High-Efficiency Polymer Tandem Solar Cells with Three-Terminal Structure

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Polymer solar cells are a promising alternative to future photovoltaic applications due to various advantages such as low cost and ease of processing. Ever since the invention of bulk heterojunctions (BHJs) utilizing a blend of donor polymer and acceptor fullerene derivative, there have been increasing efforts to enhance the power-conversion efficiency (PCE) of polymer solar cells. However, narrow absorption range and low carrier mobility of polymer solar cells limit the thickness of the active layer and, hence, the absorption efficiency. One of the strategies to increase its efficiency is to make use of tandem architectures. In a two-terminal tandem solar cell, two subcells with complementary absorption bands are connected in series through an interlayer that acts as a recombination zone for electrons from one subcell and holes from the other. The series connection leads to summation of the open-circuit voltage ($V_{OC}$); however, the overall current is limited by the subcell that delivers the smaller photocurrent. Therefore, the photocurrent-matching criterion between the two subcells must be satisfied for efficient working of a two-terminal tandem cell. Because of the current-matching criterion, the two subcells might not be readily incorporated into a tandem cell under their optimal conditions. An ideal tandem structure would consist of two subcells that operate separately, so that the efficiency of the tandem cell is simply the sum of the efficiencies of the two subcells. To circumvent the challenge of photocurrent matching in the two-terminal architecture, two solar cells can be stacked together to form a four-terminal tandem cell. In this case, the two cells can be connected either in series, to add up the $V_{OC}$, or connected in parallel (shown in Fig. 1a) to add up the short-circuit current ($J_{SC}$). However, in these devices, considerable optical losses are encountered because of the presence of an additional indium tin oxide (ITO)-coated glass substrate and semitransparent metal electrode that compensates for the gain from absorption.

In this manuscript, tandem structures with a three-terminal (3T) configuration are demonstrated, as seen in Figure 1b, in which two subcells are connected in parallel through a transparent conducting interlayer that acts as a common electrode to the two subcells. The advantage of this structure is that it is convenient to characterize the two subcells independently as well as when connected in parallel. If two subcells with similar $V_{OC}$ are used, they can be connected in parallel to sum the $J_{SC}$ without satisfying photocurrent match. Even if the $V_{OC}$ of the two subcells does not match, power can be drawn separately from the two cells. The 3T structure is relatively simple and straightforward. 3T tandem photovoltaic cells with either a common-anode or a common-cathode configuration can be fabricated. The performance of these devices is comparable to that of their two-terminal counterparts.

**Figure 1.** a) Two diodes connected in parallel with the anodes of the two diodes connected together and the cathodes connected together. b) Schematic of the three-terminal device and the dotted squares on the three electrodes denote the effective overlap areas for the two subcells. c) Transmission of 12 nm Au layer on ITO and absorbance of ITO/P3HT:PCBM, ITO/P3HT:PCBM/PEDOT:PSS/Au$_2$O$_3$, and ITO/P3HT:PCBM/PEDOT:PSS/Au$_2$O$_3$/PSBTBT:PC$_{70}$BM. P3HT: Poly-(3-hexyl)thiophene; PSBTBT: Poly[(4,4′-bis(2-ethylhexyl) dithieno[3,2-b:2′,3′-d]-silole)-2,6-diyl-alt-(2,1,3 benzothiadiazole)-4,7-diyl]; ITO: indium tin oxide; PEDOT: poly(3,4-ethylenedioxythiophene); PSS: poly(styrenesulfonate); PC$_{70}$BM: [6,6]-phenyl-C$_{71}$-butyric acid methyl ester.
common-cathode configuration based on a p- or n-type interfacial layer and Au as the middle transparent electrode have been demonstrated. The main challenge to realize such a 3T structure using the sequential layer-by-layer deposition process is to build an effective transparent and conductive interlayer as a common electrode between the two polymer BHJs. Optically, the middle electrode should allow sufficient light to pass through and, electrically, it should act as an efficient collecting contact for charge carriers from both subcells, while being strong enough to withstand the solution processing of the second polymer BHJ.

Two different polymers with complementary absorption range were used to demonstrate the device concept. P3HT, which absorbs in the wavelength range 300–650 nm, as shown in Figure 1c, was used as the front cell. PSBTBT,[16] which absorbs in the wavelength range 500–850 nm, was used for the rear cell. In this configuration, one of the subcells was an inverted cell[17] and the other a regular one. An Au layer was used as the semitransparent metal interlayer because of both its high conductivity and transparency. The resistance of the Au interlayer with thickness was measured using a two-point probe method and is shown in Figure 2a. It clearly shows that for a thickness of 12 nm, the resistance drops drastically, giving rise to a highly conductive Au layer. The thickness of the Au interlayer was kept to a minimum to achieve both high transparency and high conductivity. The PEDOT:PSS/Au (12 nm) interlayer allowed transmission of ca. 50% of the incident light in the wavelength range 400–850 nm, as shown in Figure 1c. Due to this low transmittance as well as strong absorption of the front cell at visible wavelengths, almost 50% loss in absorption from the rear cell occurred. It is also worth mentioning that the Au interlayer is resistant enough against the solution processing, preventing any damage to itself and the underlying P3HT:PC70BM film.

To collect carriers efficiently from the two subcells, the interlayer should form Ohmic contact with the subcells. In the case of the common-anode configuration PEDOT/Au(12 nm) was used as the anode contact to the front cell, while the Au surface was modified using V2O5 to form Ohmic contact with the rear cell. The work function of the modified Au layer was determined from the secondary electron onset using UPS, as shown in Figure 2b. Although Au has a high work function (ca. 5.0 eV), direct contact between Au and organic materials usually results in a significant surface dipole at the metal/organic interfaces,[18] which most likely makes it unsuitable for use as an electrode directly contacting polymer films. Instead the V2O5-modified Au surface showed a work function of 5.0 eV and was used as a common anode in the 3T device. On the other hand, in the common-cathode configuration TiO2:Cs/Al(3 nm)/Au(20 nm) was used as the cathode contact for the front cell. The 3 nm thick Al layer helped to prevent penetration and diffusion of Au into the photoactive layer of the front subcell, ensuring low leakage current and good reproducibility. A thicker Au layer was used in this case compared to the layer used in the common-anode configuration in order to compensate for the surface roughness of the TiO2:Cs layer. The roughness of the interlayer is extremely crucial for efficient functioning of the tandem device, since it is desirable to have a flat surface on which the second BHJ can be fabricated. The Au surface was modified using TiO2:Cs, shifting the work function to 3.5 eV, as shown in Figure 2b, which allows for its use as a cathode for the rear subcell.[19] As will be discussed later, the appropriate work function of the middle electrode ensures selectivity of carrier extraction, which is necessary for high performance of individual subcells.

The current–voltage (J–V) characterization of the 3T devices was carried out in ambient air and no degradation was observed during the normal testing period, which typically lasted one hour. The J–V characteristics of the individual front and rear subcells for the common-anode and common-cathode configurations and for the tandem device when connected in parallel are shown in Figure 3a,b respectively. The device parameters are summarized in Table 1 and a summed current was observed for both 3T devices when connected in parallel.

In the common-anode configuration, the front P3HT:PC70BM cell showed a PCE of 3.5% with a JSC of 10.1 mA cm–2, VOC of 0.58 V, and fill factor (FF) of 60.0%, while the rear PSBTBT:PC70BM cell exhibited a PCE of 1.3%, JSC of 5.1 mA cm–2, VOC of 0.6 V, and FF of 39.5%. The two subcells were connected in parallel with the interlayer acting as the anode, and the cathodes of the front and rear subcells were connected to form the cathode contact. The resulting tandem cell showed a JSC of 15.1 mA cm–2, VOC of 0.60 V, and FF of 52.5%, resulting in a PCE of 4.80%. The calculated J–V characteristics of the 3T device, shown in Figure 3a, constructed by adding the currents from the two single cells at each voltage, matched the J–V characteristics measured from the 3T tandem device. This match implies that the interlayer serves the efficient function of collecting the holes from both the front
Another important observation is that the FF of the parallel-connected tandem cell is dominated by the cell that delivers the higher current. As a result, very high FF values greater than 50% for the 3T device can be seen in spite of the low FF of less than 40% of the rear PSBTBT:PC70BM cell. The implication of this finding is very crucial in optimizing the thickness of the individual subcells in order to maximize the FF and photocurrent from the 3T cell.

Figure 3b shows the J–V characteristics of a successful 3T device with the common-cathode configuration. However, the front subcell exhibited a much lower photovoltaic performance than that in the common-anode cells, resulting in an overall PCE of 2.0%, which can be ascribed to two main reasons. Firstly, considering strong reflection of Au at near-IR wavelengths, the relatively thick Au middle electrode leads to a dramatic reduction in absorption of the rear subcell, resulting in a very low $J_{SC}$ (2.3 mA cm$^{-2}$). Secondly, deposition of thicker Au films leads to more pronounced Au diffusion and, hence, a small shunt resistance of the front cell that leads to a low FF. Consequently, further improvement in the surface roughness of n-type layer on the front subcell will reduce the required thickness of the Au layer and, thus, enhance the photovoltaic performance from both front and rear subcells significantly.

In this work, an ultrathin Au layer was used as a conducting interlayer; however more than 40% loss in transmission was observed because of reflectance from the 12 nm Au, especially in at near-IR wavelengths in the range 700–900 nm, as shown in Figure 1c. It is worth noting that no thermal treatment was.

Table 1. Device parameters of the 3T parallel connected tandem cell for both common-anode and common-cathode configurations. FF: fill factor.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>$J_{SC}$ [mA cm$^{-2}$]</th>
<th>$V_{OC}$ [V]</th>
<th>PCE [%]</th>
<th>FF [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Common anode</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Front subcell</td>
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<td>0.58</td>
<td>3.5</td>
<td>60.0</td>
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<tr>
<td>Rear subcell</td>
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<td>0.62</td>
<td>1.3</td>
<td>39.5</td>
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<tr>
<td>Three-terminal Device</td>
<td>15.1</td>
<td>0.60</td>
<td>4.8</td>
<td>52.5</td>
</tr>
<tr>
<td>Common cathode</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Front subcell</td>
<td>4.60</td>
<td>0.52</td>
<td>1.2</td>
<td>50.0</td>
</tr>
<tr>
<td>Rear subcell</td>
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<td>0.57</td>
<td>0.53</td>
<td>41.0</td>
</tr>
<tr>
<td>Three-terminal Device</td>
<td>7.69</td>
<td>0.50</td>
<td>2.0</td>
<td>52.0</td>
</tr>
</tbody>
</table>

Figure 3. J–V characteristics of front-cell (square), rear-cell (circle), and parallel connected tandem cell (triangles) under AM1.5G 100 mW cm$^{-2}$ of illumination for a) common-anode configuration and b) common-cathode configuration devices. The estimated J–V characteristics (solid line) of the tandem cell calculated by adding the current densities of the single cells at different voltage bias match the measured J–V characteristics of the tandem cell exactly.

Figure 4. EQE of the individual subcells and the parallel connection 3T device in a) the common-anode configuration and b) the common-cathode configuration.
performed after the deposition of the Au layer due to significant loss in conductivity which can be ascribed to aggregation of Au clusters, resulting in low FFs for the rear subcells.\cite{16} If alternative highly conductive and thermally stable electrodes with high transparency can be used, the efficiency of the 3T cells can be enhanced significantly.

Another advantage of this kind of device configuration is in enhancing the absorption range when two different polymers with complementary absorption ranges are used, or in increasing the absorption itself when two subcells of the same polymer are used. The latter is advantageous for polymers that have low carrier mobilities because of which the active layer thickness cannot be increased beyond a certain thickness. We can increase the absorption of such polymers with low mobility by connecting two subcells of the same polymer in parallel. Recently there have been reports of high-efficiency polymer photovoltaics that show only 50% absorption under optimized conditions.\cite{16,20} Utilizing the 3T tandem structure with these material systems can significantly increase the efficiencies.

In conclusion, high-efficiency 3T tandem cells have been demonstrated, in which two subcells are connected in parallel through a common conducting, semitransparent electrode. The devices were fabricated both in common-anode and -cathode configuration. In this configuration, the two subcells can be characterized individually and as well as when connected in parallel. When the subcells are connected in parallel, a short-circuit current of 15.1 mA cm\(^{-2}\) and a PCE of 4.8% was achieved in the common-anode configuration.

**Experimental**

All the 3T devices were fabricated on transparent ITO-coated glass that was cleaned sequentially using deionized water, acetone, and isopropanol, followed by drying in oven at 110 °C for 2 h.

In the common-anode configuration, the work function of ITO was modified with help of TiO\(_2\):Cs that was prepared according to our previously reported methods.\cite{16} This modification was followed by deposition of first active layer from a 1:1 weight ratio of P3HT:PC\(_{70}\)BM modified with help of TiO\(_2\):Cs that was prepared according to our previously reported methods.\cite{16} The bottom ITO, the Au interlayer, and the TiO\(_2\):Cs nanocrystals was spun-cast on the Au surface as the cathode contact for the rear subcell, followed by spin-casting of the second polymer BHJ, i.e., PSBTBT:PC\(_{70}\)BM, and deposition of the top V\(_2\)O\(_5\)(10 nm)/Al(100 nm) anode.

The absorption spectra after depositing each active layer and the interlayer were taken using a Varian Cary 50 UV-vis spectrophotometer. J–V characteristics of the tandem cell and the subcells were taken using a Keithley 4200 source unit. Bright-state J–V characteristics were taken under 100 mW cm\(^{-2}\) simulated AM1.5G illumination using an Oriel 9600 solar simulator.

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