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Surface-plasmon enhanced absorption in organic solar cells by employing a periodically corrugated metallic electrode

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We demonstrate improved efficiency of organic solar cells (OSCs) by employing a periodically corrugated metallic electrode in the OSCs. The improved efficiency can be attributed to the absorption enhancement resulted from the excitation of propagating surface-plasmon polariton (SPP) modes at the corrugated metal/organic interface. Through tuning the SPP resonance to the intrinsic absorption region, the short circuit current of the corrugated device with appropriate period has been increased from 4.1 mA/cm² for planar device to 5.5 mA/cm². The power conversion efficiency exhibits an enhancement of 35%. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4761947]

Organic solar cells (OSCs) based on conjugated polymers and small molecules are an attractive alternative to Si-based solar cells due to their advantages of low cost, light weight, simple fabrication process, and flexibility.1–5 However, the power conversion efficiency (PCE) of the OSCs is still low for commercial applications. The tradeoff between the efficiency of photon absorption and exciton harvesting is one of the main limitation factors. The active layer is generally less than 100 nm due to the short exciton diffusion length, which limits the efficiency of incident light absorption.6 A thicker active layer offers higher light absorption, however, it comes at the expense of lowered exciton harvesting. Therefore, an exploration of device design to improve light absorption without increasing the physical thickness of the photovoltaic absorber layer is required.

Recently, an interesting light-trapping strategy has been demonstrated via exploiting surface-plasmon polariton (SPP) resonances,7 which permits a considerable absorption enhancement in OSCs.8 This strategy has been explored in the previous works by employing metallic nanostructure in OSCs to excite the SPPs, such as metallic nanoparticles9–11 and periodically nanopatterned metal film.12,13 However, most of the metallic nanoparticles are fabricated by thermal evaporation14 or electrodeposition,15 which lead to poor control over particle size/shape and consequently their SPP resonance. The most absorption enhancement occurs at the SPP resonant wavelength, which means that tuning the SPP resonance to the absorption region of the absorber layer is crucial for efficiently utilizing this light-trapping strategy. In contrast to metallic nanoparticles, periodically nanopatterned metal film forms a particularly interesting class, since their periodicity can be tuned to adjust the SPP resonance and the metal film itself can be used as metallic electrode in the devices. Up to 50% increment of the absorption in the active layers of the OSCs has been predicted by previous theory analysis.16 Therefore, using the periodically nanopatterned metal to excite SPP may provide a possible way to release the tradeoff between photon absorption and exciton harvesting efficiency.

In this study, such a corrugated metallic electrode with wavelength-scale periodicity was integrated into the OSC structure to excite the SPP at the metal/organic interface with tunable resonance. The SPP resonance has been tuned by changing the grating period, so that a coincidence between the SPP resonance and the absorption wavelength region of the absorber layer can be obtained to realize a maximum absorption enhancement. Obvious improvement of absorption in the corrugated OSCs has been demonstrated by both experimentally measured and theoretically simulated absorption spectra. The short circuit current (Jsc) and the PCE were significantly improved for the corrugated OSCs with appropriate period.

A holographic lithography technique combined with vacuum thermal evaporation process provides a simple approach for the fabrication of corrugated gold and silver electrodes with high period precision and reproducibility.17 The fabrication process is shown in Fig. 1(a). The spatial period Λ is defined by the angle between the two laser beams θ and the laser wavelength λ (266 nm, MBD E-200, Coherent Inc. USA) in the form Λ = 2π(2 × sin(θ/2)). By adjusting the θ to 50°, 52.6°, 44.8°, 38.8°, the corrugated substrates with 270, 300, 350, and 400 nm spatial periods were obtained. The morphologies were characterized by an atomic force microscopy (AFM) as shown in Fig. 1(b). The groove depth of the corrugated grating is ~60 nm, which is efficient for the excitation of SPP in corrugated metal surface.18 An semi-transparent anode of Au layer (20 nm), an electron donor layer of copper phthalocyanine (CuPc 35 nm), an electron acceptor layer of fullerene (C60 70 nm), an exciton block layer of bathocuproine (BCP 10 nm), and a bi-layer cathode of Ca/Ag (3/80 nm) were deposited, sequentially, as shown in Fig. 1(a). The Ag layer is deposited as protecting layer on the top of the Ca layer. All organic compounds and electrode metals were thermally deposited under high vacuum (5 × 10−4 Pa). For comparison, we also fabricated planar device, in which

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the corrugated substrate was eliminated and all material layers were deposited in flat layers. The thickness of each layer was monitored by quartz crystal film thickness monitor\(^{15}\) and calibrated by a spectroscopic ellipsometers (J. A. Woollam Co., Inc., USA). The current density-voltage curves of the OSCs were measured by a Keithley 2400 sourcemeter under 1 sun (100 mW/cm\(^2\)) simulated AM 1.5 G illumination. The reflectance spectra of the samples were measured by a UV-Vis spectrophotometer (UV-2550, SHIMADZU Co., Inc., Japan).

The performance of the corrugated OSCs with periods of 270, 300, 350, and 400 nm are compared with that of the planar device. Figure 2 shows the statistical J\(_{sc}\) and PCE, which were acquired over 10 separate fabrication runs. Compared with the planar device, their multiple averages show positive increments for the four corrugated OSCs. Meanwhile, the J\(_{sc}\) and PCE increase with increasing period of corrugation at first, and then decrease. The OSCs with periods of 300 and 350 nm exhibit optimal performance. Table I shows the detailed results of the multiple average photocurrent density-voltage characteristics of the corrugated device with the optimal period of 350 nm and the planar device. The J\(_{sc}\) of the corrugated device is 5.5 mA/cm\(^2\), which is higher than that of the planar device (4.1 mA/cm\(^2\)). The PCE increases from 1.07% for planar device to 1.44% for corrugated device, corresponding to an enhancement of 35%.

In order to verify the origin of this enhancement, the absorption spectra of corrugated devices with the various periods were compared with that of the planar device, as shown in Fig. 3(a). Light was incoming from the semitransparent Au anode, and the reflection spectra were measured. The Ag layer with 80-nm thickness on the top of the device results in an almost zero transmittance, so that the absorption spectra can be obtained from the complementary relation between reflection and absorption. The peaks at 645 and 710 nm correspond to the intrinsic absorption of CuPc, while the peak at 550 nm is due to the resonance of the microcavity mode formed by the two metallic electrodes. Another peak at around 450 nm corresponds to the intrinsic absorption of C\(_{60}\). As can be seen, the intrinsic absorption of CuPc shows a grating period-dependent improvement for the corrugated devices.

![FIG. 1. Schematic diagram of the process steps for fabrication of periodical corrugation by holographic lithography and the structure of the solar cell (a), and AFM images of surface morphology of periodic corrugation with period of 270, 300, 350, and 400 nm (b).](image)

![FIG. 2. Multiple device statistical performance analysis of the short circuit current (a) and the power conversion efficiency (b) produced in planar device and the corrugated devices with various periods.](image)

### Table I. The multiple average photovoltaic parameters of the planar device and the corrugated device with the period of 350 nm.

<table>
<thead>
<tr>
<th>Device</th>
<th>V(_{oc}) (V)</th>
<th>J(_{sc}) (mA/cm(^2))</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>Enhancement (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planar</td>
<td>0.46</td>
<td>4.1</td>
<td>57</td>
<td>1.07</td>
<td></td>
</tr>
<tr>
<td>Corrugated</td>
<td>0.46</td>
<td>5.5</td>
<td>57</td>
<td>1.44</td>
<td>35</td>
</tr>
</tbody>
</table>

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1. These reference numbers are not present in the text provided.
SPP resonance at the corrugated metal surface can be tuned by adjusting the grating period by the following condition, when the momentum and energy of the incident light match to that of the SPP mode along the metal/organic interface:

\[
k_{spp} = \frac{k_{\text{light}} \sin \alpha \pm \frac{2\pi m}{\Lambda}}{2},
\]

where \(k_{spp}\) and \(k_{\text{light}}\) are the in-plane wavevectors of the SPP and the incident light, \(\Lambda\) is the corrugation period, \(\alpha\) is the incident angle, and \(m\) is an integer. To obtain \(k_{spp}\), we apply the transfer matrix method to calculate the eigenmodes of the Ag/BCP/C_{60} waveguide. It is known that an analytical solution could be obtained as \(k_{spp} = k_{0}(\varepsilon_{m} + i\varepsilon_{d})^{1/2}\) for SPP resonance at the metal/dielectric interface, where \(\varepsilon_{m}\) and \(\varepsilon_{d}\) are the permittivity of the metal and dielectric, respectively. In our case, the SPP exists at the interface between Ag layer and BCP layer. However, the BCP layer is only 10 nm in thickness, so that the SPP field may extend to the C_{60} layer. Thus, we treat the SPP as a mode in the Ag/BCP/C_{60} three-layer structure, and an analytical expression of the SPP wave number \(K_{spp}\) could not be obtained directly. Then we apply the optical waveguide mode theory to solve the SPP wave number \(K_{spp}\). The procedure is first to solve the scalar Helmholtz equation in each layer. Then we apply the continuity of the tangential components in the boundary to obtain the transfer matrix between each adjacent layer. When the total transfer matrix \(M\) is established, the SPP wave number \(K_{spp}\) can be obtained by solving \(|M|=0\). Based on the above procedure, the calculated SPP resonant wavelength at the Ag/organic interface from this equation peaks at 601, 644, 725, and 809 nm, respectively, for the devices with periods of 270, 300, 350, and 400 nm.

In-house generated finite-difference time-domain (FDTD) code is applied to simulate the absorption spectra. The simulated absorption spectra of the corrugated device with various periods and the planar device are shown in Fig. 3(b), which also exhibits a grating period-dependent improvement for the corrugated devices. There is an additional peak with broad band width appear in the calculated spectra for the corrugated devices, which is close to the peak wavelength of the SPP resonance calculated from Eq. (1), and can be attributed to the SPP resonance at the Ag/organic interface. The small deviation is due to that the eigenmodes obtained by waveguide mode theory are ideal enough, which could not be excited perfectly during the FDTD numerical simulation. On the other hand, the SPP at the Au anode/organic interface may also be excited, however, which should not in the intrinsic absorption region of the absorber layer. Moreover, the Au film is only 20 nm, and surface smoothness and film continuity would be poor for such a thin film, which will limit the efficiency of the SPP resonance. Therefore, the SPP resonance at the Au/organic interface has not been taken into account in this work.

The measured and FDTD-simulated absorption spectra agree with each other very well. The SPP resonance at the Ag/organic interface for the 400-nm corrugated device is around 750 nm in the absorption spectra, which blue shifts with the decreased period, eventually merges with the absorption band of CuPc. The intrinsic absorption is significantly enhanced when the period decreases to 350 nm and 300 nm, due to its appropriate overlap with the SPP resonance. Consequently, the corrugated OSCs with these two corrugation periods exhibit highest enhancement in both \(J_{sc}\) and PCE as shown in Fig. 2. While, this increment of intrinsic absorption becomes lower in case the period decreased to 270 nm, because the SPP resonance is 601 nm in this case, and has moved to the edge of the intrinsic absorption band of CuPc. This feature originates directly from the tuned characteristics of propagating SPP mode. Therefore, the enhanced absorption for the corrugated OSCs can be attributed to the corrugation-induced SPP enhancement, which results in the improved PCE.

This conclusion is also supported by the measured incident photon to current conversion efficiency (IPCE) spectra as shown in Fig. 4. The IPCE is defined as the following equation:

\[
\text{IPCE} = \frac{1024 \times I_{sc}}{\lambda \times P_{in}},
\]

where \(I_{sc}\) is short-circuit current under monochromatic light irradiation, \(\lambda\) is the wavelength of the monochromatic light.
Pin is the intensity of monochromatic light. The IPCE spectra show an obvious enhancement in the absorption region of CuPc for the corrugated device with 350 nm period compared to that of the planar device, which is consistent with their absorption spectra. Therefore, this increase should be resulted from the SPP-enabled enhanced absorption. We should note that the absorption region of C60 was also increased for the corrugated devices, which corresponds to an enhanced IPCE in this region. The SPP effect should be ruled out in this wavelength region. It is probably caused by the elongated optical path of the incident light inside the absorber material, because the light reflected by the micro-structured back cathode is no longer normal to the substrate plane. This process may also contribute to the PCE enhancement.

In summary, the optical absorption of the photovoltaic layers has been enhanced in the OSCs by introducing periodic wavelength-scale corrugation into the Ag electrode to excite propagating SPP at the Ag/organic interface. By tuning the period of the corrugation, the SPP resonance wavelength has been tuned to the intrinsic absorption peak of the photovoltaic absorber layers. As a result, the absorption of the OSCs was significantly enhanced, and the PCE exhibited an enhancement of 35%.

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