Achieving High Efficiency in Solution-Processed Perovskite Solar Cells Using C$_{60}$/C$_{70}$ Mixed Fullerenes

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ABSTRACT: Fullerenes have attracted considerable interest as an electron-transporting layer in perovskite solar cells. Fullerene-based perovskite solar cells produce no hysteresis and do not require high-temperature annealing. However, high power conversion efficiency has only been achieved when the fullerene layer is thermally evaporated, which is an expensive process. In this work, the limitations of a solution-processed fullerene layer have been identified as high crystallinity and the presence of remnant solvents, in contrast to a thermally deposited C$_{60}$ film, which has low crystallinity and no remaining solvents. As a solution to these problems, a mixed C$_{60}$ and C$_{70}$ solution-processed film, which exhibits low crystallinity, is proposed as an electron-transporting layer. The mixed-fullerene-based devices produce power conversion efficiencies as high as that of the thermally evaporated C$_{60}$-based device (16.7%) owing to improved fill factor and open-circuit voltage. In addition, vacuum-drying the mixed fullerene film, the power conversion efficiency of the solution-processed perovskite solar cells is further improved to 18.0%. This improvement originates from the enhanced transmittance and charge transport by removing the solvent effect. This simple and low-cost method can be easily used in any type of solar cells with fullerene as the electron-transporting layer.

KEYWORDS: fullerenes, perovskite solar cells, crystallinity of fullerenes, mixed fullerenes, electron-transporting layer

1. INTRODUCTION

Organometal halide perovskite solar cells (PSCs) have emerged as the next-generation thin-film solar energy harvesters with high efficiency owing to the long exciton diffusion length, high absorption coefficient, and high carrier mobility of the perovskite. Fullerenes, which have been used in organic solar cells (OSCs) for more than two decades, have attracted considerable interest as an electron-transporting layer (ETL) in PSCs. Unlike in OSCs, fullerenes are not used as an electron acceptor in the photoactive layer of PSCs; instead, fullerenes function as a charge-selective layer in PSCs and high concentration of fullerene solution is not necessary for PSCs. Furthermore, pristine fullerenes, such as [60]fullerene (C$_{60}$) and [70]fullerene (C$_{70}$), which possess intrinsically higher mobility and conductivity than fullerene derivatives, can be directly applied to PSCs without difficult and expensive chemical modification. Currently, metal oxides ETLs, such as TiO$_2$ and SnO$_2$, are widely used in PSCs. However, the use of metal oxide ETLs results in large hysteresis of devices, originating from charge accumulation and charge trapping. Moreover, their high sintering temperature limits the flexible and large-size application of PSCs. Fullerenes can be used as an ETL to avoid these problems. Fullerenes have low chemical capacitance and high electron affinity, which helps avoid hysteresis. In addition, fullerenes are reported to function as a passivation layer for perovskite grain boundaries, reducing the surface trap density. Nevertheless, high power conversion efficiencies (PCEs) were reported only when fullerenes were thermally deposited or overcoated on metal oxides; the thermal deposition is a slow and expensive process, and the overcoating process requires a metal oxide layer, which renders the use of fullerenes futile. Spin coating of fullerene solution, which is a simple and low-cost process that enables large-size application, is an ideal alternative. However, solution-processed (spin-
coated) fullerene-based PSCs cannot achieve PCEs as high as those of thermally deposited fullerene-based PSCs.

In this work, we studied the reasons for the lower performance of spin-coated fullerene-based PSCs compared with that of thermally deposited fullerene PSCs. Accordingly, we provide a method for achieving higher efficiency using spin-coated fullerenes. With regard to pristine fullerenes, we compared thermally deposited and spin-coated pristine fullerenes in PSCs and observed that C60 is a better ETL than C70 owing to its lower absorption and better morphology. In addition, thermally deposited fullerenes are a better ETL than spin-coated fullerenes owing to the amorphous state of the thermally deposited C60 films in contrast to the crystalline state of the spin-coated C60 films. Considering that the crystallinity of the fullerene films is linked to the performance of ETLs, we showed that mixing C70 into C60 reduces the crystallinity of the film. Consequently, the spin-coated mixed-fullerene-based PSC devices produced a PCE of 16.7%, which is similar to that of thermally evaporated C60-based PSCs. To enhance the performance of the spin-coated mixed-fullerene-based PSCs further, the fullerene films were subjected to vacuum drying to remove the remaining solvents. The removal of the intercalated solvent from the fullerenes improved the optical transparency and charge transport of the film. The vacuum-dried spin-coated mixed-fullerene-based PSCs produced a PCE of 18.0%, which was significantly higher than that of the thermally evaporated fullerene-based PSCs. This study not only achieved a high PCE of the spin-coated fullerene-based PSCs but also provided an insight into the fullerene engineering of PSCs through various analyses.

2. RESULTS AND DISCUSSION

2.1. Investigation of Pristine Fullene ETLs in PSCs. There have been a few reports on the comparison between C60 and C70 as the ETL in PSCs, but these comparisons were limited in terms of device architectures and deposition methods.23,26,27 Some of these reports contradicted each other in terms of PCEs and analyses. Therefore, we first comprehensively compare C60 and C70 in normal and inverted architectures using thermal and solution deposition methods (Figures 1a and S1). Table 1 shows the photovoltaic performance of the thermally deposited C60- and C70-based PSCs in the normal and inverted architectures (Figure S2). In both device types, the C60-based PSCs produced higher PCEs than the C70-based devices, which is consistent with the previous reports.23,26,27 The same open-circuit voltage ($V_{OC}$) values of the C60- and C70-based devices indicate that C60 and C70 possess similar energy disorders28−30 and similar energy levels, which are supported by the ab initio calculations (Figures 1b and S3) and photoelectron yield spectroscopy (PYS) measurements (Figure S4).31,32 The density functional theory calculations of C60 and C70 single molecules reveal that they have similar lowest unoccupied molecular orbital (LUMO) levels, whereas their highest occupied molecular orbital levels are within 0.1 eV of each other (Figure S3). This result is corroborated by the PYS data, which show that the valence levels of C60 and C70 are −6.4 and −6.3 eV.
respectively, for both thermally deposited and spin-coated films (Figure S4a–d). The short-circuit current density ($J_{SC}$) was lower for the C70-based PSCs than for the C60-based PSCs for the normal architecture but similar for both PSCs for the inverted architecture. This indicates that the lower $J_{SC}$ is due to the higher absorption of C70 (Figures S5 and S6). The fill factor (FF) of the C70-based PSCs was lower than that of the C60-based PSCs for both normal- and inverted-type devices. The lower FF of the C70-based PSCs is due to the higher series resistance ($R_s$) and lower shunt resistance ($R_{SH}$). Previous studies reported that C70 thin films have higher conductivity and electron affinity than C60 thin films. Moreover, C70 is observed to be more effective in preventing the recombination of excitons than C60, because C60 possesses many circulating circuits, resulting in inefficient quantum current distributions inside the molecules. However, based on the photoluminescence (PL) measurement (Figure 1c), it was observed that the C60 films quenched the excitons from MAPbI3 better than the C70 films. Notably, the PL peak of MAPbI3 on the C60 films is blue-shifted slightly. This blue-shift indicates the passivation of the trap states between C60 and MAPbI3 as the trap states lead to spontaneous radiative recombination at the surface. Furthermore, the full width at half-maximum (FWHM) was narrower for MAPbI3 on C60 compared with that on C70. The narrower FWHM indicates a reduction in the shallow trap density at the interface. It has been reported that the low molecular symmetry of C70 results in the smoother morphology of C60 film, which leads to better electron transfer from MAPbI3. Therefore, we can conclude that the higher FF is due to the better interface between C60 and MAPbI3, thus facilitating the use of C60 as the ETL in PSCs.

Spin-coated C60 and C70 films were compared in the normal-type PSCs. As the normal-type PSCs exhibit higher efficiency than the inverted-type PSCs (Table 2 and Table S1), we only discussed the normal architecture henceforth. The difference between the spin-coated C60- and C70-based PSCs was similar to that between the thermally deposited C60- and C70-based PSCs (Table 2 and Figure S7a); the C70-based devices showed a lower $J_{SC}$ and FF than the C60-based devices. Spin-coated fullerene-based PSCs showed lower PCEs than the thermally deposited fullerene-based PSCs (based on a comparison between Tables 1 and 2). Although the spin-coated fullerene-based PSCs resulted in lower efficiency, the solution process is preferred over the thermal deposition process owing to its lower fabrication cost, higher speed, and simplicity. Thus, it is important to determine why the spin-coated fullerene-based devices resulted in lower performance than the thermally processed PSCs and to provide a solution to this limitation.

As the lower $V_{OC}$ and FF resulted in the lower PCE of the spin-coated fullerene-based PSCs (thermally deposited C60-based PSCs: $J_{SC} = 22.7$ mA cm$^{-2}$, $V_{OC} = 1.01$ V, FF = 0.72 from Table 1; spin-coated C60-based PSCs: $J_{SC} = 23.0$ mA cm$^{-2}$, $V_{OC} = 0.99$ V, FF = 0.65 from Table 2), we attribute the lower performance mainly to the crystallinity of the fullerene films. In general, thermally deposited fullerene films are reported to be nearly amorphous, whereas spin-coated fullerene films are reported to possess high crystallinity. We used grazing-incidence X-ray diffraction (GIXRD) spectroscopy to analyze the thermally evaporated C60 films and the spin-coated C60 films (Figure S8). Figure 2a shows that the spectra of the thermally deposited C60 films do not display any peaks, but those of the spin-coated C60 films display the (111) peak at 10° and the (220) peak at 18°. This was also confirmed by the transmission electron microscopy (TEM) images. The thermally deposited C60 films exhibited an amorphous state (Figures 2b and S9a) with no crystal domains (Figure 2c), whereas the spin-coated C60 films exhibited a high crystallinity (Figures 2d and S9b) with crystal domains of sizes 20–100 nm (Figures 2e and S9c). It is known that the

**Table 2. Photovoltaic Parameters of the Normal-Type PSCs Using Spin-Coated C$_{60}$, C$_{70}$, and Mixed Fullerene with Different Ratio as the ETLs under 1 sun (AM 1.5 G, 100 mW cm$^{-2}$)***

<table>
<thead>
<tr>
<th>fullerene</th>
<th>$J_{SC}$ (mA cm$^{-2}$)</th>
<th>$V_{OC}$ (V)</th>
<th>FF</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>$R_{SH}$ (Ω cm$^2$)</th>
<th>PCE$_{best}$ (%)</th>
<th>PCE$_{average}$ (%)</th>
<th>hysteresis index $^{11}$</th>
</tr>
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<tr>
<td>C$_{60}$</td>
<td>23.0</td>
<td>0.99</td>
<td>0.65</td>
<td>42</td>
<td>$1.7 \times 10^4$</td>
<td>14.8</td>
<td>14.6% ± 0.7</td>
<td>0.03</td>
</tr>
<tr>
<td>C$_{70}$</td>
<td>19.5</td>
<td>0.97</td>
<td>0.62</td>
<td>36</td>
<td>$6.8 \times 10^4$</td>
<td>11.7</td>
<td>11.4% ± 0.6</td>
<td>0.07</td>
</tr>
<tr>
<td>C$<em>{60}$/C$</em>{70}$ (9:1)</td>
<td>22.9</td>
<td>1.02</td>
<td>0.71</td>
<td>30</td>
<td>$1.5 \times 10^5$</td>
<td>16.7</td>
<td>16.6% ± 0.5</td>
<td>0.04</td>
</tr>
<tr>
<td>C$<em>{60}$/C$</em>{70}$ (5:5)</td>
<td>21.2</td>
<td>1.02</td>
<td>0.55</td>
<td>65</td>
<td>$5.7 \times 10^5$</td>
<td>11.8</td>
<td>11.4% ± 0.5</td>
<td>0.05</td>
</tr>
<tr>
<td>C$<em>{60}$/C$</em>{70}$ (1:9)</td>
<td>20.4</td>
<td>1.00</td>
<td>0.55</td>
<td>60</td>
<td>$6.8 \times 10^5$</td>
<td>11.1</td>
<td>11.0% ± 0.5</td>
<td>0.05</td>
</tr>
</tbody>
</table>

*The data on inverted-type PSCs are given in Table S1.

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**Figure 2.** (a) GIXRD 2θ scan (incident angle $\omega = 1°$) of thermally deposited C$_{60}$ film (blue line), spin-coated C$_{60}$ film (black line), and spin-coated mixed fullerene film (red line). TEM images of (b, c) thermally deposited C$_{60}$ film; (d, e) spin-coated C$_{60}$ film with an SAED as an inset; and (f, g) spin-coated mixed fullerene film with an SAED as an inset. Structures of (h) C$_{60}$ in face-centered cubic (fcc) crystal structure and (i) C$_{70}$ in hexagonal close-packed (hcp) crystal structure.
boundaries between crystal domains hinder the charge flow, whereas charge mobility may be high within a crystal domain. Therefore, unless a film is in a predominately single-crystalline phase, amorphous films are expected to have better charge transport. This explains the higher series resistance ($R_s$) and lower FF of the spin-coated C$_{60}$-based PSCs as compared with those of the thermally deposited C$_{60}$-based PSCs. The lower charge transport indicates more charge recombination; thus, lower $V_{oc}$ was obtained for the spin-coated fullerene-based PSCs.

2.2. Improvement of Spin-Coated Fullerene ETLs in PSCs. Considering that the crystallinity of the C$_{60}$ films leads to lower device performance, we added a small amount of C$_{70}$ into the C$_{60}$ solution to suppress the crystallinity of the spin-coated C$_{60}$ film. C$_{60}$- and C$_{70}$-mixed fullerene films (referred to as "mixed fullerene films" hereafter) are reported to possess lower crystallinity than pure C$_{60}$.$^{37,44}$ Furthermore, the native C$_{60}$ and C$_{70}$ mixtures obtained during fullerene synthesis are considerably less expensive than the pure compounds.$^{49}$ GIXRD spectra in Figure 2a show that the mixed fullerene film exhibits much weaker (111) and (220) peaks. The TEM analysis also reveals that the mixed fullerene film (Figure 2f) displays suppressed crystallinity in contrast to the spin-coated C$_{60}$ film (Figure 2d). This is evident from the selected-area electron diffraction ring patterns (SAED); the SAED pattern of the spin-coated C$_{60}$ film (Figures 2d inset and S9e) shows stronger crystallinity than that of the mixed fullerene film (Figures 2f inset and S9f). Moreover, crystal domains were not observed in the mixed fullerene films (Figures 2g and S9d). To the best of our knowledge, the low crystallinity of mixed fullerene has not been discussed in detail in the literature so far. We can explain this phenomenon in terms of their packing. Theoretically, C$_{60}$ packing is more stable in a face-centered cubic (fcc) form (Figure 2h) than in a hexagonal close-packed (hcp) form, whereas C$_{70}$ is more stable in the hcp form (Figure 2i).$^{35}$ However, in reality, C$_{60}$ is present in both hcp and fcc forms, whereas C$_{70}$ only exists in the hcp form.$^{34}$ Therefore, in mixed fullerene, as C$_{60}$ molecules attempt to form an fcc structure, C$_{70}$ molecules existing between C$_{60}$ molecules may prevent the formation of fcc packing. For C$_{60}$ in the hcp form, which is less stable, the larger and asymmetric C$_{70}$ molecules distort the packing, inhibiting the crystallization. The morphologies of the films were investigated using the topography and adhesion modes of atomic force microscopy (AFM). The mixed fullerene film showed lower surface roughness with a roughness average ($R_s$) of 2.43 nm compared with the spin-coated C$_{60}$ films, which showed the $R_s$ of 7.19 nm (Figure 3a,b). We could also detect the crystal domain boundaries of the fullerene films by probing the adhesion of the film surface. From the high adhesion force of the crystal boundaries, we could conclude that the C$_{60}$ films possessed many domains of ca. 50 nm (Figure 3c). In the case of mixed fullerene, the boundaries were much less defined (Figure 3d). This is evident from the three-dimensional (3D) images in which the mixed fullerene films have a much flatter topography.

PSCs with normal architecture were fabricated using the spin-coated mixed fullerene ETLs with different C$_{60}$-to-C$_{70}$ ratios (Table 2 and Figure S7b). The best PCE of 16.7% was achieved with the native C$_{60}$ and C$_{70}$ mixture ratio (C$_{60}$/C$_{70}$ = 9:1 in weight). This PCE is as high as that of the thermally deposited C$_{60}$-based PSCs (Table 1). The devices with a greater C$_{70}$ content exhibited a lower $J_{sc}$ and a lower FF (Table 2). The UV−vis spectra with different C$_{60}$/C$_{70}$ ratios showed that the increase in the amount of C$_{70}$ reduces the transmittance of the film (Figure 3e), thus reducing the $J_{sc}$. The C$_{60}$/C$_{70}$ films with the weight ratio 9:1 showed almost the same absorption as that of the pure C$_{60}$ as indicated by the similar $J_{sc}$ values. The lowering trend of FF is observed because the charge transfer between C$_{70}$ and the perovskite layer is not favored as discussed in Section 2.1. We used solid-state ab initio calculations to assess the energy-level change when C$_{60}$ and C$_{70}$ are mixed and the contributions from each component to the density of states (DOS) in the conduction band. Solid-state calculations were performed at the dispersion-corrected density functional tight binding level (Figure S3). The DOS of C$_{60}$ and C$_{70}$ solids (Figure S10a) show the same energy levels to C$_{60}$ and C$_{70}$ similar to the comparison at the single-molecule level in Figure S3. Mixing C$_{60}$ and C$_{70}$ yielded a similar result in that the energy contributions from C$_{70}$ and C$_{60}$ to the conduction band are similar (Figures 1b and S10b), indicating that there is no LUMO offset within the mixed film, which could potentially inhibit charge transport. This is corroborated experimentally by the PYS measurement.
We also conducted simulations of selected low-index surfaces and confirmed that there is no change in DOS owing to the presence of the mixed fullerene interface (Figure S11). In addition, the ab initio calculations suggest that the mixed system is only approximately 0.03 eV/molecule above the convex hull (Figure S12), which is approximately kT at room temperature; there is, therefore, no significant driving force for segregation or desegregation. In addition, devices in which mixed fullerenes were used resulted in higher $V_{OC}$ than the pure C$_{60}$-based or C$_{70}$-based devices. This is another evidence pointing to the lower recombination between the perovskite and the mixed fullerene due to its amorphous nature possessing more efficient charge transfer than the pure fullerene films. Consequently, we can conclude that the native mixed fullerene weight ratio of 9:1 is the optimized ratio, and mixing too much C$_{70}$ undermines the device performance (Figure 4a).

### 2.3. Further Enhancement of Mixed Fullerene ETL.

Considering that the mixed fullerene ETLs can achieve PCE as high as that of the thermally deposited C$_{60}$ ETLs, we report a method to improve the PCE of these mixed fullerene ETLs even further. In addition to the amorphous state, a favorable...
aspect of the thermally evaporated C_{60} is that it is solvent free. By removing the trapped solvents from the spin-coated mixed fullerene films, we postulate that the fullerene can be packed in a more compact manner, improving the charge transport and eliminating the solvent effects.\textsuperscript{52,53} To remove the ortho-dichlorobenzene (ODCB) effectively, we applied three different treatments to the spin-coated mixed fullerene films: thermal annealing (TA) at 100 °C, TA at 200 °C, and TA at 100 °C under a light vacuum (0.01 MPa). Table 3 shows the photovoltaic performances of the PSCs with different post-treatments applied to the spin-coated mixed fullerene ETls. The PSCs treated with TA at 100 °C did not exhibit a significant change in the device performance (Figure S13). We suspect that this temperature is not sufficiently high to remove ODCB (boiling point of 180 °C). In contrast, the PSCs treated with TA at 200 °C exhibited reduced device performance (Table 3 and Figure S13). According to the AFM morphology analysis in Figure S14a, TA at 200 °C resulted in aggregation of the fullerene films. Although such a high temperature is effective for removing ODCB, it leads to strong crystallization, which severely roughens the morphology as indicated by the low FF.\textsuperscript{54,55} Finally, we vacuum-dried the film at 100 °C for 10 min. The device performance increased to 18.0% with the increase in J_{SC} and V_{OC}, whereas FF remained the same (Figure 4a–d, Table 3, and Figure S13). The AFM roughness image and the corresponding R_{s} value reveal that the morphology of the fullerene film improved with the vacuum-drying treatment (Figure S14b). However, the improvement in morphology does not explain the improvements in J_{SC} and V_{OC}. X-ray photoelectron spectroscopy (XPS) was used to confirm the removal of solvents via vacuum-drying. The data indicate that the chlorine from ODCB solvent, which was detectable in films treated with TA at 100 °C, was not detectable in the films treated with TA at 200 °C and vacuum-dried films (Figure 4e). UV–vis absorption spectra in Figure 4f indicate that the vacuum-drying treatment reduced the absorption of the film significantly. We conjecture that the removal of ODCB increased the transmittance of the film by removing solvatochromism.\textsuperscript{54,55} Cross-sectional scanning electron microscopic (SEM) image of the spin-coated mixed fullerene film, with a magnified image as an inset, shows that the fullerene film has a thickness of approximately 32 nm (Figure 4g), which is similar to the optimized thickness, i.e., 35 nm of the thermally deposited C_{60} film (Figure S15). After the vacuum-drying treatment, we can observe that the thickness of the same mixed fullerene film decreased to ca. 12 nm (Figure 4h). The GIXRD spectra showed a decrease in the crystallinity of the spin-coated mixed fullerene films upon vacuum-drying treatment, thus resembling the thermally evaporated C_{60} film (Figure S8). This confirms that the removal of solvent affected the packing and crystallinity of the fullerenes. The combination of enhanced transmittance and charge transport led to the increase in J_{SC} and V_{OC}. Ultimately, the PCE of the vacuum-dried solution-processed mixed-fullerene-based PSC (18.0%) exceeded that of the thermally evaporated C_{60}-based PSC (16.7%). Moreover, the vacuum-dry method is not limited to the mixed fullerene. It demonstrated its effectiveness in solution-processed C_{60} film and C_{70} film as well (Table S2 and Figure S16).

3. CONCLUSIONS

We compared C_{60} and C_{70} in PSCs. The comparison was extended to thermally evaporated and solution-processed deposition methods of fullerenes in normal and inverted architectures of PSCs. C_{60} as an ETl in PSC exhibited a higher photovoltaic performance than C_{70}. The thermally deposited C_{60}-based normal-type PSCs showed a PCE of 16.7%. By investigating the mechanism behind the efficiency enhancement, we discovered that the high performance of the thermally deposited C_{60}-based PSCs is attributed to the crystallinity of the fullerene and the presence of remnant solvents. By mixing a small amount of C_{70} into a solution of C_{60}, the crystallinity of the spin-coated fullerene films decreased substantially, resulting in a PCE close to that of the thermally deposited C_{60}-based PSCs. Furthermore, by vacuum-drying the mixed fullerene film, a PCE of 18% without the hysteresis was achieved, which exceeds that of the thermally deposited C_{60}-based PSCs.

4. EXPERIMENTAL SECTION

4.1. Mixed-Fullerene Solution Preparation. C_{60} and C_{70} were dissolved in a solution of ODCB in different ratios with a mass concentration of 20.0 mg mL\textsuperscript{-1}. The solution was filtered through a 0.45 μm poly(tetrafluoroethylene) filter before use.

4.2. Spiro-MeOTAD Solution Preparation. A solution was prepared by mixing 85.8 mg spiro-MeOTAD (Lumtech), 19.3 μL of a stock solution of 520 mg mL\textsuperscript{-1} lithium bis(trifluoromethanesulfonyl)imide (Aldrich) in anhydrous acetonitrile, and 33.8 μL of 4-tert-butylpyridine (Aldrich) in 1 mL anhydrous chlorobenzene.

4.3. Poly(3,4-ethylenedioxythiophene):Polystyrene Sulfonate (PEDOT:PSS) Solution Preparation. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) solution was produced by adding 0.5 wt % polyoxymethylene(6) trieclyl ether (Sigma-Aldrich Chemical Co., Inc.) to a PEDOT:PSS dispersion in water (Clevios P VP, Heraeus Precious Metals GmbH & Co.). The solution was filtered through a 0.45 μm poly(tetrafluoroethylene) filter before use.

4.4. Perovskite (MAPb\textsubscript{I\textsubscript{3}}) Precursor Solution Preparation. CH\textsubscript{3}NH\textsubscript{3}I (TCI), PbI\textsubscript{2} (TCI), and anhydrous dimethyl sulfoxide (TCI) (molar ratio 1:1:1) were mixed in anhydrous N,N-dimethylformamide (TCI) with a concentration of 50 wt %. The solution was filtered through a 0.45 μm poly(tetrafluoroethylene) filter before use.

4.5. Fabrication of Inverted-Type Planar Heterojunction Perovskite Solar Cells. Indium tin oxide (ITO) patterned glass substrates with a size of 15 × 15 mm\textsuperscript{2} and sheet resistance of 6 Ω sq\textsuperscript{-1} (Techno Print Co., Ltd.) were cleaned and sonicated with a detergent, distilled water, acetone, and isopropanol in an ultrasonic bath for 15 min. Subsequently, the substrates were treated with

**Table 3. Photovoltaic Parameters of the Normal-Type PSCs Using Mixed Fullerene as the ETL with Different Film Treatments under 1 sun (AM 1.5 G, 100 mW cm\textsuperscript{-2}**

<table>
<thead>
<tr>
<th>Fullerene</th>
<th>Treatment</th>
<th>J_{SC} (mA cm\textsuperscript{-2})</th>
<th>V_{OC} (V)</th>
<th>FF</th>
<th>R_{S} (Ω cm\textsuperscript{2})</th>
<th>R_{sh} (Ω cm\textsuperscript{2})</th>
<th>PCE\textsubscript{max} (%)</th>
<th>PCE\textsubscript{average} (%)</th>
<th>Hysteresis Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin-coated C_{60}/C_{70} (9:1)</td>
<td>None</td>
<td>22.9</td>
<td>1.02</td>
<td>0.71</td>
<td>42</td>
<td>1.7 × 10\textsuperscript{4}</td>
<td>16.7%</td>
<td>16.6% ± 0.5</td>
<td>0.04</td>
</tr>
<tr>
<td>100 °C TA</td>
<td></td>
<td>23.2</td>
<td>1.04</td>
<td>0.71</td>
<td>33</td>
<td>1.7 × 10\textsuperscript{4}</td>
<td>16.9%</td>
<td>16.0% ± 0.4</td>
<td>0.04</td>
</tr>
<tr>
<td>200 °C TA</td>
<td></td>
<td>22.3</td>
<td>1.05</td>
<td>0.66</td>
<td>20</td>
<td>4.0 × 10\textsuperscript{4}</td>
<td>15.7%</td>
<td>14.8% ± 1.0</td>
<td>0.13</td>
</tr>
<tr>
<td>Vacuum-dry at 100 °C</td>
<td></td>
<td>24.3</td>
<td>1.03</td>
<td>0.73</td>
<td>28</td>
<td>1.5 × 10\textsuperscript{4}</td>
<td>18.0%</td>
<td>17.7% ± 0.6</td>
<td>0.01</td>
</tr>
</tbody>
</table>
ultraviolet/ozone (UV/O3) for 15 min before use. Thereafter, 25 \( \mu L \) of PEDOT:PSS solution was spin-coated on UV/O3-treated ITO substrates at 3000 rpm for 30 s. The coated ITO substrates were subsequently annealed at 105 °C for 10 min. Thereafter, 25 \( \mu L \) of the perovskite precursor solution was spin-coated on the PEDOT:PSS layer at 3000 rpm for 30 s, and 0.5 mL of anhydrous diethyl ether was slowly dripped onto the substrate 10 s after the start of the spin-coating process. Subsequently, the film was annealed at 100 °C for 10 min to obtain a dense brown MAPbI3 film. Subsequently, C60 or C70 was thermally deposited on the perovskite film to obtain a thickness of 30 nm at a constant evaporation rate of 0.02 nm s\(^{-1}\). Similarly, bathocuprine was thermally deposited to obtain a thickness of 10 nm at the same evaporation rate. Finally, a 70 nm-thick Ag cathode was fabricated via thermal deposition at a constant evaporation rate of 0.05 nm s\(^{-1}\).

### 4.6. Fabrication of Normal-Type Planar Heterojunction Perovskite Solar Cells

ITO patterned glass substrates were cleaned and sonicated with detergent, distilled water, aceton, and isopropanol in an ultrasonic bath for 15 min, respectively. Subsequently, 25 \( \mu L \) of mix-fullerene solution was spin-coated on ITO substrates at 3000 rpm for 30 s. The coated ITO substrates were used without any treatment or were followed by different processes, such as (1) annealing at 100 °C for 1 h; (2) annealing at 200 °C for 1 h; and (3) drying up at 100 °C under vacuum condition (\( \sim 10^{-3} \) MPa) for 1 h. If thermally deposited fullerene film was used, C60 or C70 was thermally deposited on ITO substrates in a thickness of 30 nm at a constant evaporation rate of 0.02 nm s\(^{-1}\). Then, 25 \( \mu L \) of perovskite precursor solution was spin-coated on the fullerene layer at 3000 rpm for 30 s, with 0.5 mL of anhydrous diethyl ether slowly dripped onto the substrate 10 s after the start of the spin-coating process. Next, the film was annealed at 100 °C for 10 min to obtain a dense brown MAPbI3 film. The hole-transporting layer was spin-coated from the spiro-MeOTAD solution at 4000 rpm for 30 s. Finally, a 70 nm thick Au anode was fabricated by thermal deposition at a constant evaporation rate of 0.05 nm s\(^{-1}\).

### 4.7. Characterizations

The \( J-V \) characteristics were measured using a software-controlled source meter (Keithley 2400 Source-Meter) under dark conditions and the simulated sunlight irradiation of 1 sun (AM 1.5G; 100 mW cm\(^{-2}\)) using a solar simulator (EMSS35AAA, Ushio Spax Inc.) with a Ushio Xe short arc lamp 500. The source meter was calibrated using a silicon diode (BS-520BK, Bunkokeiki). The SEM analysis of the perovskite films was performed using an S-4800 (Hitachi). The TEM images are taken by JEM-2010F with an electron emission gun operated at 200 keV. The selected area electron diffraction (SAED) patterns are recorded using an Cu K\( \alpha \) source. In the 2\( \theta \) scans, the scattering angle 2\( \theta \) between incident beam and diffracted beam changes, whereas the incident angle \( \omega \) between the incident beam and the sample surface is fixed at 1°. The valence band and the Fermi levels measurements were performed using Riken Keiki PYS-A AC-2 and Kelvin probe spectroscopy in air (ESA), respectively. The photoemission measurements were performed using XPS (PHIS0000, Versa Probe) with monochromatic Al K\( \alpha \) radiation. The water contact angle measurements were performed using a contact angle meter (DMO-501, Kyowa Interface Science Co., Ltd.).

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**Author Contributions**


**Notes**

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