the pictures in Fig.1 (d)

As shown in Fig.1d, for pristine and PEAI passivated perovskite, the HTM solution spontaneously spread to the corner of the substrate after dropping the solution onto the perovskite layer, while it did not for OAI passivated perovskite over for 30 s. Fig.S1 depicts CA of HTM solutions over perovskite layer so indicates this trend in more detail. CA for the pristine and PEAI passivated perovskite were less than 5°, representing the spontaneous spread. To the contrary, CA for the OAI passivated perovskite resulted in 33°, indicative of the retention of the droplet not to be spread over the perovskite as shown in the Fig.1d (center).

The CA value for OAI sample with HTM solution (Fig.S1, 33°) was slightly higher than that with pure CB (Fig.2c, 27°). Hence, the prediction that practical HTM solution possesses higher polarity than the pure CB, which exists in main script at page 3, is plausible.

3. Current-voltage property of the fabricated solar cells

Table S1 Averaged current-voltage properties under backward scan

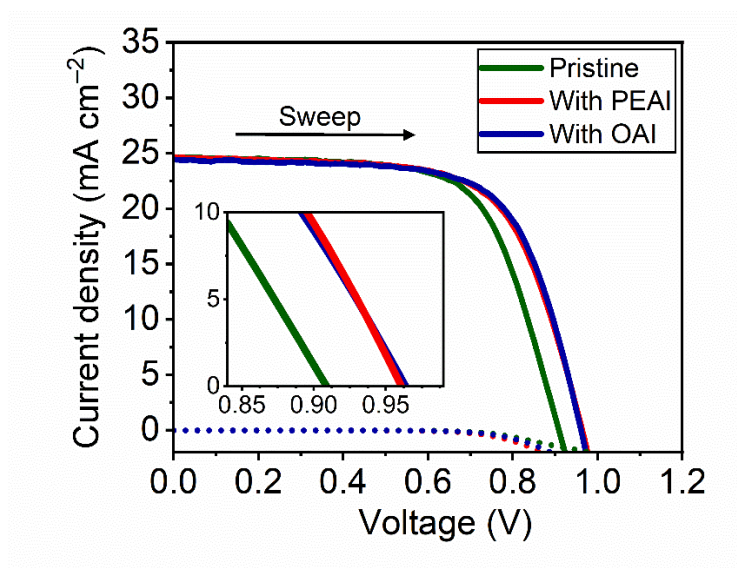| Sample	Jsc (mA/cm^2)	Voc (V)	FF	η (%)
Pristine	23.97 ± 0.37	1.00 ± 0.03	0.74 ± 0.01	17.66 ± 0.84
With PEAI	23.94 ± 0.38	1.02 ± 0.01	0.74 ± 0.01	18.04 ± 0.51
With OAI	23.93 ± 0.43	1.03 ± 0.02	0.72 ± 0.02	17.73 ± 0.91

Fig. S2 current-voltage curves of the best cells consisting of perovskite layer (a) pristine, (b) with PEAI-, or (c) OAI-treatment under forward scan (the dotted lines denote dark currents)

Table S2 Solar cell properties of the best samples in the series of the cells under forward scan

Sample	Jsc (mA/cm^2)	Voc (V)	FF	η (%)
Pristine	24.65	0.91	0.67	14.91
With PEAI	24.42	0.96	0.68	15.87
With OAI	24.67	0.96	0.66	15.70

Table S3 Averaged current-voltage properties under forward scan

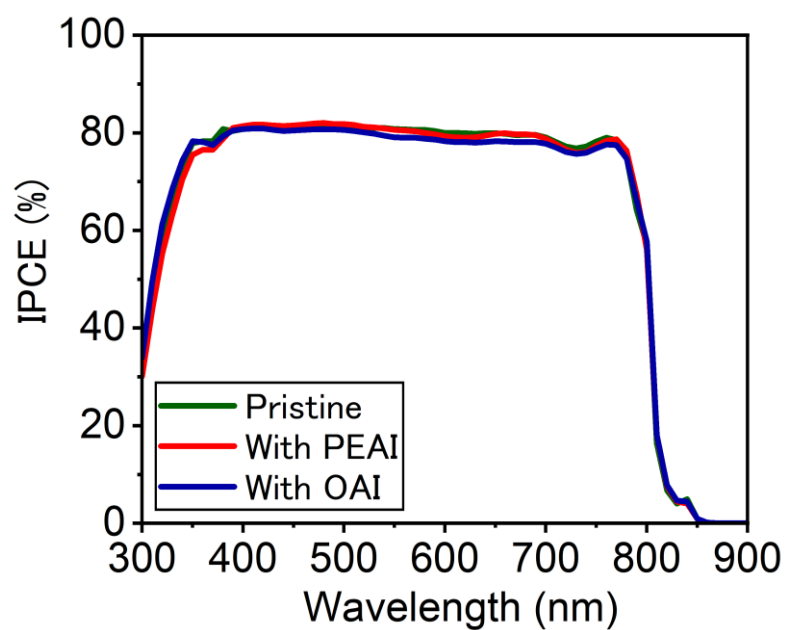| Sample	Jsc (mA/cm^2)	Voc (V)	FF	η (%)
Pristine	24.03 ± 0.45	0.89 ± 0.05	0.66 ± 0.03	14.32 ± 1.44
With PEAI	24.00 ± 0.41	0.94 ± 0.02	0.68 ± 0.02	15.33 ± 0.59
With OAI	24.04 ± 0.46	0.94 ± 0.03	0.64 ± 0.03	14.61 ± 1.13

Fig. S3 EQE action spectra

The integrated photocurrent densities were estimated to be 21.87, 21.85, and 21.61 mA cm^{-2} for samples pristine, with PEAI, and with OAI, respectively. Therefore, the IPCE values were similar among the samples.

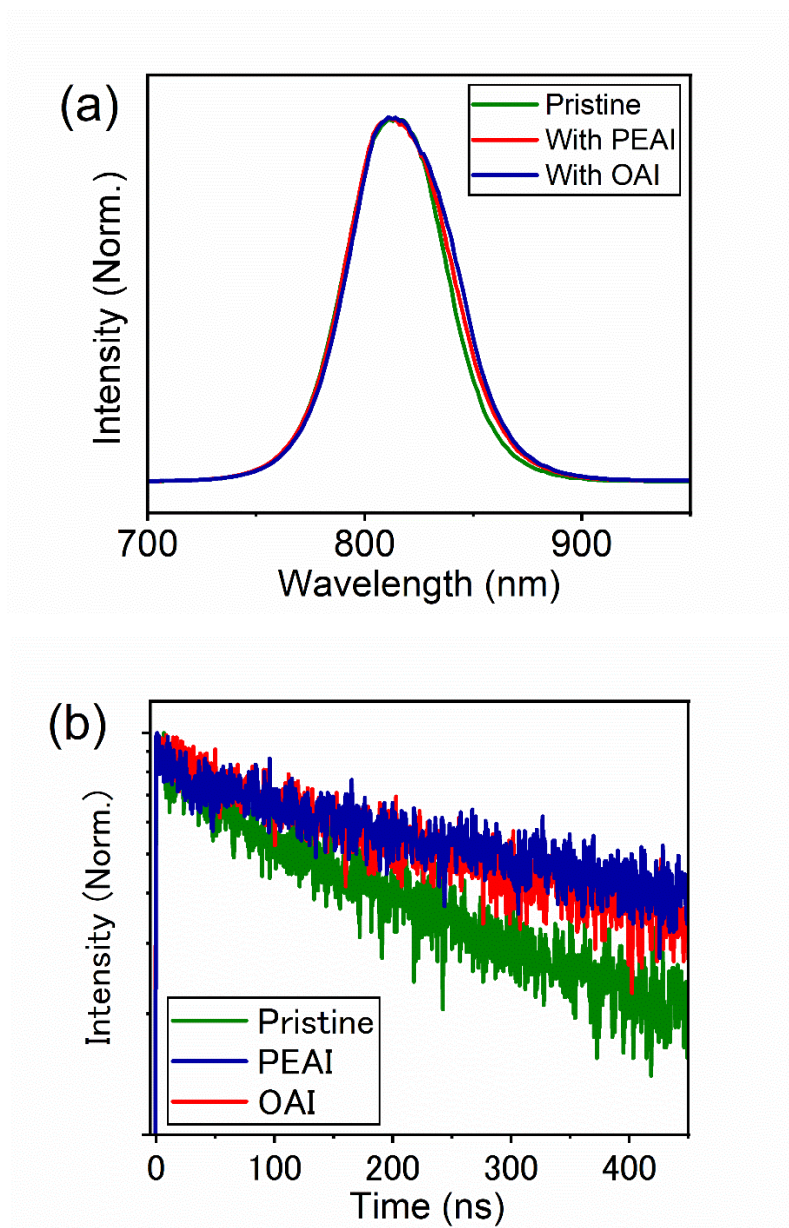**4. PL from perovskite layer with or without passivation**

Fig. S4 (a) steady state PL from perovskite samples pristine, with PEAI or OAI treatment, (b) lifetime

of their PL.

Table S4. Estimated PL lifetime

Sample	PL lifetime; τ (ns)
Pristine	135 ± 2
With PEAI	269 ± 26
With OAI	249 ± 15

For steady state PL, similar PL spectra with peaks around 820 nm were observed among the samples.

Meanwhile, in terms of the PL lifetime, the passivation both of PEAI and OAI significantly improved

the PL lifetime (τ)from 135 ± 2 ns from to 269 ± 26 ns for PEAI and 249 ± 15 ns for OAI, which is

indicative of cancelation of defects in perovskite layer via the passivation and consistent with the

previous reports. Therefore, this results also supports that the passivation treatment employed in this

work was typical.

5. Estimated adhesive work between CB and perovskite surface

Table S5   Divided adhesive work (W_A) between CB and perovskite layer

Sample	$2(\gamma_S^{a}\,\gamma_L^{a})^{1/2}$ Non-polar (N/cm^2)	$2(\gamma_S^{b}\,\gamma_L^{b})^{1/2}$ Diplole (N/cm^2)	Sum (N/cm^2)
Pristine	59.2	16.5	75.7
With PEAI	59.2	14.8	74.0
With OAI	57.2	4.2	61.5

CB, which is the major solvent of HTM solution, is a type (ii) solvent. Hence, the passivation treatment significantly decreases γ_S^{b} such as OAI passivation results in drop of W_A of polar term γ^{b} (e.g., from pristine: 16.5 N/cm^2 to OAI-treated: 4.2 N/cm^2) can reduce wettability of the HTL precursor solution over perovskite layer as shown in Fig. 1d

6. Wettability control of HTM solutions over perovskite layers for the scalable solar cell fabrication

For the scalable wet process, high wettability of precursor solutions over the layers to be coated is vital. If a precursor solution cannot spontaneously spread, meticulous adjustment of the printing process would also be required, leading to a narrow process window. As the broad process window is preferable for industrialization, this issue would hamper large-scale cell fabrication. Moreover, especially for coating the HTM layer, much portion of the precursor solution, which is relatively expensive, will be wasted if the perovskite layer has low wettability. Indeed, in the HTM deposition process in the present work, OAI passivated perovskite layer necessitated dropping much portion of HTM solution in order to spread this solution over the substrate, compared to the amount toward pristine or PEAI passivated layers (see experimental section). Consequently, wettability control of HTM solution over passivated perovskite layer (Fig. 1c) would be one of the keys to industrialization, and this work provides insights to sort it out.

Reference

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