Dual-periodic-corrugation-induced broadband light absorption enhancement in organic solar cells

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ABSTRACT

We demonstrate an efficient approach to realize broadband light trapping in organic solar cells (OSCs) by integrating two-dimensional dual periodic corrugations. The dual-periodic corrugations consist of two set different periodic gratings, and have the effect to excite the surface plasmon-polariton (SPP) resonance associated with the cathode/organic interface in broadband wavelength region by adjusting befitting periods of the microstructures. Experimental and numerical results demonstrate that light absorption in OSCs has been enhanced in broadband owing to the effect of SPP-induced field enhancement. The short-circuit photocurrent density is improved from 4.072 to 5.365 mA/cm², and a 31% enhancement of power conversion efficiency has been obtained compared to the conventional planar devices.

1. Introduction

Organic solar cells (OSCs) have come into international research focus owing to the promising properties such as low cost, flexibility, light weight, transparency and large-area manufacturing compatibility [1–7]. However, the low power conversion efficiency (PCE) of the OSCs is one of the primary limitations for their feasibility of commercial use. Increasing the thickness of active layer could realize efficient absorption of the solar radiation to achieve high efficiency of the OSCs [8]. Unfortunately, the thicker active layer brings about lowered exciton harvesting due to the short diffusion length of exciton in organic materials [9]. Plasmonic nanostructures have been introduced into solar cells to enhance light harvesting without increasing the thickness of active layer by light-scattering mechanism and strong surface plasmon-polariton (SPP) effects [10–14]. Metallic gratings based light-trapping schemes have been investigated in traditional photovoltaic cells [15,16]. For wavelength-scale mono-periodic metallic nanogratings introduced into the OSCs, light absorption enhancement in specific narrow wavelength range can be achieved [16–18]. Considering the broadband of the sunlight, extending the wavelength region of the enhanced light absorption in OSCs is necessary, however, mono-periodic plasmonic corrugations are powerless for broadband light trapping.

Broadband light absorption enhancement has been reported by using dual plasmonic nanostructures with Au nanoparticles and periodic gratings [19]. Multiple SPP excited at the interface of a metallic grating and photonic crystal with the designed refractive index variation has also been demonstrated for broadband trapping of light in OSCs [20]. However, nanoimprinting process has limitations in the devices based on small molecule materials, and both the dual plasmonic nanostructures and composite structure of grating and photonic crystal need complicated fabrication processes, which limit their commercial applications. In this article, effective broadband light trapping in OSCs has been achieved by introducing two-dimensional (2-D) dual periodic corrugations into metallic electrodes by holographic lithography technique [21,22]. The 2-D dual periodic corrugation has two sets of corrugations with different periods and rotated 90° with respect to each other. Our experimental and theoretical results demonstrate that the 2-D dual periodic corrugations can broaden the SPP resonance associated...
with the cathode/organic interface as shown Fig. 1, and a 31% enhancement in PCE compared to that of the traditional planar devices has been realized arising from the broadband light absorption enhancement in OSCs.

2. Experimental details

2.1. Fabrication of the dual periodic corrugations

The holographic lithography technique is used to fabricate the microstructures. The technological process of introducing periodic microstructure on substrates is shown in Fig. 2a. The glass substrates were cleaned using standard procedure. The photoresist film (SU-8 2025, Norland Inc.) was spin-coated onto the substrate and the thickness of the film is about 110 nm. The wavelength of the laser (Coherent Inc.) is 266 nm, which is used as the irradiance light source, and the substrates covered with photoresist were exposed by two beams interference. To fabricate the 2-D corrugation, the photoresist film was exposed for the second time after rotation of 90°. The morphologies of the one-dimensional (1-D) and 2-D corrugations have been detected by an atomic force microscopy (AFM, Dimension Icon, Bruker Corporation) in tapping mode as shown in Fig. 2b–f. The groove depth was around 70 and 60 nm for the 1-D and 2-D grating, respectively, which is the optimized depth to excite the SPP mode effectively in OSCs [10].
2.2. Fabrication and evaluation of the OSCs

The anode of 15 nm Au film was deposited on the substrate in a thermal evaporation chamber at a base pressure of $5 \times 10^{-4} \text{ Pa}$. A 5 nm MoO$_3$, 15 nm boron subphthalocyanine chloride (SubPc), 40 nm fullerene (C$_{60}$), 3 nm bathocuproine (BCP), and LiF (1 nm)/Al (80 nm) were evaporated sequentially. UV–Vis spectrophotometer (UV-2550, SHIMADZU) was used to measure the absorption spectra. The angular dependent absorption spectra were measured by a converted UV–Vis spectrophotometer with a rotation stage.

The device performance of solar cells was measured by a source-meter (Keithley 2400) under 1 sun simulated AM 1.5 G illumination (100 mW/cm$^2$).

3. Results and discussion

The effect of filed enhancement induced by SPP is believed to be a highly effective solution to enhance light trapping in an OSC.

![Fig. 3](image1.png)

**Fig. 3.** (a) Absorption spectra of the SubPc and C$_{60}$ films. Experimentally measured (b) and theoretically calculated (c) normalized absorption spectra of the OSCs structures with various periods of corrugations.

![Fig. 4](image2.png)

**Fig. 4.** (a) Absorption spectra of the 2-D dual periodic corrugated OSCs. (b)–(c) Angular dependent absorption spectra of the dual-periodic corrugated OSCs. The rotating orientation is shown in the insets of (b) and (c). The rotation axis is perpendicular to one of the gratings of the microstructure.
device without increasing the thickness of the active layers. SPPs can be excited by introducing a metallic nanostucture in solar cells, such as a periodic corrugated metal film. By changing the period of the microstructures, the SPP resonance in the corrugated metal/organic interface can be tuned. Its consistence with the absorption spectra of active materials is crucial for the efficient improvement of light absorption in OSCs devices. In this work, the donor material has been chosen to be SubPc, and the acceptor material was C60. The absorption spectra of SubPc and C60 planar films are shown in Fig. 3a, and the absorption peaks are around 450 nm for C60 and 595 nm for SubPc, respectively. To determine the desired grating period, both experimental measurement and theoretical simulation of the normalized absorption spectra for the OSCs with grating period from 200 to 400 nm are compared at normal direction (Fig. 3b and c). In the absorption measurement, we decreased the thickness of the Al cathode from 80 nm to 40 nm. In order to exclude the intrinsic absorption of the planar metal films and the organic materials at the observed wavelength region and to distinguish the peaks originated from the SPP resonance supported by the periodic corrugations clearly, we chose a planar OSC as the reference sample for the absorption measurement of the corrugated devices. The absorption spectra exhibit red shift with the increasing grating period as shown in Fig. 3b. The absorption spectra was simulated by in-house generated finite-difference time-domain (FDTD) code as shown in Fig. 3c, and the peak positions of the measured and simulated spectra show excellent coincidence [23]. According to the absorption spectra of SubPc and C60, the suitable periods of the corrugations were determined to be 200 and 350 nm since the corresponding SPP resonance can be tuned to 450 and 595 nm, respectively.

According to the determined periods, we fabricated 2-D dual periodic corrugations by the holographic lithography technique, and the AFM images of surface morphologies of the corrugations are shown in Fig. 2f. The 2-D grating consists of two set corrugations with periods of 200 and 350 nm. The absorption spectra of the dual periodic corrugated OSCs has been measured (Fig. 4a), and it exhibits broadband light absorption as expected. The absorption spectra of the devices with 2-D dual periodic corrugations as a function of the observation angle have been examined using a transverse-magnetic (TM) and a transverse-electric (TE) polarized light source as shown in Fig. 4b and c, respectively. TE and TM polarization have been defined here by the incidence with the electric and magnetic component vertical to the xz plane as describe in the insets of Fig. 4b and c. Using the polarized light source, only a specific narrow absorption peak at normal direction could be observed which is different from the nonpolarized absorption spectra, and the absorption peak splits into two peaks and shifts in wavelength by changing the observation angle. At normal direction, the absorption peak under TM polarized light source is around 450 nm and identical with the SPP resonance supported by 200 nm periodic corrugations, and the peak in TE polarized absorption spectra is the same with SPP resonance peak associated with 350 nm corrugated interface as shown in Fig. 3b. The angular-dependent absorption spectra demonstrate clearly that the broadband absorption of the dual periodic corrugated device comes from the combined action of 200 and 350 nm periodic corrugations in cathode/organic interface.

In order to establish the principle of absorption enhancement in theory and to verify the optical modes supported by the microstructures in OSCs to be SPP modes, the dispersion maps and field intensity distributions of the devices with 2-D dual periodic corrugations were simulated by using the FDTD codes. The dispersion

![Fig. 5. Simulated dispersion relations of the 2-D dual periodic corrugated OSCs under TM (a) and TE polarization (b), and distributions of the magnetic field intensity across the 2-D dual periodic corrugated OSCs under the 450 nm TM polarized normal incident light (c) and 595 nm TE polarized normal incident light (d). The experimental dispersion relations extracted from the angular dependent absorption spectra (circles) are also shown in (a) and (b).](image-url)
maps exhibiting the relationship of absorption intensity with both incident angle and absorption wavelength are shown in Fig. 5a with TM polarized incident light and in Fig. 5b with TE polarized incident light. The plots in Fig. 5a and b shows the dispersion relations constructed from the experimental spectra in Fig. 4b and c, and we can observe an excellent agreement between the numerically simulated and experimentally measured results. The spatial steady-state Hz field intensity distributions across the device with 2-D dual periodic corrugations under the normal incident light for the TM polarization with wavelength of 450 nm is shown in Fig. 5c, and the TE polarization with wavelength of 595 nm is shown in Fig. 5b, respectively. The field intensity exhibits its maximum at the Al/organic interface and decays along the direction perpendicular to it in accord with the characteristics of SPP modes, demonstrating that the peaks at 450 and 595 nm in absorption spectra both supported by SPP modes. We can conclude from the numerical simulations that broadband light absorption enhancement arising from the excitation of broadband SPP modes associated with Al/organic interface by using the 2-D dual periodic microstructures in OSCs.

The current density-voltage (J–V) characteristics of the OSCs devices with and without periodic microstructures were measured and are shown in Fig. 6a, and the photovoltaic parameters are list in Table 1. The performance of OSCs devices with 1-D and 2-D mono-periodic corrugations with the same device structure were also compared in Fig. 6a and Table 1. The open-circuit voltage (Voc) and fill factors (FF) of the planar and corrugated devices remain constant, and it suggests that the microstructures do not violently affect the interface resistance and charge-transfer interface [5]. However, the PCE of the corrugated devices shows obvious enhancement compared with that of the planar devices, which originates from the improvement of short-circuit current density (Jsc). The Jsc is increased from 4.072 mA/cm² for the planar device to 4.302 mA/cm² for the 1-D 200 nm periodic device, 4.531 mA/cm² for the 1-D 350 nm periodic device, 4.887 mA/cm² for the 2-D 200 nm mono-periodic device, 5.129 mA/cm² for the 2-D 350 nm mono-periodic device, and 5.365 mA/cm² for the dual-periodic device, respectively. As a result, the PCE has been improved from 2.652% to 3.487%, and it reveals a 31.49% enhancement in PCE by integrating the 2-D dual-periodic corrugated microstructures. The incident photon to current conversation efficiency (IPCE) spectra has been measured as shown in Fig. 6b. The IPCE spectra of the dual periodic corrugated device shows obvious enhancement compared to those of the planar device in the absorption region of C60 around 450 nm and SubPc around 595 nm. We can conclude that the improvement of OSCs performance could arise from the broadband light trapping by the excitation of the broadband SPP modes at the dual-periodic corrugated cathode/organic interface in OSCs.

4. Conclusions

In summary, we have introduced the 2-D dual periodic corrugations into OSCs and broadband light harvesting has been realized. The dual periodic corrugations have the effect to excite the SPP resonance over a broadband wavelength region at the corrugated Al/organic interface by tuning the periods of the microstructures. The experimental and theoretical results demonstrate that broadband optical absorption has been enhanced by using the dual periodic corrugations, and the photocurrent and efficiency of the OSCs have been improved. As a result, a 31% enhancement in PCE compared to that of the conventional planar devices has been obtained. Therefore, the 2-D dual periodic corrugated OSCs will contribute to their practical application for photovoltaics.

Acknowledgments

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Table 1

<table>
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<tr>
<th>Device</th>
<th>Voc [V]</th>
<th>Jsc [mA/cm²]</th>
<th>FF [%]</th>
<th>η [%]</th>
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<td>1.067</td>
<td>4.072</td>
<td>61.03</td>
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<tr>
<td>Dual periodic</td>
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<td>60.86</td>
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References


