

Article

Effects of Polysilane Addition to Chlorobenzene and High Temperature Annealing on $\text{CH}_3\text{NH}_3\text{PbI}_3$ Perovskite Photovoltaic Devices

Takeo Oku ^{1,*} , Masaya Taguchi ¹, Atsushi Suzuki ¹ , Kaede Kitagawa ¹, Yugo Asakawa ¹, Satoshi Yoshida ¹ , Masanobu Okita ², Satoshi Minami ², Sakiko Fukunishi ² and Tomoharu Tachikawa ²

¹ Department of Materials Science, The University of Shiga Prefecture, 2500 Hassaka, Hikone, Shiga 522-8533, Japan; of21mtaguchi@ec.usp.ac.jp (M.T.); suzuki@mat.usp.ac.jp (A.S.); ov21kkitagawa@ec.usp.ac.jp (K.K.); ov21yasakawa@ec.usp.ac.jp (Y.A.); satoshi.glass.jp@gmail.com (S.Y.)

² Osaka Gas Chemicals Co., Ltd., 5-11-61 Torishima, Konohana-ku, Osaka 554-0051, Japan; okita@ogc.co.jp (M.O.); s-minami@ogc.co.jp (S.M.); fukunishi@ogc.co.jp (S.F.); t-tachikawa@ogc.co.jp (T.T.)

* Correspondence: oku@mat.usp.ac.jp; Tel.: +81-749-28-8368

Abstract: $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite photovoltaic devices treated with a polysilane layer were fabricated and characterized. Decaphenylcyclopentasilane (DPPS) in chlorobenzene solution was deposited at the surface of the perovskite layer, and the resulting device was annealed at 140–260 °C. The photoconversion efficiencies of the DPPS-treated device remained high even after 255 days in ambient air. Raman scattering spectroscopy and ab initio molecular orbital calculations of DPPS suggested that it increased hole transport efficiency in the treated devices, which was confirmed from the high shunt resistances of the DPPS-treated devices.

Keywords: perovskite; $\text{CH}_3\text{NH}_3\text{PbI}_3$; solar cells; polysilane; decaphenylcyclopentasilane; stability; chlorobenzene; calculation; Raman scattering



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1. Introduction

Si-based photovoltaic cells are a widely used energy technology. However, the manufacture of Si-based devices is complex, and the band structure of silicon involves an indirect transition type. Conversely, $\text{CH}_3\text{NH}_3\text{PbI}_3$ (MAPbI_3) has the advantages of a direct bandgap, a high conversion efficiency, and an ability to be solution processed [1–5]. Hence, perovskite compounds are regarded as candidates for new generation photovoltaic materials. However, perovskites are normally unstable in air. The instability of MAPbI_3 has been attributed to migration and desorption of CH_3NH_3 (MA) and reactions with moisture in air [6,7]. Therefore, the stability of perovskite solar cells must be improved to enable their practical application in modules [8,9].

Various doped perovskite crystals have been widely studied with the aim of improving their stability and photovoltaic properties [10–13]. Although perovskite solar cells doped with $\text{CH}_3(\text{NH}_2)_2$ [14–16], $\text{CH}_3\text{CH}_2\text{NH}_3$ [17,18], or $\text{C}(\text{NH}_2)_3$ [19,20] have been developed and studied, these organic molecules may still induce instabilities. Substitutions of CH_3NH_3 by doping sodium [21], potassium [22–24], rubidium, or cesium are expected to be effective for suppressing desorption of CH_3NH_3 sites in the MAPbI_3 . Doping Rb^+ or Cs^+ to the MAPbI_3 also reduced defect densities and increased grain sizes [25–28]. First-principles calculation also indicated that co-doping of alkali metals and copper at the MA and Pb sites, respectively, lowered the distortion and energies of the crystal structures [29,30]. In fact, photovoltaic properties of the co-doped perovskite solar cells were improved and stable, even after one year [31].

Another approach to improving the stability of perovskite solar cells is incorporating polymeric materials into the perovskite devices [32–37]. Polymers have been shown to promote device stability in perovskite cells [38]. For example, coating a thin layer of

poly(methyl methacrylate) on top of the perovskite layer forms a cross-linked network structure, which protects the cell from moisture and oxygen [38–40]. Poly(propylene carbonate) is similarly effective for improving stability, owing to the formation of large crystals of crosslinked perovskite particles with few defects [34].

The stability of the MAPbI₃ compounds is affected by moisture and oxygen in the air and is also influenced by the hole transport layer (HTL). A common HTL in perovskite solar cells is 2,2',7,7'-tetrakis-[N,N-di(p-methoxyphenyl)amine]-9,9'-spirobifluorene (spiro-OMeTAD); however, this HTL is expensive and has poor stability. Alternative low cost and more stable HTLs have been developed [36,37], and other HTL materials, such as polysilanes, have also been utilized with organic photovoltaic devices [41,42].

In contrast to organic polymers, polysilanes have two important features. First, polysilanes are *p*-type semiconductors, which promote hole transfer. Second, polysilanes are more stable at elevated temperatures above 300 °C than ordinary organic materials. Polysilanes may function as a protective layer when deposited on perovskite compounds. Hence, polysilanes, such as decaphenylcyclopentasilane (DPPS), have been applied as HTLs [43,44] and as additives in the photoactive layer [45] of MAPbI₃ perovskite devices. DPPS has been found to promote a uniform perovskite morphology, which increases device power conversion efficiencies. However, chlorobenzene is typically used to dissolve and deposit DPPS by solution processing. Chlorobenzene can also have effects on device performance, which have not been investigated separately from its use as a solvent for DPPS [46–48]. Thus, there is a need to separately investigate the effects of DPPS and chlorobenzene in detail.

The purpose of the present work was to investigate the photovoltaic properties and stabilities of perovskite photovoltaic devices treated with a DPPS layer. The cells were treated by high temperature annealing in ambient air. The effects of treating devices with DPPS in chlorobenzene on the photovoltaic properties and microstructures were investigated. When only the DPPS is used as the HTL, the obtained conversion efficiencies are not enough; consequently, the DPPS/spiro-OMeTAD bilayer was applied in the present work. The chlorobenzene-treated devices were also compared to investigate the effect of the chlorobenzene. To increase the conversion efficiency by raising the fabrication temperatures of the devices, the device preparation time was shortened.

2. Experimental and Calculation Procedures

Figure 1a shows the fabrication process of the devices. Detailed conditions for the fabrication process have been described in previous reports [10,48–51]. All fabrication processes were performed under atmospheric conditions in ambient air, and the temperature and humidity were ~20 °C and ~30%, respectively. A compact TiO₂ layer and a mesoporous TiO₂ layers were formed on a fluorine-doped tin oxide (FTO) substrate by annealing at 550 °C. To prepare the perovskite compounds, solutions of PbCl₂ (Sigma Aldrich, Tokyo, Japan, 111.2 mg) and CH₃NH₃I (Tokyo Chemical Industry, 190.7 mg) with the desired molar ratio were mixed in *N,N*-dimethylformamide (Sigma Aldrich, 0.5 mL) at 60 °C for 24 h. These perovskite precursor solutions were normally spin-coated during the first coating. During the second and third spin-coating steps, an air-blowing method was employed [50], as illustrated in Figure 1b. The cells were maintained at 90 °C during the air-blowing. DPPS (Osaka Gas Chemicals, OGSOL SI-30-15, Osaka, Japan, 10 mg) solutions were prepared in chlorobenzene (0.5 mL) and dropped onto the perovskite layer during the last 15 s of the third spin-coating of the perovskite precursor solutions, as shown in Figure 1b. A suitable temperature to initiate the reaction of the starting materials (3CH₃NH₃I and PbCl₂) for forming MAPbI₃ and 2CH₃NH₃Cl (as a gas) is 140 °C [10,50]. The devices with DPPS layers were annealed at temperatures in the range of 140 to 260 °C for 1 to 30 min. Then, a spiro-OMeTAD layer was formed as an HTL by spin-coating, and the spiro-OMeTAD layer was formed below the gold electrodes for all the fabricated devices in the present work. Finally, gold (Au) electrodes were formed by evaporation.

All the fabricated cells in the present work were put into dark storage at a temperature of 22 °C and ~30% humidity in ambient air.

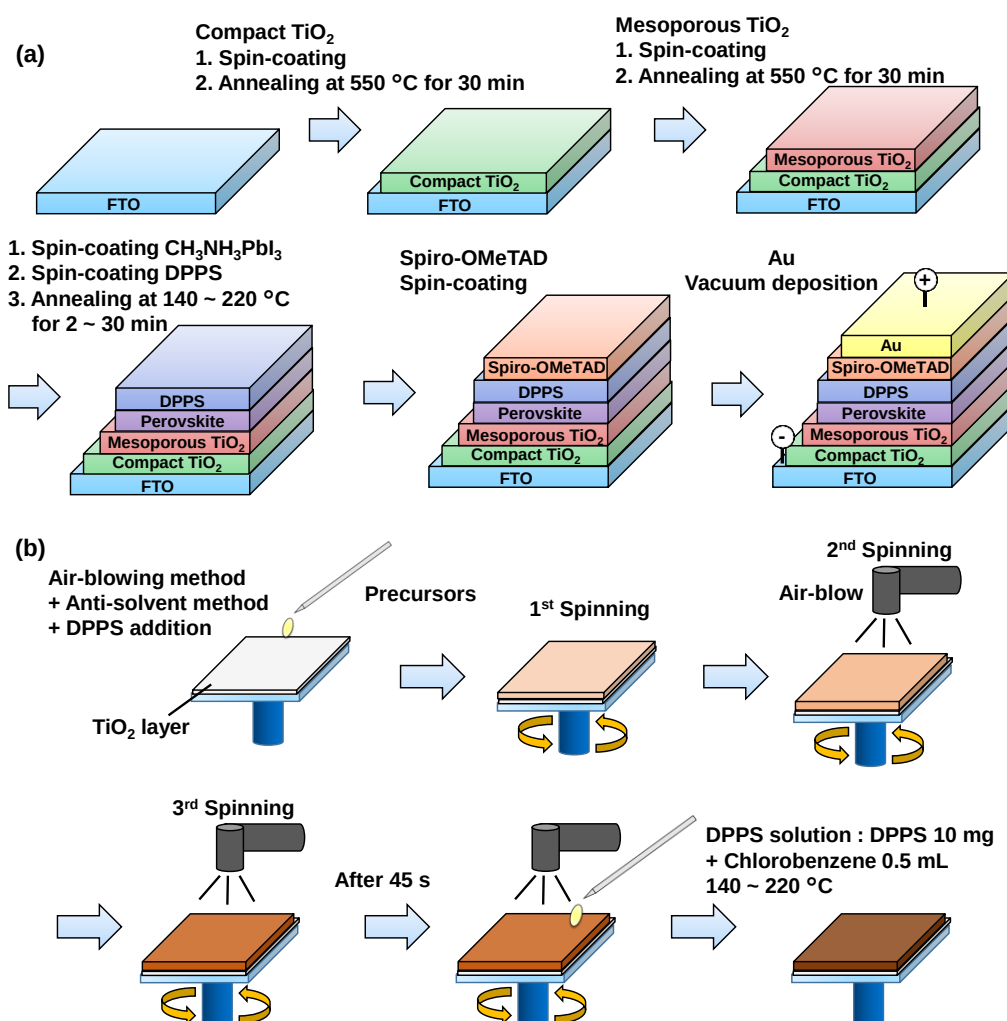


Figure 1. (a) Schematic illustration of the fabrication process of the perovskite photovoltaic devices. (b) Detailed illustration of DPPS insertion process.

Detailed conditions for the characterization of the devices have been described in previous reports [51–53]. Microstructural analysis was conducted by an X-ray diffractometer (Bruker, Billerica, MA, USA, D2 PHASER). Raman scattering spectra were measured with a Raman microspectrometer (JASCO, Tokyo, Japan, NRS-5100). The surface morphologies of the perovskite layers were examined using an optical microscope (Nikon, Tokyo, Japan, Eclipse E600). The current density voltage characteristics of the fabricated devices were measured (Keysight, Santa Rosa, CA, USA, B2901A) under a solar simulator (San-ei Electric, Osaka, Japan, XES-301S) with irradiation at 100 mW cm^{−2}. Geometry optimization and energy calculation of the DPPS molecule were performed by the ab initio calculation using the restricted open-shell Hartree–Fock (RHF) method as the approximated wavefunctions with STO-3G* basis set (Gaussian 09) [21,54,55]. The electron density distributions around the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) were calculated from total self-consistent-field density. The isovalue for the MO on the surface were adjusted to be 0.02 Hartree. The hybrid orbital was widely mapped on the atoms, yielding delocalization. The detailed electron density and Mulliken charge was described in the log file. The electrostatic potential was calculated from the Mulliken population analysis. As the Mulliken population analysis, the charge distribution

of atoms was calculated while considering the atomic orbital overlapping and molecular orbital coefficient. The electrostatic potential was displayed on the surface of the isoelectron density and was mapped with electron density from total self-consistent-field density. The density of electrostatic potential was adjusted to be 0.03. Maximum and minimum energy values with the Hartree unit are shown by scale bars. The positive charge was distributed as blue electrostatic potential around the atom. Raman scattering spectra and the vibration modes were calculated by RHF with STO-3G* using frequency mode.

3. Results and Discussion

Figure 2a shows current density voltage (J - V) curves of the fabricated solar cells. The performance of the cells is summarized in Table 1. The measured parameters were as follows: V_{OC} : open-circuit voltage, J_{SC} : short-circuit current density, FF: fill factor, η : conversion efficiency, η_{ave} : averaged efficiency of four cells, R_S : series resistance, and R_{SH} : shunt resistance. Devices prepared with only chlorobenzene had an η of 3.87% after annealing at 140 °C. To enable a comparison of the chlorobenzene-treated devices with the DPPS-treated devices, a pair of these devices were annealed at 190 °C. The device prepared with DPPS in chlorobenzene had η of 9.40%. The same device fabricated at 220 °C had an initially higher η value of 10.04%. All cell parameters were improved for the devices treated with DPPS in chlorobenzene. The J_{SC} and FF markedly increased compared with those values of the chlorobenzene-treated devices.

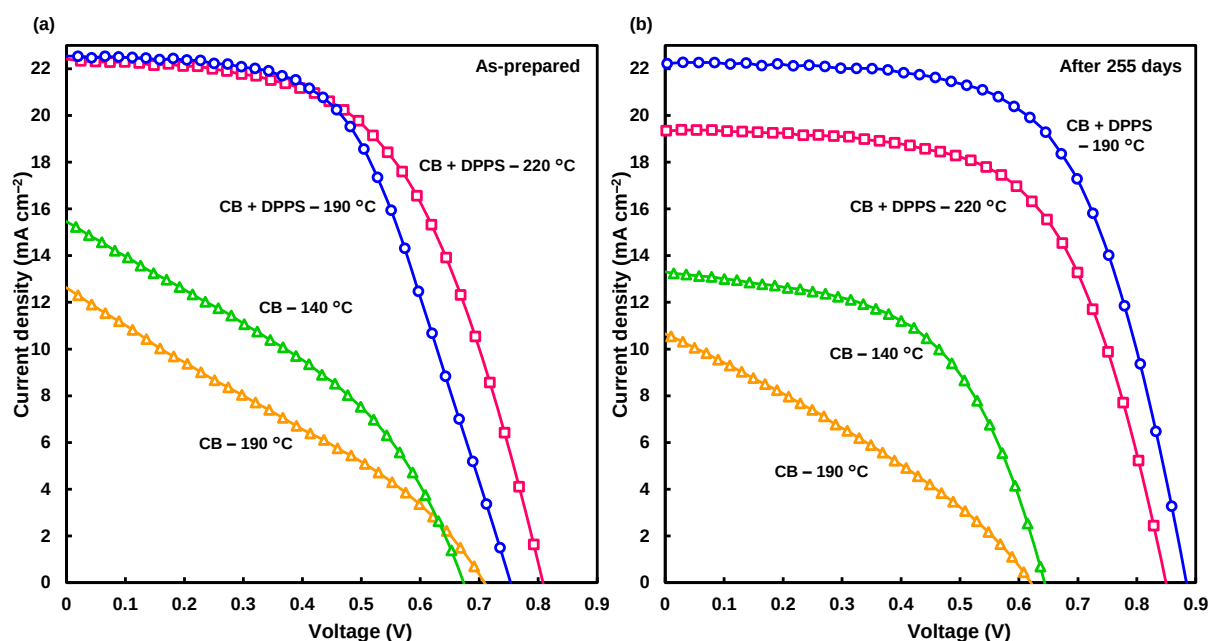


Figure 2. Current density voltage curves of the devices (a) as-prepared and (b) after 255 days in ambient air without encapsulation.

Stabilities of the photovoltaic parameters after preparation in ambient air were measured for the cells over 255 days, and J - V characteristics are shown in Figure 2b. After 255 days, the highest photoconversion efficiency of 12.4% was obtained for the DPPS device prepared at 190 °C (Table 1). The DPPS device prepared at 220 °C had good stability over the extended time, as shown in Figure 3. Whereas the photoconversion efficiency of the chlorobenzene-treated devices prepared at 190 °C decreased over time, η for the devices prepared with DPPS in chlorobenzene at 190 °C increased; hence, DPPS effectively increased the photovoltaic properties when subjected to high temperature annealing. Although the FF values increased for all the devices, V_{OC} decreased for the chlorobenzene-treated device after 255 days. Conversely, V_{OC} for the DPPS-treated devices increased. The hysteresis index (HI) is also calculated and listed in Table 1. The HI values were estimated from the next equation [56]: $HI = (J_{RH} - J_{FH})/J_{RH}$, where J_{RH} is the current density at the

half open-circuit voltage for the reverse scan, and J_{FH} is the current density at the half open-circuit voltage for the forward scan. When there is no hysteresis, the HI is equal to 0. Although the HI values of CB devices were lower than those of CB + DPPS devices for the as-prepared cells, HI values of CB + DPPS and CB devices decreased and increased after 255 days, respectively. The parameters of the DPPS devices either remained stable or increased over time, which is attributed to the reduced influence of moisture, oxygen, and spiro-OMeTAD in the DPPS protected perovskite layers. Shunt resistances were high for the DPPS-added devices, which is likely because of the effects of DPPS on hole transport and electron blocking [45,48].

Table 1. Photovoltaic parameters of perovskite photovoltaic devices. * Prepared from $\text{CH}_3\text{NH}_3\text{I}:\text{PbI}_2 = 1:1$ and without air blowing.

Solution	Annealing (°C, min)	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	R_S ($\Omega \text{ cm}^2$)	R_{Sh} ($\Omega \text{ cm}^2$)	η (%)	η_{ave} (%)	HI
*	100, 15	15.8	0.800	0.550	8.89	525	6.94	6.76	0.029
CB	140, 12	15.4	0.674	0.373	12.35	72	3.87	3.65	−0.082
CB	190, 6	12.6	0.708	0.298	18.87	71	2.66	2.30	−0.034
CB + DPPS	140, 60	12.6	0.903	0.660	8.13	916	7.51	6.06	0.076
CB + DPPS	190, 30	22.5	0.753	0.554	11.92	5670	9.40	8.99	0.334
CB + DPPS	220, 2	22.4	0.808	0.554	9.33	831	10.04	9.40	0.125
CB + DPPS	250, 1.5	20.5	0.875	0.524	9.90	268	9.40	8.71	0.043
CB + DPPS	260, 1	13.5	0.884	0.483	24.37	709	5.75	5.42	0.327
After 255 days	-	-	-	-	-	-	-	-	-
CB	140, 12	13.3	0.643	0.543	8.35	330	4.64	4.54	0.102
CB	190, 6	10.6	0.620	0.311	23.71	86	2.05	1.70	−0.087
CB + DPPS	190, 30	22.2	0.884	0.634	7.35	5830	12.44	11.84	0.086
CB + DPPS	220, 2	19.3	0.849	0.618	8.03	2700	10.15	9.39	0.044

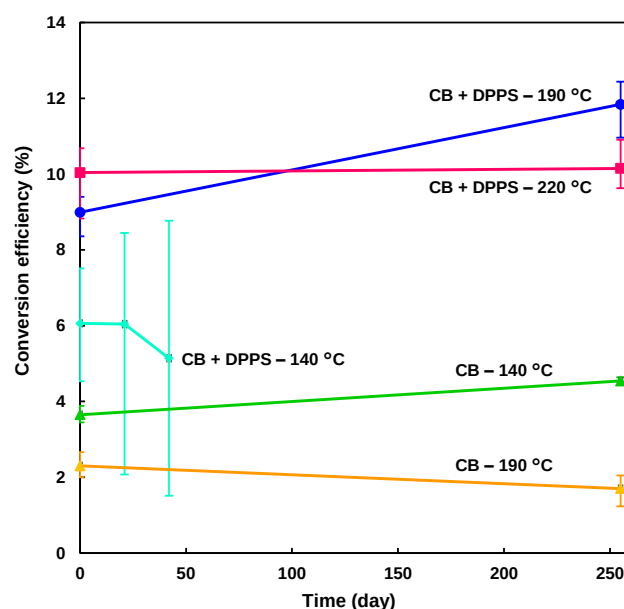


Figure 3. Stabilities of the present devices.

Optical microscope images of the perovskites in the present devices measured after 255 days are shown in Figure 4. The perovskite grains were dispersed and divided by space for the chlorobenzene-treated devices, as observed in Figure 4a,b. On the other hand, the morphologies of the perovskite changed drastically by adding DPPS, and the perovskite grains seem to form smoother surface. Hence, the DPPS-treated devices had fewer grain boundaries and a greater surface coverage of grains. This morphology should suppress

carrier recombination and reduce carrier losses. These effects were confirmed by the low R_S and high R_{Sh} values for the DPPS-treated devices.

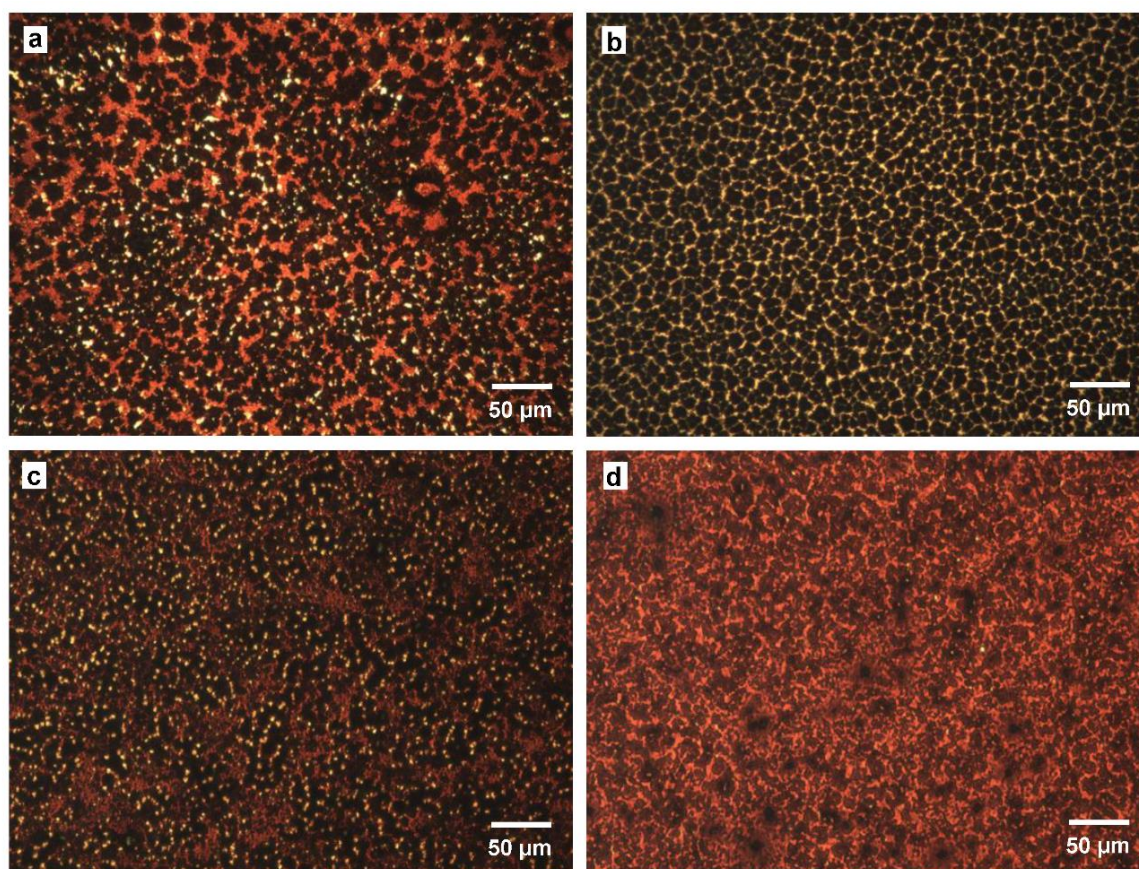


Figure 4. Optical microscope images of cells prepared with chlorobenzene and annealed at (a) 140 °C and (b) 190 °C; and cells prepared with DPPS in chlorobenzene annealed at (c) 190 °C and (d) 220 °C.

Figure 5a shows X-ray diffraction (XRD) results of the devices after 255 days. The diffraction patterns were indexed to a cubic perovskite structure [10,49]. The (100) diffraction peaks were higher for both the devices treated with chlorobenzene and DPPS in chlorobenzene prepared at 190 °C, as observed in the enlarged XRD patterns in Figure 5b.

The lattice constant of the perovskite compound decreased slightly at 220 °C (Table 2), which indicated desorption of MA. The lattice constant was smallest for the chlorobenzene device prepared at 190 °C, indicating that the MA desorption was associated with a decrease in conversion efficiency. The device treated with DPPS in chlorobenzene at 190 °C had the largest lattice constant, indicating that the MA desorption was suppressed, contributing to the high efficiency.

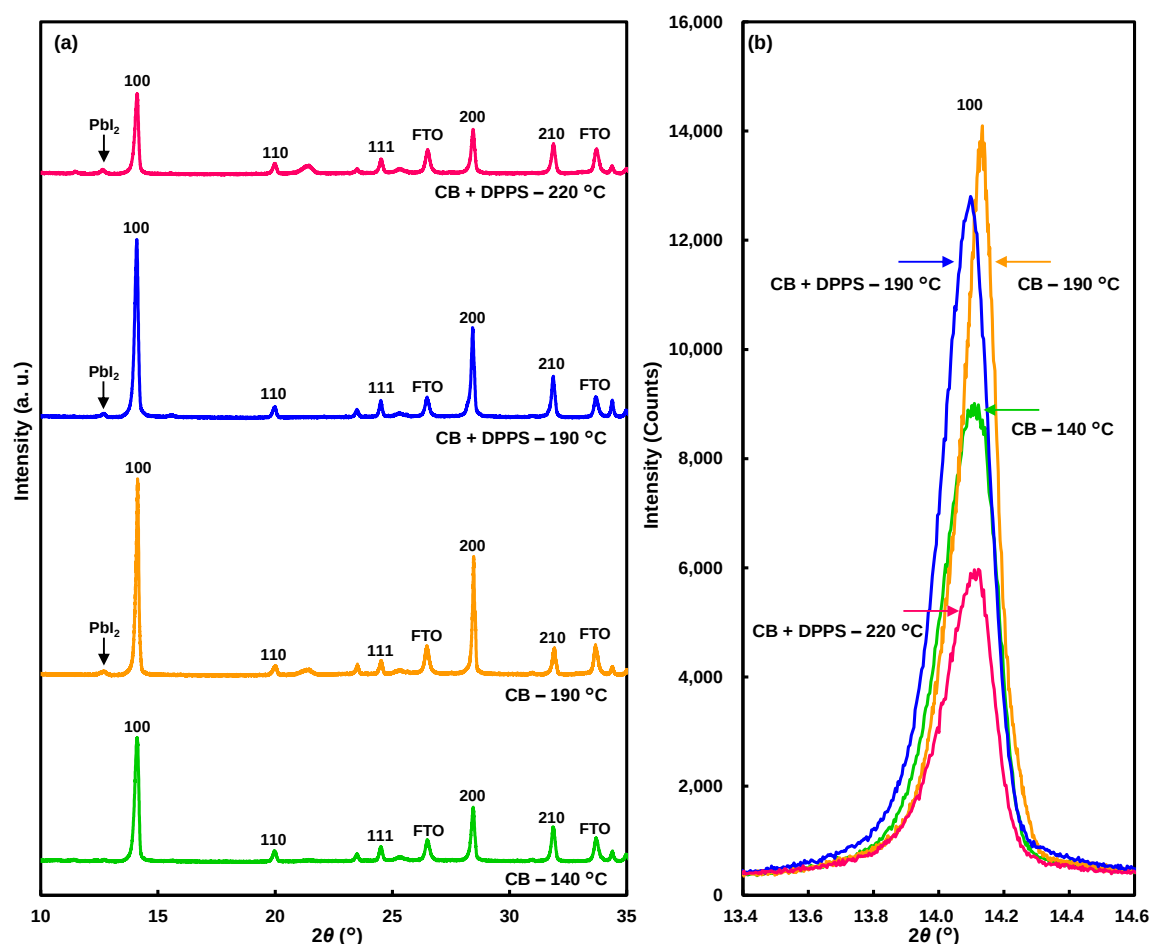


Figure 5. (a) X-ray diffraction patterns of the devices. (b) Enlarged patterns of 100 reflections.

Table 2. Crystallographic data of perovskite films.

Solution	Annealing (°C, min)	Lattice Constant a (Å)	Orientation I_{100}/I_{210}
CB	140, 12	6.270(0)	3.6
CB	190, 6	6.265(1)	7.5
CB + DPPS	190, 30	6.276(0)	4.4
CB + DPPS	220, 2	6.270(1)	2.7

The crystal orientation of the perovskite grains was estimated from the ratios of the 100 intensity (I_{100}) to the 210 intensity (I_{210}) in the XRD patterns, as summarized in Table 2. When the crystal planes in the perovskite crystallites were randomly aligned, the intensity ratio of I_{100}/I_{210} was 2.08 [10]. For the device prepared with chlorobenzene at 190 °C, I_{100}/I_{210} was 7.5, which indicates that the (100) planes were comparatively well aligned with the FTO substrate. For the devices treated with DPPS in chlorobenzene, I_{100}/I_{210} decreased to 4.4 after annealing at 190 °C to 2.7 for devices annealed at 220 °C. Hence, the DPPS treatment of the perovskite promoted more randomly aligned structures. Small PbI₂ peaks were observed for both devices treated with chlorobenzene and DPPS in chlorobenzene after annealing at 190 °C. Further formation of PbI₂ was suppressed during annealing at 220 °C, which indicates that the DPPS protected the MAPbI₃ crystals against decomposition to PbI₂.

Raman spectroscopy measurements of DPPS and the present as-prepared photovoltaic devices are shown in Figure 6, together with calculated data for the DPPS. The Raman scattering peaks at ~600, ~1100, ~1540, and ~3040 cm⁻¹ are respectively assigned to Si-Si,

phenyl-Si, phenyl group, and phenyl C-H groups of the DPPS. Several peaks were assigned to MA, CH₃, and NH₃ for the devices treated with chlorobenzene and DPPS in chlorobenzene. These peaks derive from internal vibrations of MA relating to its local symmetry in the crystal symmetry [57,58]. Because the amount of DPPS was quite small, no clear differences were apparent in the Raman spectra of the devices treated with chlorobenzene and DPPS in chlorobenzene.

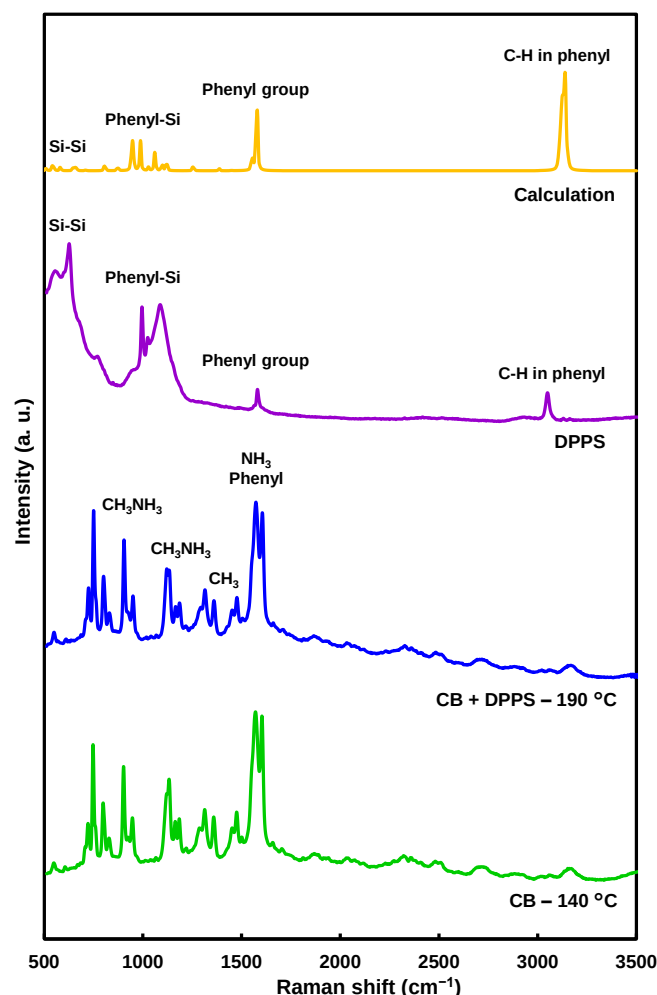


Figure 6. Raman spectra of DPPS and devices.

In this study, the DPPS was dissolved in chlorobenzene, which is often used as an antisolvent to promote grain growth and form smooth surface structures on perovskite films, resulting increased current densities [59–61]. Although temperatures around ~100 °C are commonly used to fabricate perovskite devices, high temperatures above ~180 °C are required to improve the efficiencies of DPPS-treated cells. Thus, DPPS affects the morphology and photoelectronic properties by a different mechanism from that of chlorobenzene. The DPPS layer suppresses MA desorption and DPPS is also a *p*-type semiconductor, which has hole transporting properties that inhibit hole and electron recombination.

The *J-V* characteristics of the champion DPPS-treated device with the highest conversion efficiency in the present work are also shown in Figure 7, and the measured photovoltaic parameters are listed in Table 3. The device was annealed at 190 °C for 5 min. Although the conversion efficiency of this as-prepared device was lower than that prepared at 190 °C for 30 min, its efficiency increased to ~15% after 66 days. Changes of the (100) XRD reflections for the champion device in the present work are shown in Figure 7b, and the crystallographic data are summarized in Table 4. The perovskite crystallites were randomly aligned after 10 days, and the intensity ratio of I_{100}/I_{210} increased from 1.9 to 2.6

after 66 days, which indicates that the (100) planes were comparatively well aligned. In addition, the crystallite size increased from 486 to 617 Å after 66 days. This indicates that the increase of the conversion efficiencies would be caused by the crystal growth of the perovskite compounds during room temperature aging. This crystallization mechanism even after the annealing at the high temperature of 190 °C would be explained by the DPPS treatment, which might slow the diffusion of ions and crystal growth during annealing. Then, the non-crystallized phase that remained might contribute to the crystal growth during the aging.

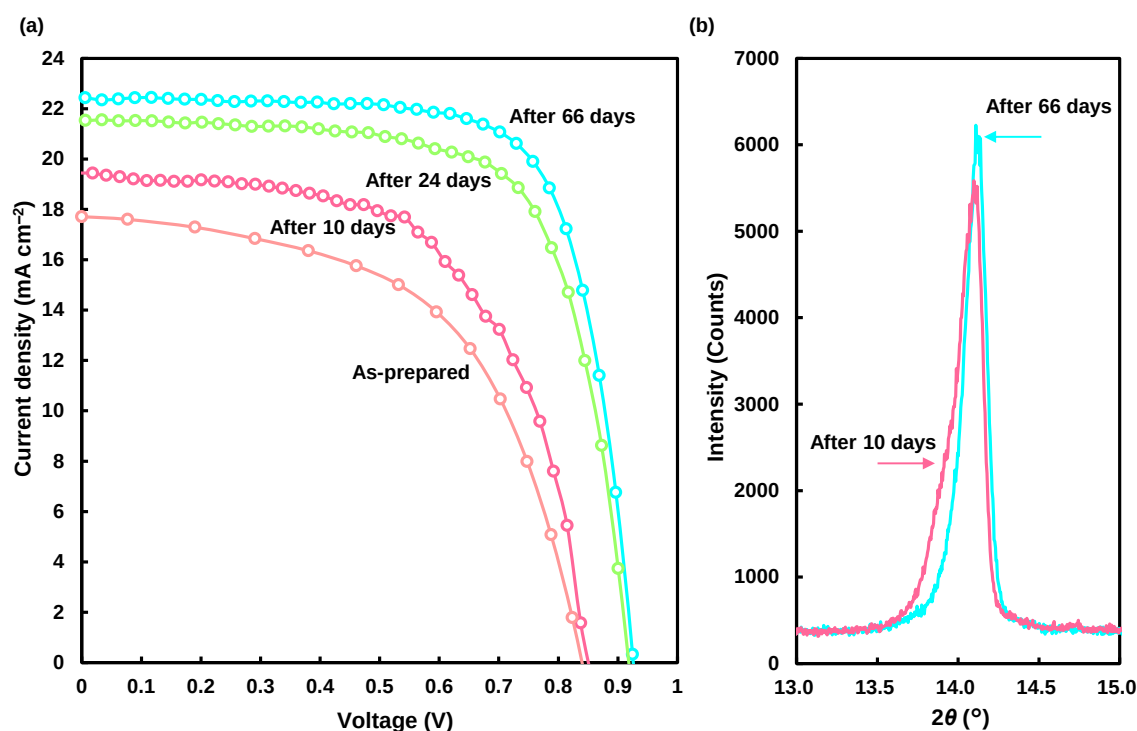


Figure 7. (a) Changes of the J - V curves for the champion device in the present work. (b) X-ray diffraction patterns of 100 reflections.

Table 3. Photovoltaic parameters of champion device, treated with DPPS in chlorobenzene and annealed at 190 °C for 5 min.

Time (Day)	J_{SC} (mA cm^{-2})	V_{OC} (V)	FF	R_S ($\Omega \text{ cm}^2$)	R_{Sh} ($\Omega \text{ cm}^2$)	η (%)	η_{ave} (%)	HI
0	17.7	0.839	0.558	4.41	908	8.30	6.58	0.268
10	19.4	0.850	0.593	3.49	1440	9.80	8.81	0.034
24	21.6	0.918	0.699	3.96	1610	13.82	12.48	0.046
58	22.3	0.930	0.724	3.66	2120	15.03	13.31	0.073
66	22.4	0.923	0.727	3.72	3070	15.10	13.38	0.085

Table 4. Changes of crystallographic data of perovskite films.

Time (Day)	Lattice Constant a (Å)	Orientation I_{100}/I_{210}	Crystallite Size D_{100} (Å)
10	6.272(1)	1.9	486
66	6.268(1)	2.6	617

Schematic and optimized structural models of DPPS are shown in Figure 8a,b, respectively. Pentagonal Si bonding is present in both models. Figure 8c,d shows an electrostatic potential map of DPPS and its cutaway view, respectively, as calculated by ab initio methods

based on the HF. The electrostatic potential was positive (blue) around the cyclopentasilane and proton, as shown in Figure 8c,d. Calculated electronic structures of the DPPS at the HOMO and the LUMO energy levels are shown in Figure 8e,f, respectively. The phases of electron densities in the Si-3p and C-2p orbitals were inverted, as indicated by the green and red coloration. The electronic charge of the HOMO was broadly distributed over the phenyl rings and Si-Si chains, which contributed to the carrier transport and electronic properties. The length of the main Si-Si chain also affects the localization of σ electrons, which determines the LUMO level.

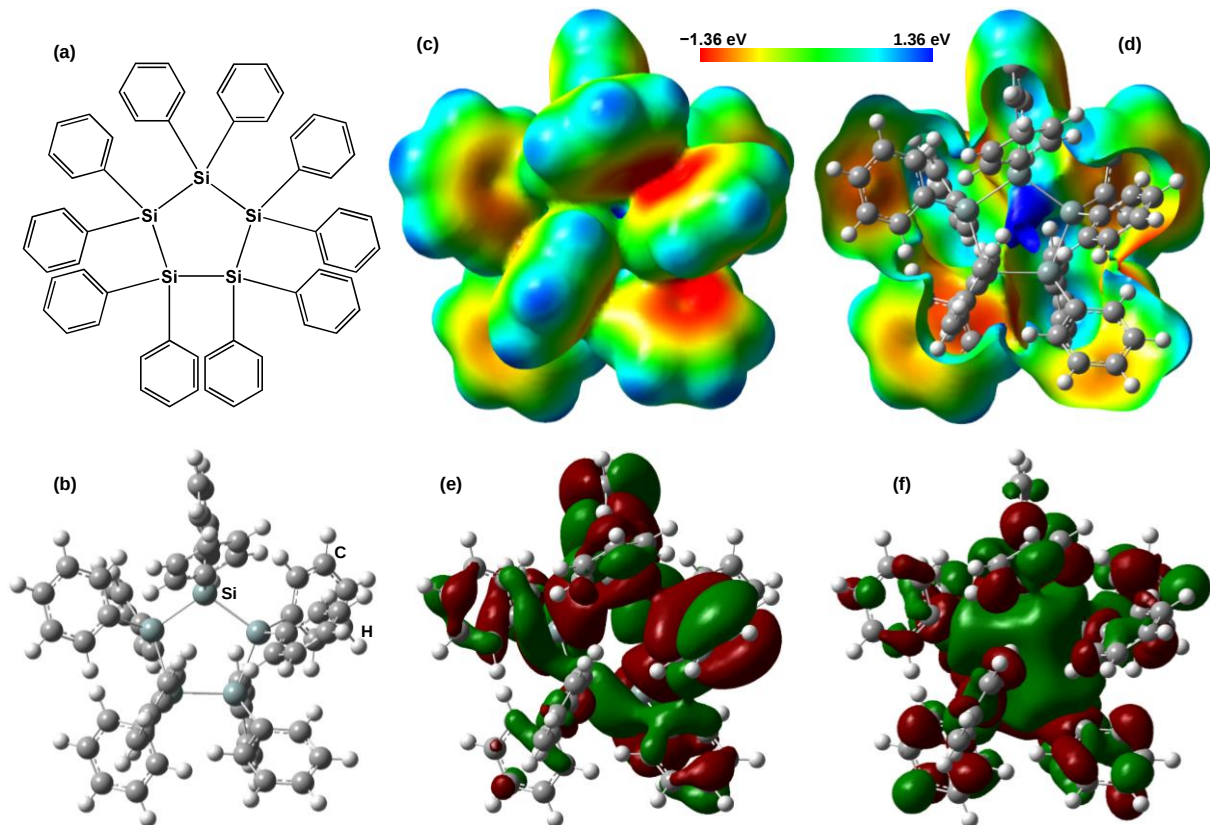


Figure 8. (a) Schematic and (b) optimized models of DPPS. (c) Electrostatic potential, (d) cutaway view of (c), (e) HOMO, and (f) LUMO.

An energy level diagram of the present DPPS-treated perovskite cells is shown in Figure 9. The energy levels of the valence band maximum, conduction band minimum, HOMO, and LUMO are indicated in the diagram [62,63]. When the device was irradiated from the FTO glass side, carriers (holes and electrons) separate at the interfaces. Holes separated in the perovskite layer are carried through the PbI_2 , DPPS, and spiro-OMeTAD to the gold electrode. Conversely, electrons are transported through titanium dioxide to the FTO. By inserting a DPPS layer between the photoactive layer and the HTL, holes are effectively transported from the valence band maximum of the MAPbI_3 to the Fermi level of Au. High shunt resistances were obtained for the DPPS-treated devices, which are attributed to the hole transporting and formation of smoother surface morphology by DPPS. Efficient carrier transport is likely caused by the specific arrangement of the phenyl group around the cyclopentasilane in the DPPS [41].

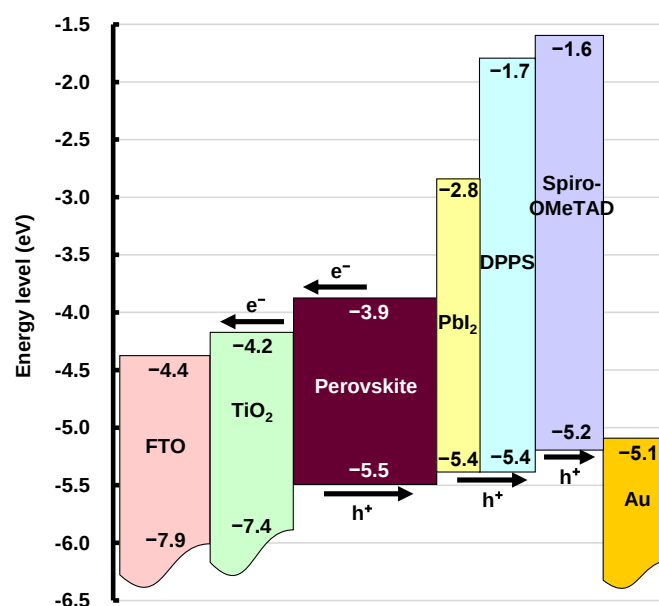


Figure 9. Energy level diagram of the present cell.

A small PbI₂ layer might be formed by MA desorption at the perovskite/DPPS interface at high temperatures. If this thin PbI₂ layer forms at the perovskite/DPPS interface during or after annealing, PbI₂ may act as a p-type semiconductor and an HTL [64,65]. Activation energies of ion migration of MA⁺, I[−] and Pb²⁺ in the MAPbI₃ were reported to be 0.84, 0.58, and 2.31 eV, respectively [66]. Since the activation energy of Pb²⁺ migration is higher than those of other ions, the formed PbI₂ layer may remain around the surface of the perovskite. The increased efficiency of the DPPS-treated devices might also be related to crystallization of amorphous grains. During the spin-coating of DPPS, a composite layer of DPPS and amorphous pre-perovskite compounds forms, which provides a solid interface for room temperature aging. Because DPPS can also function as a hole transport material [41], holes are efficiently transported at the interface, to improve the R_{sh} and V_{OC} . Since all the processes in the present work were performed in the ambient air, further improvement of photovoltaic properties is expected by controlling the environmental conditions.

4. Conclusions

In summary, the effects of a DPPS treatment on perovskite solar cells were investigated. The DPPS layer was inserted at the perovskite/spiro-OMeTAD interface. Conversion efficiencies improved by inserting the DPPS layer during spin-coating of MAPbI₃ and annealing above 190 °C. A cell fabricated at 220 °C had the highest photoconversion efficiency among the as-fabricated cells, and the conversion efficiencies of all devices remained stable over more than 8 months in air. In addition, a device fabricated at 190 °C had the highest efficiency following room temperature aging. The DPPS layer acts as both a protective layer for the perovskite and as an HTL. Although a small amount of PbI₂ was detected by XRD, the PbI₂ layer likely also functioned as an HTL. The perovskite grains grew more densely, and their surface coverage increased compared with that resulting from the ordinary chlorobenzene anti-solvent method. The DPPS treatment promoted fewer lattice defects and grain boundaries, which suppressed the leakage current and increased the JSC. The effectiveness of the DPPS on hole transport was also confirmed by ab initio molecular orbital calculations. These findings indicate that high temperature annealing of devices treated with DPPS in chlorobenzene is an effective and easy method for improving the photoconversion efficiencies and stability of MAPbI₃ solar cells.

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