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Broadband light absorption enhancement in moth’s eye nanostructured organic solar cells

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A comprehensive study on inverted organic solar cells (OSCs) with a moth’s eye nanostructured (MEN) active layer was carried out. Performance of the MEN-based OSCs and the corresponding control planar cells, fabricated with blend of poly[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl] [3-fluoro-2,6-diyl] [3-fluoro-2,6-diyl] carbonyl[thieno[3,4-b]thiophenediyl] (PTB7):[6,6]-phenyl-C70-butyric-acid-methyl-ester (PC70BM) was analyzed. The efficiency of the MEN-based OSCs was optimized by adjusting the height of MEN pattern in the active layer. Our experimental and theoretical results reveal that the MEN pattern enhances light absorption in the PTB7:PC70BM active layer, especially over the long wavelength region. This leads to a 7.8% increase in short circuit current density and a 6.1% increase in power conversion efficiency over those of the control planar cell.

As a clean and non-exhaustible energy source, solar energy is becoming ever more important in reducing energy prices and influencing the global climate change. Compared to conventional Si solar cells, conjugated polymer-based organic solar cells (OSCs) are more cost effective, enabling productions on a larger scale at a low-cost. However, due to the mismatch between the optical absorption depth and the charge transport scale in OSCs, light absorption in OSCs is limited. This severely restricts the power conversion efficiencies (PCE) of OSC. To solve this problem, many efforts have been devoted to improving light absorption in the active layer without increasing its thickness through different light trapping effects.

Various approaches have been reported including incorporating metal nanoparticles, photonic structures and textured substrate templates in OSCs to boost light absorption. Incorporation of these nano-structures for absorption enhancement in regular configuration OSCs has been demonstrated. An inverted architecture has processing advantages compared to the regular structured OSCs. OSCs with a reverse geometry also possess enhanced absorption and stability comparing to the corresponding OSCs having a regular configuration. Recently, performance enhancement in inverted OSCs with a thick sol-gel zinc oxide (ZnO) grating buffer layer, formed by imprinting following with a sintering treatment, was demonstrated. However a sintering process required for forming the sol-gel ZnO buffer layer is not a favorable approach for application in fabrication of large area flexible OSCs. A solution-processed annealing-free thin ZnO nanoparticle-based buffer layer has advantages for producing efficient inverted OSCs. In a related work, we found that Al/organic contact in regular OSCs always hampers the electron collection, proven by the transient

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photocurrent measurements, due to the unfavorable interfacial exciton dissociation occurred at the (Al)/organic cathode interface. However, this is not observed in inverted OSCs.\textsuperscript{20}

In this work, moth’s eye (MEN)-based two-dimensional (2-D) periodic nano-structures were incorporated for attaining light absorption enhancement in inverted OSCs. The nano-structured OSCs were fabricated by imprinting 2-D MEN pattern in the active layer without additional post-annealing or vacuum treatment, a process that can be easily adopted for application in large area and flexible OSCs. The patterning of MEN structure in the inverted OSCs was optimized by controlling the mold pressure during the imprinting process. Performance of the MEN-based OSCs is closely related to the period and the height of the imprinted structures. The optimized MEN-based OSCs produced an average short circuit current density ($J_{SC}$) of $15.2 \pm 0.1 \text{ mA/cm}^2$, with an increase of $7.8\%$ compared to that measured for the optimized control planar cells ($14.1 \pm 0.2 \text{ mA/cm}^2$). The improvement in $J_{SC}$ is primarily attributed to the enhanced light absorption, resulting in a $PCE$ of $7.0 \pm 0.2\%$, increased by $6.1\%$ compared to that of the best performing control planar cell ($6.6 \pm 0.1\%$).

Indium tin oxide (ITO)/glass substrates, with a sheet resistance of 10 $\Omega$/square, were cleaned by ultrasonication sequentially with detergent, deionized water, acetone and isopropanol each for 20 min. The ZnO nanoparticles with diameter around 5.0 nm in methanol were synthesized following the processes described in a previous work.\textsuperscript{21} A 10 nm thick ZnO electron extract layer (EEL) was then fabricated on ITO/glass by spin-coating inside a N$_2$-purged glove-box with O$_2$ and H$_2$O levels < 0.1 ppm. The donor poly[4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b]dithiophene-2,6-diyl]-[3-fluoro-2-[(2-ethylhexyl) carbonyl]thieno[3,4-b]-thiophenediyl] (PTB7) (1 Material) and the acceptor [6,6]-phenyl-C$_{70}$-butyric-acid- methyl-ester (PC$_{70}$BM) (Nano C) were blended in a weight ratio of 1:1.5 in chlorobenzene (CB) (Sigma-Aldrich, 99.8\%) with 3\% 1, 8-Diodooctane (DIO) (Sigma-Aldrich) additive in the PTB7:PC$_{70}$BM blend formulation. All chemicals were used as received. The donor/acceptor blend solution was stirred to full dissolution on a hotplate at 60 $^\circ$C before use. A PTB7:PC$_{70}$BM bulk heterojunction layer was then deposited on ZnO (10 nm) modified ITO/glass substrates by spin-coating inside the glove-box. The thickness of the PTB7:PC$_{70}$BM photoactive layer was optimized to achieve the best PCE for both MEN-OSCs ($95 \pm 2$ nm) and the control planar cells ($82 \pm 2$ nm). MEN structure in the PTB7:PC$_{70}$BM active layer was formed by imprinting process using a perfluoropolyether mold. The height of the 2-D MEN pattern in the active layer was optimized by controlling the mold pressure during the imprinting process for achieving high efficiency MEN-based OSCs. The imprinting was carried out at room temperature with duration of 5 minutes. After the mold was removed, samples were then transferred to an adjacent vacuum evaporator, with a base pressure of $5.0 \times 10^{-5}$ Pa, for the deposition of a 2 nm thick MoO$_X$ anode interlayer and a 100 nm thick Ag top contact. Thicknesses of the MoO$_X$ and the Ag layers were monitored in-situ using a calibrated Fil-Tech QI8010 quartz crystal microbalance. The optimized control planar cells with an identical layer structure of ITO/ZnO (10 nm)/PTB7:PC$_{70}$BM (82 $\pm$ 2 nm)/MoO$_X$ (2 nm)/Ag (100 nm) were also made for comparison studies. After the cell fabrication, the MEN-based and control OSCs were then transferred back to the adjacent glove-box for in-situ photocurrent density-voltage ($J$–$V$) characteristic measurement, using an Agilent U2722 SMU, under a SAN-EI XEC-301S AM 1.5G solar simulator (100 mW/cm$^2$), calibrated with a KG5 filtered silicon diode.

The schematic three-dimensional (3-D) drawing of the imprinted MEN-based OSCs is shown in Fig. 1(a). The details of the corrugated cell structure are: glass/ITO/ZnO (10 nm)/PTB7:PC$_{70}$BM (95 $\pm$ 2 nm)/MoO$_X$ (2 nm)/Ag (100 nm). The nano-structured OSCs with different MEN heights in the active layer were made, along with the control planar cells for comparison studies. Considering the wettability and the capillary effect during the cell fabrication via the one-step imprint process, a mold with a periodicity of 480 nm was used. Apart from the periodicity of the pattern, it is found that the structure depth is a very important factor on the device performance. For the same mold, nano-structure with different depths, which can be controlled by the pressing pressure, had a great impact on the performance of the cells. AFM images measured for the top surface of the PTB7:PC$_{70}$BM layer, formed by the imprinting process with a pressure of 9.68 kPa, and the Ag cathode surface of the MEN-cells are shown respectively in Figs. 1(b) and 1(c). The AFM images confirm the creation of the periodic structure in the PTB7:PC$_{70}$BM active layer, formed by the
FIG. 1. (a) Schematic diagram of a MEN-based OSC. 3-D AFM images measured for (b) the PTB7:PC \(_{70}\)BM active layer imprinted with a pressure of 9.68 kPa, and (c) the Ag cathode surface of the corresponding MEN-OSC, revealing Ag layer being conformal with 3-D MEN pattern with a periodicity of ∼480 nm.

simple imprinting process, and silver layer being conformal with the 3-D MEN pattern having a period of ∼480 nm and a height of ∼51 nm. In this work, the periodic pattern with different MEN heights in the active layer was controlled by adjusting the imprinting pressure over the range from 1.94 kPa to 19.36 kPa, with the corresponding average height of the MEN pattern in the active layer ranging from 42 nm to 64 nm. The modulation parameters of the MEN pattern obtained in the AFM measurements were then used in the simulation.

The \(J–V\) characteristics measured for a series of the imprinted and control planar OSCs are shown in Fig. 2(a). Regardless of the variation in the structure of the active layer, these OSCs yielded a consistent \(V_{OC}\) of 0.71 V to 0.72 V, which are in good agreement with the reported values. The \(J_{SC}\) of 15.2 ± 0.1 mA/cm\(^2\) was obtained for imprinted cells having an average MEN height of 51 nm in the active layer, showing a 7.8% increase in short circuit current density compared to that of a structurally identical control planar cell (14.1 ± 0.2 mA/cm\(^2\)). The statistical analyses of \(J_{SC}\) and PCE with the corresponding measurement errors are summarized in Table I, revealing that there is an obvious enhancement in the performance of the MEN-based cells, as compared to the best performing (optimized) control planar cells. 7.8% enhancement in \(J_{SC}\) is an improvement averaged from more than 10 cells, not the result from the champion device. Although the figure
of 7.8% is less aggressive, it could be impactful as the enhancement in $J_{SC}$ is realized via a very simple one-step imprinting process without acquiring any post annealing treatment. There is a small reduction in the $FF$ of the imprinted devices, induced by a slight increase in the series resistance ($R_S$) and a small decrease in the shunt resistance ($R_{SH}$). For example, compared to the control planar cell, 5% increase in $R_S$ and 3% decrease in $R_{SH}$ were observed in the imprinted OSCs with a 51 nm height MEN pattern in the active layer. The optimized MEN-based OSCs with a $PCE$ of 7.0 ± 0.2% were obtained, showing a 6.1% increase in power conversion efficiency compared to that of a structurally identical best performing control planar cell (6.6 ± 0.1%).

In order to better understand the origin of the enhancement in the performance of the MEN-based OSCs compared to the control planar cells, the recombination characteristics in the OSCs

### Table I

<table>
<thead>
<tr>
<th>MEN height (nm)</th>
<th>$V_{OC}$ (V)</th>
<th>$FF$ (%)</th>
<th>$J_{SC}$ (mA/cm²)</th>
<th>$PCE$ (%)</th>
<th>$R_S$ (Ω·cm²)</th>
<th>$R_{SH}$ (Ω·cm²)</th>
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</thead>
<tbody>
<tr>
<td>64</td>
<td>0.71</td>
<td>63.3</td>
<td>15.0 ± 0.2</td>
<td>6.7 ± 0.2</td>
<td>71</td>
<td>6569</td>
</tr>
<tr>
<td>55</td>
<td>0.72</td>
<td>65.2</td>
<td>14.7 ± 0.1</td>
<td>6.9 ± 0.1</td>
<td>40</td>
<td>8212</td>
</tr>
<tr>
<td>51</td>
<td>0.72</td>
<td>64.3</td>
<td>15.2 ± 0.1</td>
<td>7.0 ± 0.2</td>
<td>43</td>
<td>7649</td>
</tr>
<tr>
<td>44</td>
<td>0.72</td>
<td>64.0</td>
<td>14.9 ± 0.2</td>
<td>6.9 ± 0.1</td>
<td>43</td>
<td>6889</td>
</tr>
<tr>
<td>42</td>
<td>0.71</td>
<td>62.7</td>
<td>15.0 ± 0.1</td>
<td>6.7 ± 0.1</td>
<td>46</td>
<td>6640</td>
</tr>
<tr>
<td>Planar</td>
<td>0.72</td>
<td>65.1</td>
<td>14.1 ± 0.2</td>
<td>6.6 ± 0.1</td>
<td>41</td>
<td>7893</td>
</tr>
</tbody>
</table>
were analyzed. Fig. 2(b) shows the double logarithmic plot of the net photocurrent density generated, $J_{\text{ph}}$, $J_{\text{ph}} = J_l - J_d$, where $J_l$ and $J_d$ are the photocurrent and dark currents, as a function of the effective voltage $V_\text{eff}$ ($V_\text{eff} = V_0 - V_b$, where $V_0$ is the built-in voltage measured at $J_{\text{ph}} = 0$, and $V_b$ is the applied bias), measured for an imprinted OSC and a control planar cell. As $V_\text{eff}$ decreases, charge recombination would increase and not all the photo-generated carriers could be collected by the electrodes. Thus, under specific $V_\text{eff}$, charge extraction efficiency $P$ can be expressed as

$$P(I, V_\text{eff}) = \frac{J_{\text{ph}}(I, V_\text{eff})}{J_{\text{ph, sat}}(I)}$$

$P$ approaches unity at a high $V_\text{eff}$, corresponding to the complete collection of the photo-generated charges. In this regime, recombination is negligible. The recombination becomes increasingly important at low $V_\text{eff}$ as $P$ decreases with $V_\text{eff}$. As shown in Fig. 2(b), monomolecular recombination is the dominant recombination mechanism at the high $V_\text{eff}$, while bimolecular recombination is the dominant recombination process at the low $V_\text{eff}$. $J_{\text{ph}} - V_\text{eff}$ characteristics of the MEN-based OSCs are almost identical to that measured for the control planar cell over the $V_\text{eff}$ range from 1 V to approximately 0.25 V that is close to the maximum power point of the cells. This suggests that both MEN-based and control planar OSCs possess the same charge collection efficiency in this $V_\text{eff}$ region. The value of $P$ reflects an overall measure of the loss in the photo-generated charges in the OSCs. The results shown in Fig. 2(b) reveal clearly that the MEN-based OSCs had similar charge collection properties to that of the control planar cell, suggesting that the creation of the periodic structure in the active layer of the MEN-based OSCs does not affect the charge recombination process and the charge collection properties.

The IPCE spectra measured for the MEN-based OSCs and control planar cells are shown in Fig. 3(a). Comparing the IPCE spectra measured for the imprinted and the control planar OSCs, the enhancement factor on IPCE due to the MEN structure at different wavelengths is shown in

![FIG. 3. (a) IPCE spectra measured for the MEN-based and the control planar OSCs. (b) Experimental results of enhancement factor on IPCE of MEN-based OSCs over a control planar cell.](image-url)
Fig. 3(b). It can be observed that the enhancement factor on \textit{IPCE} is wavelength dependent. The enhancement occurs at specific wavelengths, e.g., at 379 nm and 544 nm. There is a spectral region with decrease in absorption, e.g., at 455 nm. For OSCs with periodic nano-structures, light diffraction and light scattering play an important role contributing to the absorption enhancement in the cells, although the improved spectral response due to light scattering effect is not wavelength dependent. The results in Fig. 3 imply that absorption enhancement in the MEN-based OSCs is mainly attributed to the 2-D periodic grating effect, as the absorption enhancement is wavelength dependent.

In order to better understand the origin of the enhancement in the photocurrent of the corrugated OSCs, light absorption in the active layer of the different OSCs was analyzed using the finite-difference-time-domain (FDTD) simulation method. The unit cell in $x$-$y$ plane used in FDTD simulation is shown in the inset in Fig. 4(a), and the cross section of the field distribution is set at $y = 0$ in the FDTD simulation. The simulated absorption spectra and the corresponding enhancement factor of the active layer at normal incidence for different OSCs are plotted in Figs. 4(a) and 4(b). The results, shown in Fig. 4(b), reveal that the enhancement factor on absorption calculated for the imprinted OSCs over the control planar cell agrees with the enhancement factor on \textit{IPCE} measured for the OSCs shown in Fig. 3(b). It is clear that absorption enhancement in MEN-based OSCs is wavelength dependent and occurs at specific wavelengths.

For MEN-based OSCs with an optimized MEN height of 51 nm in the active layer, the electric $|E|$ and magnetic $|H|$ field distributions at $x$-$z$ plane when $y = 0$ for the imprinted cell at incident wavelengths of 379 nm, 455 nm, and 544 nm are illustrated in Fig. 5. It can be seen that the electric and magnetic field distributions in the active layer of the imprinted cells are clearly modified at these wavelengths. The profile of the field distributions arises from the distorted Bloch/cavity hybridization modes, caused by the distinct optical phenomena in periodic nano-structures, e.g., the MEN-OSCs, and the multilayer interference effect.\(^{24}\) At 379 nm, the resonant optical modes of the...
electric field distribution cover exactly within the active layer, explaining the observed 15.2 ± 0.1% enhancement in the absorption. However, at longer wavelength (e.g., 544 nm), part of the electric field concentration locates outside active layer, resulting in only ~2% increase in absorption. It shows that the absorption enhancement in MEN-based OSCs occurs at the specific wavelengths, e.g., at 379 nm and 544 nm. A decrease in absorption over a spectral region was also observed, e.g., at 455 nm, as compared to a control planar cell, observed in both experiments and the simulation. The behavior of such a wavelength-dependent absorption enhancement is mainly due to the distinct optical phenomena in the OSCs containing periodic patterns. The electric and magnetic field distributions calculated for the MEN-based and the control planar OSCs at 455 nm are shown in Figs. 5(b) and 5(e). FDTD simulation reveals that a large portion of the field enhancement at 455 nm is distributed outside the active region in MEN-based cells. This imposes a limitation in the absorption over a spectral region near 455 nm. However, PTB7 does not have a strong absorption below 500 nm. MEN-based cells still benefit from an overall absorption enhancement due to
the 2-D periodic grating effect over the wavelength region from 500 to 750 nm, attaining a 7.8% increase in $J_{SC}$ as compared to the control planar cell.

In summary, annealing-free high performance inverted MEN-based OSCs were demonstrated. Charge collection and absorption enhancement in the 2-D photonic structured OSCs were investigated. The enhancement in the $PCE$ of MEN-based OSCs (7.0 ± 0.2%) over a control planar OSC (6.6 ± 0.1%) was mainly due to the broadband absorption enhancement in the active layer. FDTD simulation supported the experimental findings in showing that the enhancement in $J_{SC}$ is mainly from the absorption enhancement in the MEN-based OSCs.

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