

High-Performance Organic Solar Cells with Broadband Absorption Enhancement and Reliable Reproducibility Enabled by Collective Plasmonic Effects

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Broadband absorption enhancement in metal nanomaterials for high-performance organic solar cells (OSCs) is highly desirable in the plasmonic-enhanced OSCs. Here, a new dual plasmonic device is proposed by strategically designing device structures and managing two types of plasmonic structures (e.g., metal grating and metal nanoparticles (NPs)) in one device to achieve the broadband enhancement with better reproducibility, including (a) selecting Ag grating with 600 nm period as an anode, (b) introducing metal NPs into the electron transport layer (not active layer), and (c) adopting ZnO as the electron transport layer (not TiO₂). The device shows broadband absorption enhancement in the range of 350–800 nm due to multiple plasmonic effects. As a result, the maximum power conversion efficiency (PCE) of 9.62% has been achieved from the device, which is one of the highest efficiencies in plasmonic OSCs reported for a single junction OSC. Importantly, the as-proposed dual device in this work shows an excellent reproducibility of high PCE in experiment, which is much more applicable for practical applications. This work demonstrates the significance of rational design of the device structure and plasmonic nanostructures in achieving high-performance plasmonic OSCs with broadband plasmonic absorption enhancement and reliable reproducibility.

surface plasmon (LSP) of metal nanoparticles (NPs), (2) propagation of surface plasmon polariton (SPP) modes, and (3) plasmon-enhanced scattering.^[2,14–16] LSPs are the oscillation of conduction electrons in finite-sized particle, while SPPs are surface electromagnetic waves propagating along the metal surface. Recently, incorporation of plasmonic NPs into the active layers or an interlayer (hole transport layer or/and electron transport layer) to enhance the light absorption by LSPs resonance and the introduction of plasmonic metal grating as an electrode to promote the optical absorption by SPPs effect are extensively studied in OSCs.^[11,12,17–39] Each type of metal nanostructure has its distinct optical resonances, collectively exciting the various optical modes and integrating all enhancements in one device will be beneficial for achieving a considerable absorption enhancement. It is desirable to achieve a light absorption enhancement in a broadened wavelength region of sun-

light spectrum through a cooperative utilization of plasmonic nanostructures.^[40–43]

Recently, some cooperative plasmonic nanostructures have been progressively reported for high performance OSCs,^[16,17,21,23,24,27,30,33,36–38,40,44,45] including blending Au and Ag NPs into PEDOT:PSS,^[23,33] Ag NPs and Ag nanoprisms into an active layer,^[40] Au NPs and Al NPs into an active layer,^[38] Ag nanoprisms into both the hole transport layer and the electron

1. Introduction

Light trapping is an important topic for organic solar cells (OSCs) to improve light absorption of ultrathin active layers and then photocurrent of OSCs.^[1–8] Recently, plasmonic nanostructures have been introduced into bulk heterojunction (BHJ) OSCs for highly efficient light harvesting.^[1–3,9–13] Generally, the enhanced optical absorption based on the plasmonic effect can be obtained through the routes of (1) excitation of localized

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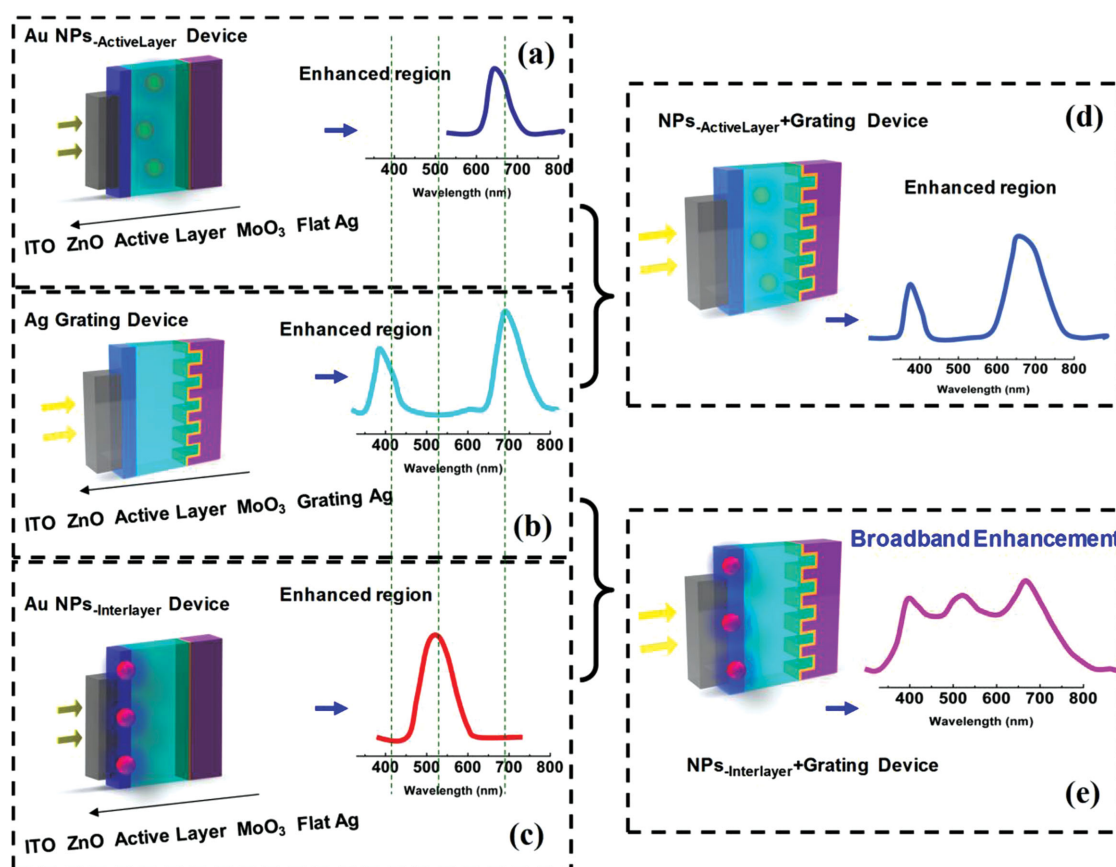


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transport layer.^[24,36] In fact, we have previously demonstrated a fabrication of dual plasmonic nanostructures of ITO/TiO₂/active layer:metal NPs/MoO₃/Ag grating by embedding metal NPs into the active layer and introducing a metal grating as the back electrode in a single-junction device and achieved a power conversion efficiency (PCE) of over 9% for plasmonic-enhanced OSCs.^[46] To further improve the performance of the plasmonic solar cells for reaching the practical application, two important issues should be considered. (1) Broadband light absorption enhancement in a single-junction OSC should be further considered. Generally, the LSP resonance peak of metal NPs incorporating into an active layer is obviously redshift because of the large refractive index of the active layer compared to water (Scheme 1a).^[40,47] For grating device, the absorption enhancement induced by the SPP mode of metal grating locates around infrared region (Scheme 1b).^[31,32,48] As a consequence, light is trapped only around infrared region in the dual device (Scheme 1d). (2) The reproducibility of device performance is also an important issue. Metal NPs should be first introduced into an active layer and subsequently grating structures are fabricated on the top of the active layer by using the polydimethylsiloxane (PDMS) nanoimprinted method.^[46] During a fabrication process, the composite of the active layer and metal NPs will be possibly encountered damage after applying PDMS

mold onto the active layer, thus deteriorating device performance. Therefore, the key step in achieving high-performance plasmonic-enhanced OSCs is to rationally design device structures and manage the plasmonic nanostructures with simultaneously achieving high reproducibility of devices and exhibiting broadband absorption enhancement.

In this paper, we design a plasmonic OSC of ITO/ZnO:Au NPs/Active layer/MoO₃/Ag grating (600 nm period) that consists of Au NPs (with size about 35 nm) incorporated ZnO interlayer and a nanopatterned Ag metal electrode with 600 nm period as back reflectors in the inverted solar cells. Through a carefully strategic analysis of absorption enhancement region from two types of plasmonic nanostructures including metal grating (e.g., grating period) and metal NPs (e.g., Au NPs and Ag NPs) located in different regions (e.g., active layer and electron transport layer) in OSCs, the Ag grating with 600 nm period (not other period) and ZnO interlayer (not TiO₂ interlayer) are selected. Especially, the Au NPs are rationally incorporated into ZnO interlayer (not active layer) in our current design, which is different from our previous work.^[46] In our previous design, the device structure is ITO/TiO₂/active layer:Au NPs/MoO₃/Ag grating (700 nm period). As a result, a broadband absorption enhancement ranging from 350 to 800 nm has been achieved. Herein, we demonstrate a combination of two key advances:



Scheme 1. Plasmonic absorption enhancement of devices with different metal nanostructures: a) for the Au NPs_{ActiveLayer} device, the plasmonic peak drastically shifts from 512 nm to 675 nm. b) For the grating device, the main enhancement region is before 400 nm and after 600 nm. c) For the Au NPs_{Interlayer} device, the plasmonic peak slightly shifts from 512 nm to 530 nm. d) For the Dual Type II device, there are only two absorption enhancement regions around 300–400 nm and 600–700 nm. e) For the Dual Type I device, a broadband absorption enhancement has been achieved.

(1) the broadband plasmonic absorption enhancement has been attributed to collectively plasmonic effects of SPPs and plasmon-enhanced forward scattering. This advance allows us to report an appreciable enhancement in light harvesting of active layers associated with the optical effects resulting in a significant improvement in the maximum PCE to 9.62% and an average 9.34% PCE up from 7.7% for control devices without any plasmonic nanostructures. (2) High reproducibility of the device fabrication procedure is achieved, which is much more applicable for the practical applications.

2. Results and Discussions

2.1. Theoretical Analysis of Absorption Enhancement Region from Two Types of Plasmonic Nanostructures

For optimization of device for the grating device and the NPs device, respectively, a theoretical analysis of an absorption enhancement region from two types of plasmonic nanostructures including Ag grating with different periods and metal NPs (Au or Ag NPs) located in different regions in OSCs will be conducted first. The control device and the plasmonic devices with single plasmonic nanostructures are designed as follows:

1. control device: ITO/ZnO or TiO₂ interlayer (40 nm)/active layer (100 nm)/MoO₃ (8 nm)/flat Ag,
2. device with grating: ITO/ZnO or TiO₂ interlayer (40 nm)/active layer (100 nm)/MoO₃ (8 nm)/Ag (grating with different periods),
3. device with metal NPs introduced into active layer: ITO/ZnO or TiO₂ interlayer (40 nm)/active layer: Au or Ag NPs (100 nm)/MoO₃ (8 nm)/flat Ag,
4. device with metal NPs introduced into interlayer: ITO/ZnO or TiO₂ interlayer: Au or Ag NPs (40 nm)/active layer (100 nm)/MoO₃(8 nm)/flat Ag.

To investigate the grating effect on the plasmonic absorption enhancement of a device, we have calculated the active layer absorption for the devices with or without a grating (Figure 1c,d). We first studied the effect of the grating period on the absorption enhancement region. The grating period is tuned from 400 to 800 nm with the duty cycle being 0.7. According to the enhancement of absorption, we have found that there are two significant absorption enhancement regions around 350–450 nm and 600–800 nm when common absorbing materials including poly(3-hexylthiophene) (P3HT):[6,6]-phenyl-C60-butyric acid methyl ester (PC₆₀BM) and 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):PC₇₀BM are used in our current design. The absorption enhancement region around 350–450 nm is attributed to guided modes because of the different dielectric constants of each layer (see the dielectric constant of each material and near field distribution as shown in Figures S1 and S2 in the Supporting Information, respectively), while the SPPs resonances induced by the Ag grating contribute to the absorption enhancement region after 600 nm.^[31,32,46] These SPP resonances in favor of absorption enhancement are relevant to the period of grating struc-

tures and also slightly vary with the surrounding active layer. For P3HT:PC₆₀BM and PTB7:PC₇₀BM, the dielectric constant is around 1.9 (see Figure S1 in the Supporting Information), these SPP resonances are almost after the wavelength of 600 nm (Figure 1a,b). Because a grating structure with a 600 nm period shows a strong enhancement around the absorption shoulder of P3HT:PC₆₀BM and PTB7:PC₇₀BM in this work (Figure 1c,d), the grating structure with the 600 nm period has been chosen for grating devices in the experimental design below. In addition, it is worth noting that these SPP resonances are typically narrow bands and around 100 nm (Figure 1a,b). Thus, we should adopt another type of plasmonic effect, LSP induced by metal NPs to cooperate with the grating devices to ultimately achieve a broadband absorption enhancement.

After achieving the two distinct absorption enhancement regions around 350–450 nm and 600–800 nm, the absorption region around 500–600 nm should further be enhanced. Generally, the plasmonic resonance peak of metal NPs is strongly affected by the dielectric constant of surrounding environment.^[22,24,33,35,36,49] We first take Au NPs with 35 nm as an example. To elucidate the absorption spectra of the Au NPs, the finite difference time domain method has been employed to calculate the absorption enhancement for Au NPs embedded into an active layer.^[40] The absorption enhancement by incorporating Au NPs into an active layer is shown in Figure 1e. Since most of the active layers show a relatively large refractive index (i.e., P3HT:PC₆₀BM, PTB7:PC₇₀BM is around 1.9 as shown in Figure S1 in the Supporting Information), the plasmonic resonance peak shows a redshift upon transferring from water to an active layer (Scheme 1a, Figure 1e, Figure S3, Supporting Information). For example, when we embed the Au NPs into the P3HT:PC₆₀BM, we find the peak of enhancement induced by LSPs dramatically shift to 650 nm because of the relatively large refractive index of P3HT:PC₆₀BM, which overlaps with the enhancement region induced by the metal grating (Figure 1e). Similarly, when introducing the Au NPs into another active layer PTB7:PC₇₀BM, the absorption enhancement introduced by the LSP resonance also occurs around the near infrared region (Figure 1e). Furthermore, the enhancement region of Ag NPs incorporated into the active layer (P3HT:PC₆₀BM and PTB7:PC₇₀BM) has also been theoretically investigated. The absorption enhancement induced by the LSP resonance of Ag NPs is redshifted to the near-infrared region compared to the extinction peak of 400 nm of Ag NPs in water (Figure 1e). Therefore, based on our theoretical analysis, metal NPs including Au NPs and Ag NPs introduced into an active layer cannot enhance the middle region around 450–600 nm.

In addition to the absorption improvement provided by the metal NPs directly blended into an active layer, metal NPs incorporated into an interlayer can also be possible to indirectly enhance absorption of the active layer by their plasmon-enhanced forward scattering effect. The Mie theory is used to theoretically model the optical response of Au NPs embedded into dielectric materials such as interlayer ZnO and TiO₂, which are two prevalent electron-transporting layers.^[50] Regarding their refractive indices in visible range, as shown in Figure S1 (Supporting Information), TiO₂ (around 2.6) has a larger refractive index than ZnO (≈ 1.4). When Au NPs are incorporated into the ZnO interlayer, the plasmon-enhanced scattering

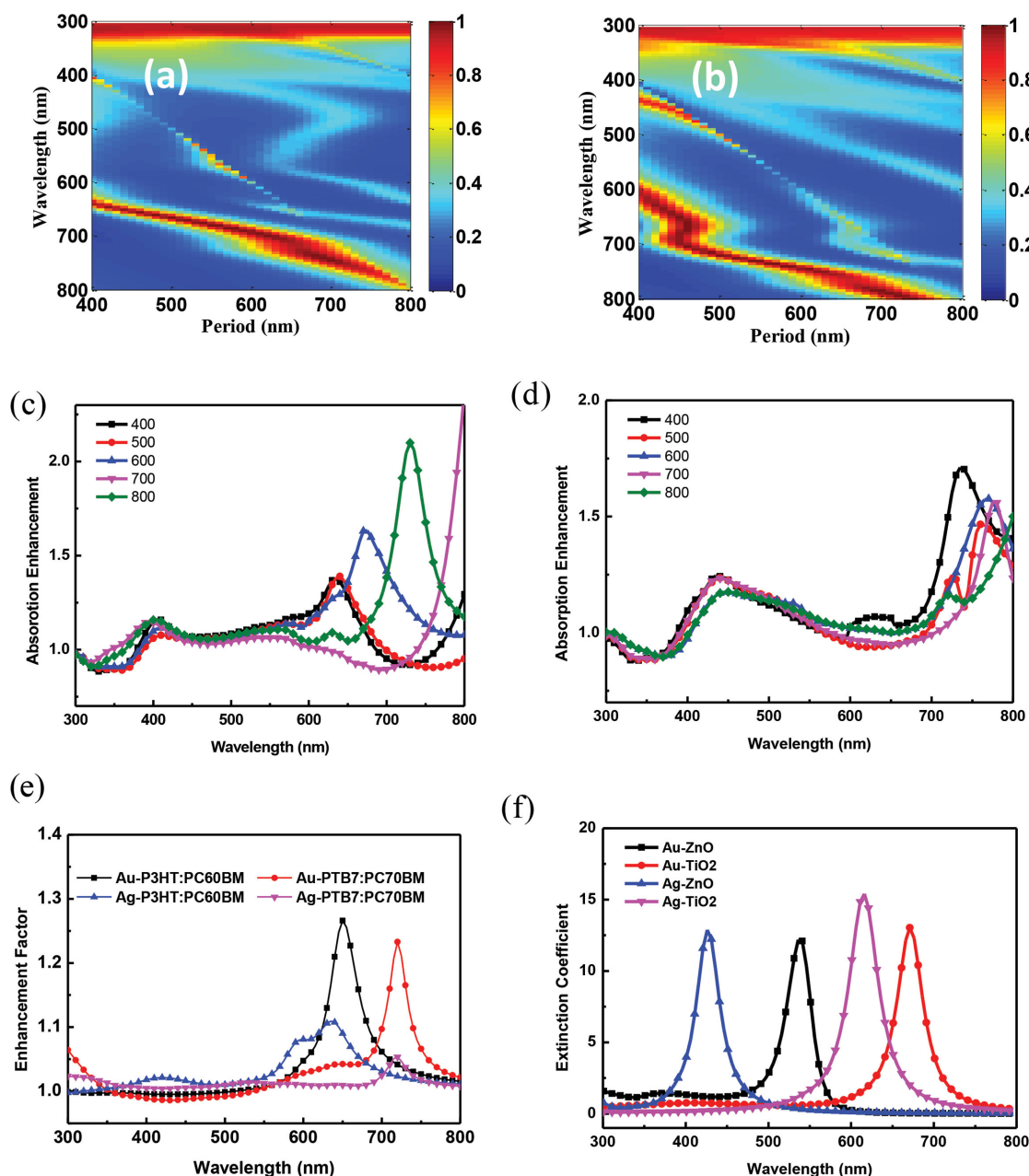


Figure 1. Theoretical investigation of grating period and wavelength on the grating absorption with coating material a) P3HT:PC₆₀BM and b) PTB7:PC₇₀BM. The extinction coefficient of active layer was set as $k = 0$; the duty cycle of grating is 0.7. Theoretical absorption enhancement of c) P3HT:PC₆₀BM devices with different grating periods and d) PTB7:PC₇₀BM devices with different grating periods. e) Theoretical absorption enhancement of metal NPs in different active layers. f) Theoretical extinction coefficient of metal NPs in different interlayers. The diameter of Au and Ag NPs is about 35 nm.

peak of Au NPs just slightly shifts to 540 nm, indicating an enhancement region different from that of the metal grating (before 450 nm and after 650 nm) (Figure 1f). It is noteworthy that the near field of plasmonic Au NPs is horizontally localized around NPs in the ZnO layer and does not contribute to the any absorption enhancement in the active layer;^[25] however, the plasmonic resonances of Au NPs with large size about 35 nm incorporated into the ZnO layer would enhance the forward scattering and then improve light absorption. In contrary,

when small Au NPs with size of 18 nm are introduced into the ZnO interlayer, absorption enhancement of device is not obviously observed due to a weak forward scattering effect of Au NPs, which is agreed with our previous report.^[25] In addition, the theoretical calculation reveals an absorption enhancement region around 450–650 nm when Au NPs with 35 nm are introduced into the ZnO interlayer that again confirms the existence of plasmon-enhanced forward scattering effects (Figure S6, Supporting Information). When ZnO is substituted by TiO₂

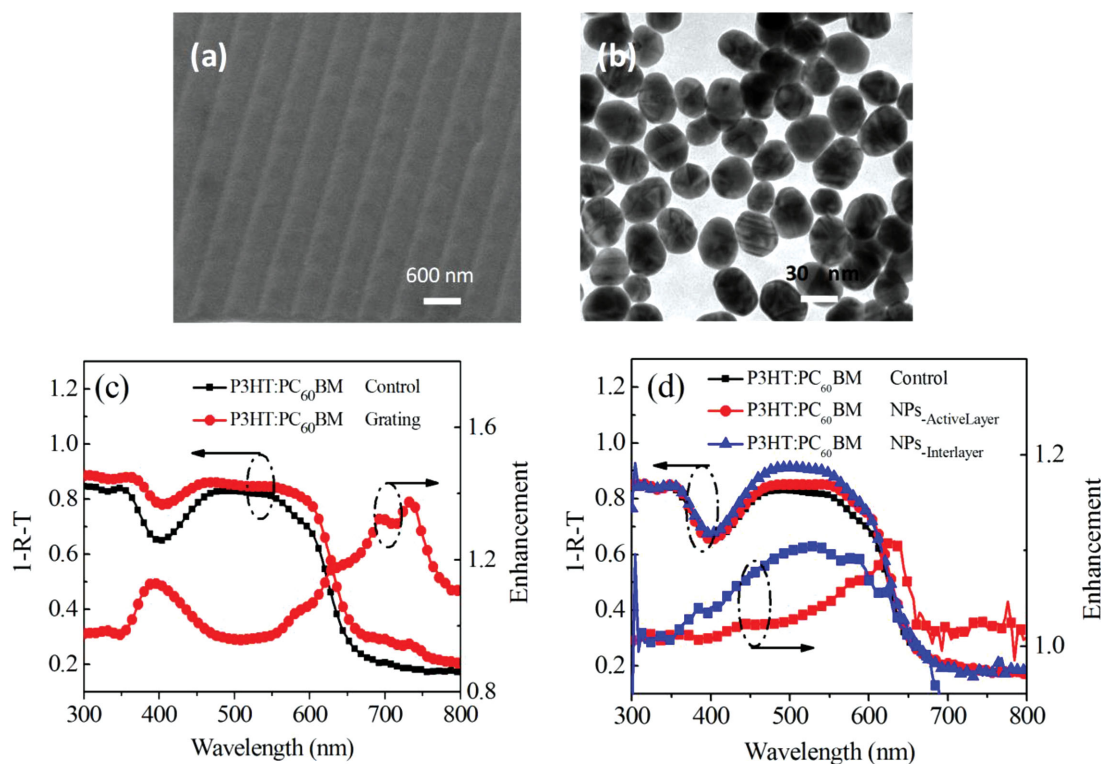


Figure 2. a) SEM image of P3HT:PC₆₀BM film after applying grating pattern on it. The period of the mold is about 600 nm. b) TEM image of Au NPs. The diameter of Au NPs is about 35 nm. c) Experimental absorption spectra of P3HT:PC₆₀BM device with or without grating (i.e., 1-reflection (R)-transmission (T)) and their corresponding ratios (i.e., (1-R-T of grating device)/(1-R-T of control)). d) Experimental absorption spectra of P3HT:PC₆₀BM device with or without Au NPs and their corresponding ratios.

as the interlayer, the plasmon-enhanced scattering resonance peak of Au NPs would show a considerable redshift to 670 nm, which is overlapped with the enhancement region of the metal grating (Figure 1f). Furthermore, incorporation of Ag NPs into ZnO and TiO₂ interlayers has also been investigated. The scattering peak regions are found around 420 nm and 625 nm, respectively, indicating that Ag NPs are not suitable for enhancing light absorption around a wavelength region of 500–600 nm (Figure 1f). As a result, choosing ZnO (not TiO₂) as the interlayer and introducing Au NPs (not Ag NPs) into the ZnO interlayer (not active layer) is the only feasible way to finally enhance the active layer absorption in the wavelength region of 500–600 nm.

2.2. Experimental Investigation: Individual Plasmonic Effect of Au NPs and Ag Grating and Their Cooperative Effects

Experiments have also been conducted to verify the theoretical analysis that the Ag grating with 600 nm period as the back electrode and the incorporation of Au NPs into a ZnO interlayer will result in achieving a broadband plasmonic enhancement. The systematical experiments have been conducted through fabricating six types of devices, including (1) grating device (Scheme 1b), (2) NPs_{ActiveLayer} device (Scheme 1a), (3) NPs_{Interlayer} device (Scheme 1c), (4) Dual Type I device (Scheme 1e), (5) Dual Type II device (Scheme 1d), and (6) the device without any metal

nanostructures as a control device. For devices including a grating structure, the PDMS nanoimprinted method is applied to produce a plasmonic Ag grating back electrode.^[31,32] For devices involving NPs, Au NPs are incorporated into an active layer or an interlayer through the spin-coating method. Scanning electron microscope (SEM) image of the PDMS mold is shown in Figure S4 (Supporting Information), which exhibits the grating period of 600 nm. After applying a PDMS mold on the smooth film of the active layer, the grating feature can obviously be observed as shown in Figure 2a and the period of the grating is ≈600 nm. The diameter of Au NPs used here is ≈35 nm (Figure 2b), and the plasmonic resonance peak of Au NPs with a diameter of 35 nm in water is about 512 nm (Figure S5, Supporting Information).

We have experimentally measured the reflection spectra of the grating device to further confirm the enhancement region contributed by the Ag grating. Figure 2c shows the reflection spectra of the P3HT:PC₆₀BM device with or without a grating; two enhancement regions around 350–450 nm and 650–800 nm have been observed after applying the grating structure, which is consistent with the theoretical results (Figure 1c). For the NP devices, an absorption ratio is obtained by dividing the absorption of P3HT:PC₆₀BM with incorporation of Au NPs with that of P3HT:PC₆₀BM without Au NPs. As shown in Figure 2d, the incorporation of Au NPs into the P3HT:PC₆₀BM active layer only shows a narrow enhancement peak around 650 nm, while embedding Au NPs into the ZnO interlayer shows an obvious

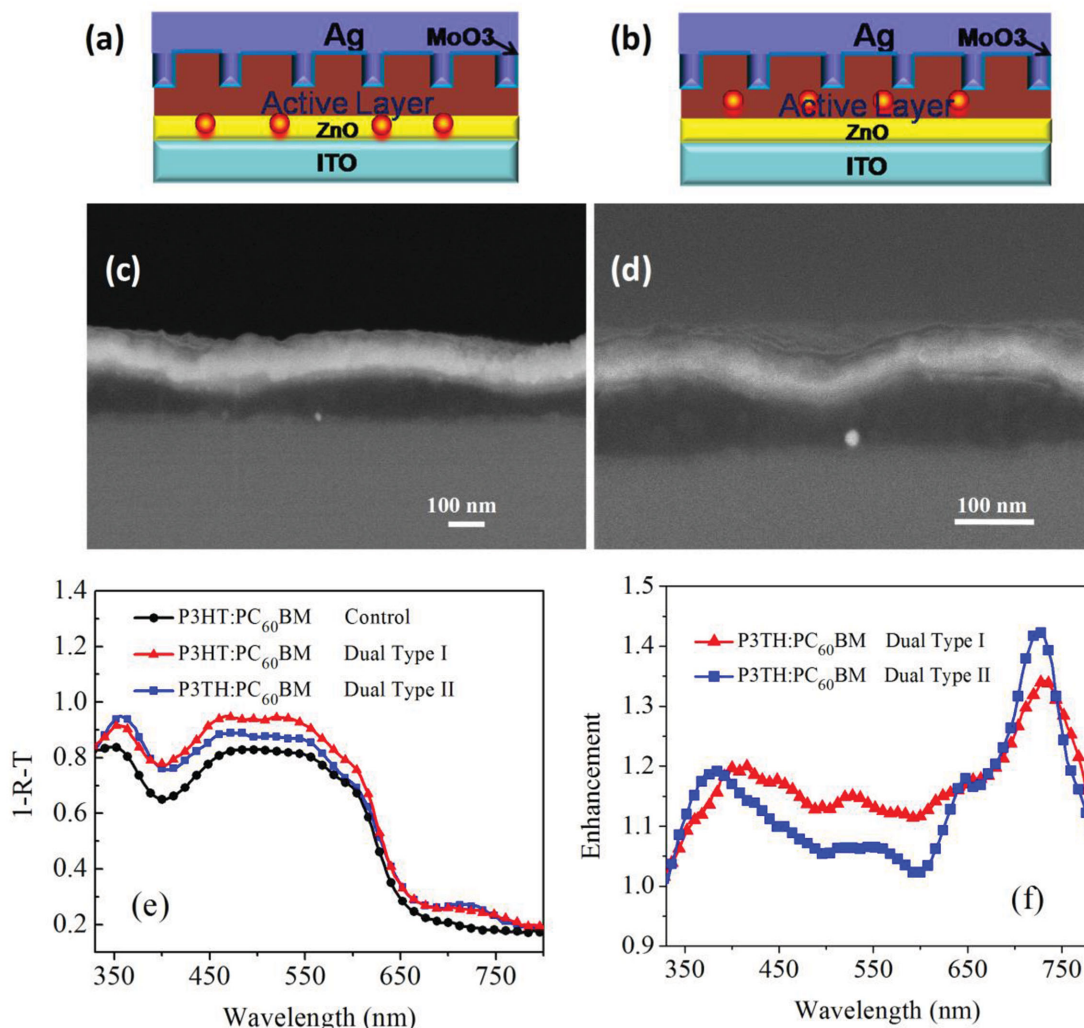


Figure 3. Schematics of dual devices: a) Dual Type I device and b) Dual Type II device. Cross-sectional SEM image of dual device: c) Dual Type I device and d) Dual Type II device. e) Experimental absorption spectra of dual plasmonic P3HT:PC₆₀BM devices and f) their corresponding enhancements.

enhancement region around 450–600 nm. The wavelength dependence of the enhanced absorption region of the Grating device, the NPs_{ActiveLayer} device, and the NPs_{Interlayer} device is in good agreement with the theoretical results. Taking LSP resonance of Au NPs in water as a reference, the shift of plasmonic peak is very small for the Au NPs incorporated into the ZnO interlayer compared to that of Au NPs introduced in the active layer. As a result, the strategy of introducing Au NPs into the ZnO interlayer effectively harvests the light around the 450–600 nm regions, which is an important complement to the enhancement region by the grating structure.

After two metal plasmonic nanostructures of Au NPs and Ag grating are studied individually, integrating both of them into a single device would be favorable to achieve a broadband plasmonic absorption enhancement. **Figure 3a,b** shows schemes of two types of dual devices: Dual Type I device and Dual Type II device, respectively. The cross-sectional SEM images of the Dual Type I and Dual Type II devices are shown in **Figure 3c,d**, respectively. When the Dual Type II device was fabricated through first blending metal NPs into P3HT:PC₆₀BM

and subsequently introducing a grating structure on the top of the composite active layer by using the PDMS nanoimprinted method, the dual device enhances absorptions mainly around 350–450 nm and 600–800 nm and cannot achieve a broadband absorption enhancement (**Figure 3e,f**). Interestingly, when the Dual Type I device is designed with simultaneously embedding Au NPs into ZnO and fabricating the nanopatterned Ag back reflector in one device, a broadband plasmon-induced absorption enhancement has been achieved (**Figure 3e,f**). For the absorption enhancement of Dual Type I device, the two plasmonic structures (Au NPs and Ag grating) emphasize particularly on optical absorption in the specific wavelength regions (**Figure 2**).

Furthermore, we also evaluate the performance of another type of active layer PTB7:PC₇₀BM, which is a low-bandgap material.^[37,54,58] **Figure 4** shows the absorption spectra of the two types of dual devices. The optical enhancements are found to be around 600–750 nm for Dual Type II device and 350–750 nm for Dual Type I device, matching well with the results of P3HT:PC₆₀BM devices. As a consequence, rationally managing

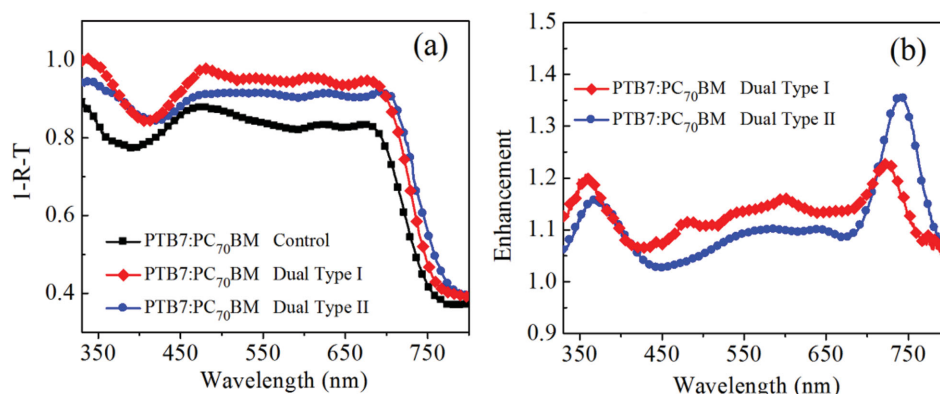


Figure 4. a) Experimental absorption spectra of dual plasmonic PTB7:PC₇₀BM OSCs and b) their corresponding enhancements.

these two plasmonic structures (e.g., (a) selecting Ag grating with 600 nm period, (b) introducing Au NPs into interlayer (not active layer), and (c) adopting ZnO as electron transport layer (not TiO₂)) into one device collectively leads to a broadband absorption enhancement.

2.3. Device Performance: PCE and Reliability of Devices

In order to demonstrate the collective effects of the Au NPs and the Ag grating on device performance, the current density–voltage (*J*–*V*) characteristics of the above six types of P3HT:PC₆₀BM devices are distinguished. It is worth noting that over 100 separate devices for each type of device are fabricated and tested to ensure the reproducibility of the result. Histograms of the cell-performance characteristics are shown in Figure S7 (Supporting Information), the average device parameters are summarized in Table 1, and *J*–*V* curves of an average-performance device are shown in Figure 5a. As seen from the histograms, the devices with a single metal nanostructure (i.e., grating device, NPs_{ActiveLayer} device, and NPs_{Interlayer} device) show a good reproducibility of the device performance (all of them with relative standard deviation in PCE below 4%). Regarding the case of a grating device, PCE of the device with a grating obviously improves from 3.07% (control device) to 3.60% (grating device). The PCE improvements are originated from the FF improvement and the *J*_{sc} improvement. The higher

fill factor is a consequence of the nanoimprinted pattern, which increases the interface area and reduces the effective distance for hole traveling to the electrodes, resulting in a better charge collection.^[31,51] Regarding the optical properties, absorption enhancement around 350–450 nm and 600–700 nm owing to the SPP mode induced by the metal electrode is the main reason for the increased *J*_{sc}, as shown in the absorption spectra in Figure 2. After embedding metal NPs into the P3HT:PC₆₀BM active layer (NPs_{ActiveLayer} device) and ZnO interlayer (NPs_{Interlayer} device), the PCEs are improved to 3.38 and 3.49, respectively, which are mainly attributed to the increased FF and *J*_{sc}. The increased FF is mainly attributed to the improved charge transport for the NPs_{ActiveLayer} device and charge extraction for the NPs_{Interlayer} device, respectively.^[25,26,38,52] *J*_{sc} increment is mainly due to the strong plasmon-enhanced scattering effect of Au NPs, which enhances the light absorption of the active layer and then increases the amount of photogenerated electron–hole pairs and hence increases the *J*_{sc} of OSCs.^[16,18,37,45,49,50,53–57]

The device performance of the dual plasmonic structures has been characterized. First, the Dual Type I device with a 3.8% relative standard deviation (RSD) in PCE shows a better reproducibility than that of the Dual Type II device with a 17.2% RSD in PCE (see Figure 6a,b). In 100 separate devices, there are only five devices with PCE below 3.07% for the Dual Type I device, while there are 27 devices with PCE below 3.07% for the Dual Type II device (PCE of control device is 3.07%). In addition, it is worth noting that the average PCE for the Dual Type

Table 1. Photovoltaic parameters of the OSCs with different plasmonic structures in different regions under AM 1.5G illumination at 100 mW cm^{−2}.

Donor	Device	<i>V</i> _{OC} [V]	<i>J</i> _{sc} [mA cm ^{−2}]	FF [%]	PCE [%]
P3HT	Control	0.66 ± 0.01	7.63 ± 0.09	61.16 ± 0.45	3.07(3.15)
	Grating	0.66 ± 0.01	8.49 ± 0.20	64.14 ± 0.66	3.60(3.75)
	NPs _{ActiveLayer}	0.66 ± 0.01	7.90 ± 0.15	64.22 ± 0.54	3.38(3.50)
	NPs _{Interlayer}	0.66 ± 0.01	8.15 ± 0.20	65.04 ± 0.66	3.49(3.65)
	Dual Type II device	0.66 ± 0.01	8.78 ± 0.35	66.30 ± 1.02	3.85(4.05)
	Dual Type I device	0.66 ± 0.01	9.10 ± 0.35	67.15 ± 1.02	4.06(4.20)
PTB7	Control	0.75 ± 0.01	16.30 ± 0.12	63.23 ± 0.25	7.65(7.81)
	Dual Type II device	0.75 ± 0.01	17.62 ± 0.43	67.34 ± 1.02	8.43(9.04)
	Dual Type I device	0.75 ± 0.01	18.11 ± 0.15	68.81 ± 1.02	9.34(9.62)

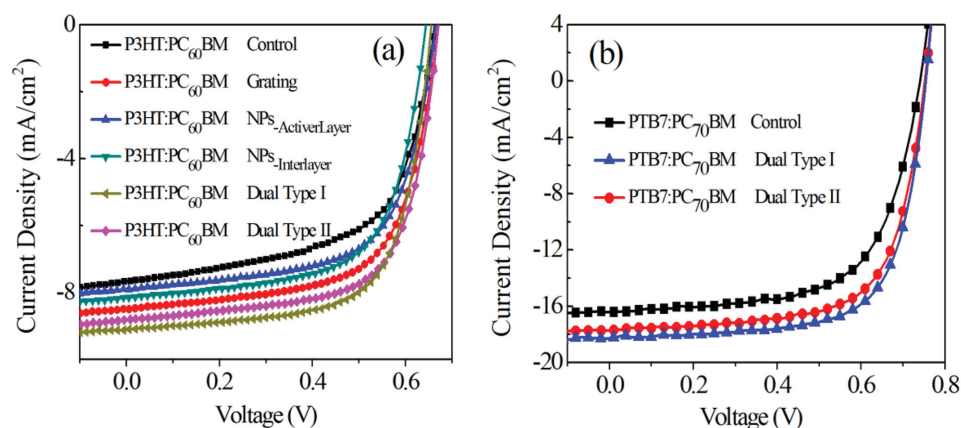


Figure 5. a) J - V characteristics of P3HT:PC₆₀BM OSCs with various metal nanostructures. b) J - V characteristics of PTB7:PC₇₀BM OSCs with various metal nanostructures.

I device is 4.06%, while the average PCE for the Dual Type II device is only 3.62%. The reason for the different reliabilities of these two type dual devices might be attributed to the fabrication process. In the fabrication of the Dual Type II device, the Au NPs should be first introduced into an active layer and subsequently grating structures are fabricated on the composite of the active layer and metal NPs by using the PDMS nanoimprinted method. During the fabrication process in the nanoimprinted method, the composite will encounter some

degree of damage after the PDMS mold applied and the device performance will be deteriorated. To visualize this hypothesis, a cross-sectional SEM image of a Dual Type II device with a bad device performance (PCE = 1.52%) is shown in Figure S8 (Supporting Information), which clearly shows an aggregation of Au NPs embedded in the bottom of the active layer and the grating feature is seriously damaged.

In addition, the device performance of the dual devices based on PTB7:PC₇₀BM is also shown in Figure 5b and is summarized

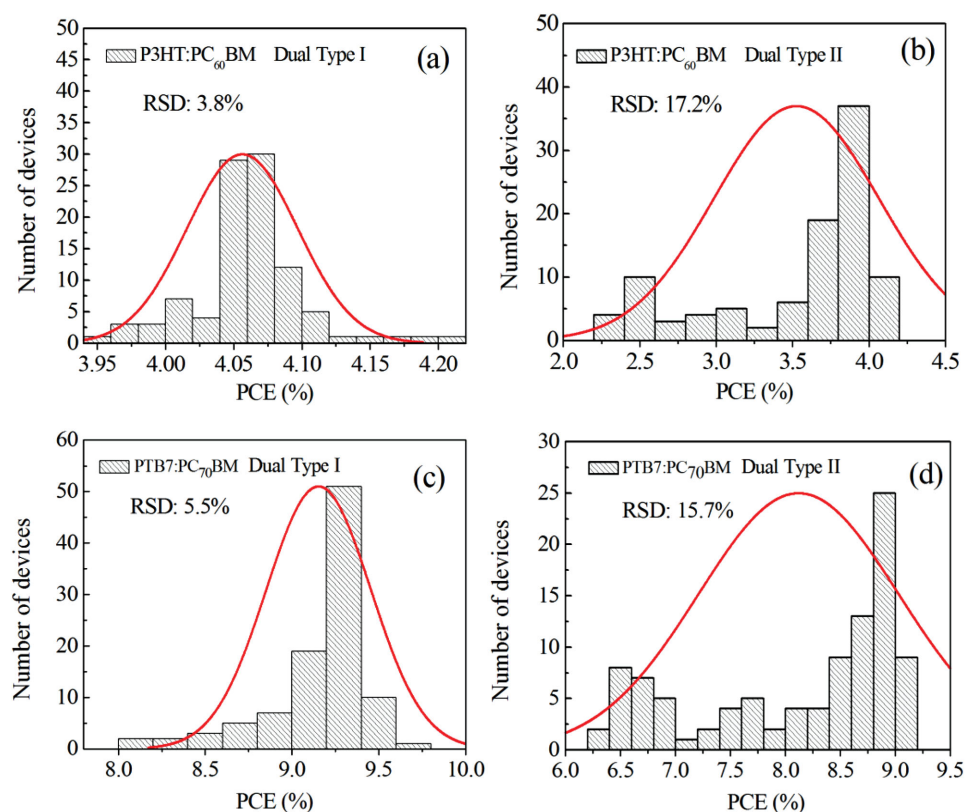


Figure 6. Histograms of PCE measured for two dual plasmonic OSCs. a) Dual Type I device for 100 separate P3HT:PC₆₀BM OSCs. b) Dual Type II device for 100 separate P3HT:PC₆₀BM OSCs. c) Dual Type I device for 100 separate PTB7:PC₇₀BM OSCs. d) Dual Type II device for 100 separate PTB7:PC₇₀BM OSCs.

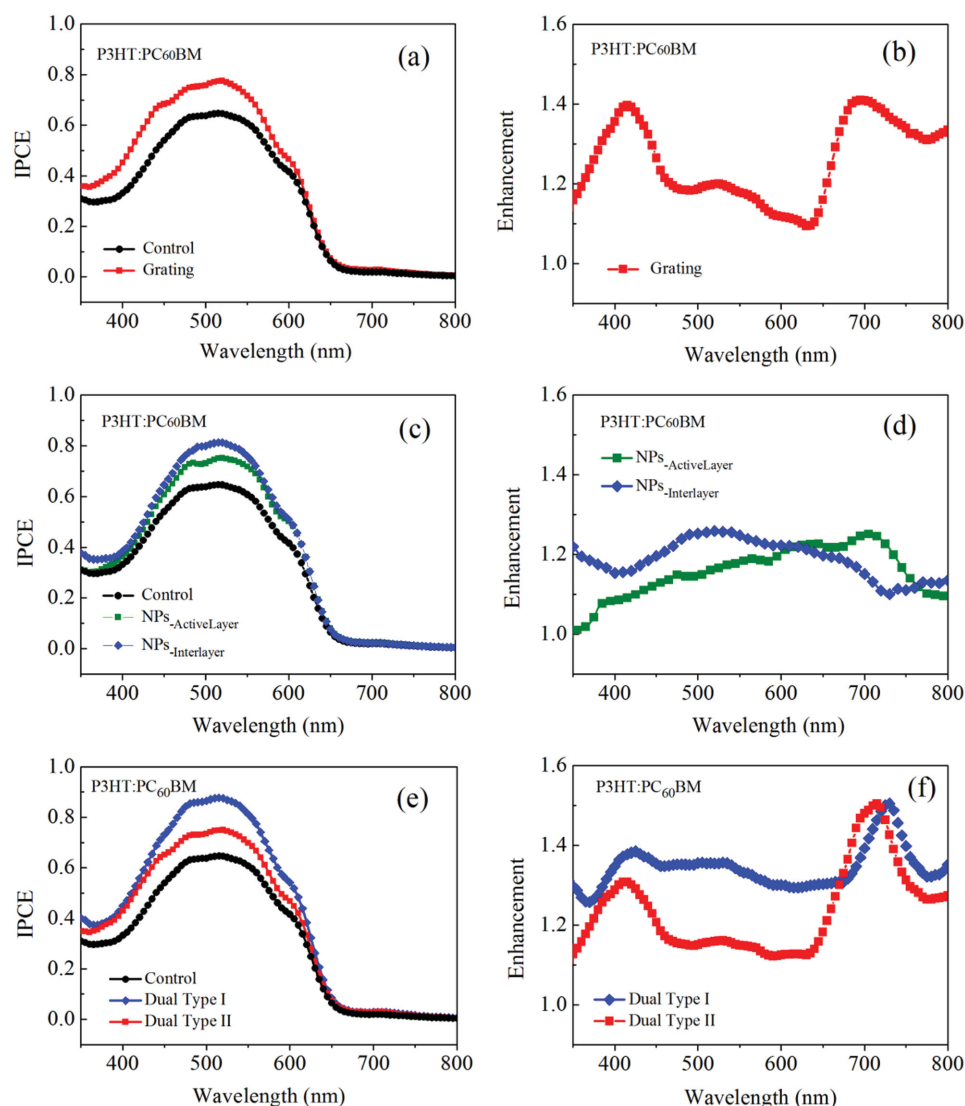


Figure 7. Experimental IPCE of different P3HT:PC₆₀BM devices and their corresponding enhancement. a,b) Grating device. c,d) NPs devices. e,f) Dual devices.

in Table 1. The PCE of control device is 7.7%. The Dual Type I device shows a much better reliability and reproducibility (a 5.5% RSD in PCE) than that of the Dual Type II device (a 15.7% RSD in PCE) (Figure 6c,d). There are only nine devices with PCE below 7.7% for the Dual Type I device, while there are 31 devices showing PCE below 7.7% for the Dual Type II device. The average PCE for the Dual Type I device is substantially improved from 7.7% to 9.34% (average) (21.2% enhancement) and 9.62% (maximum) when counting all of the 100 devices. In contrast, the average PCE for the Dual Type II device is enhanced to 8.4% (10% enhancement). Notably, this PCE is among the highest values reported to date for a plasmonic single-junction OSC device using metal NPs or a metal grating. Table S1 (Supporting Information) further highlights the advantages of using dual plasmonic nanostructures with a broadband plasmon-induced absorption enhancement. Especially, both the reproducibility of the device fabrication

procedure and the excellent PCEs are highly encouraging in future applications.

2.4. Device IPCE

To further demonstrate the cooperative effects from SPPs of metal grating and plasmon-enhanced scattering of metal NPs on the device performance, especially J_{sc} , we then measured the incident photon-to-current efficiency (IPCE) spectra for the P3HT:PC₆₀BM devices (see Figure 7) and the PTB7:PC₇₀BM devices (see Figure 8), respectively. As shown in Figure 7, three P3HT:PC₆₀BM devices with individual metal nanostructures (grating device, NPs_{ActiveLayer} device, and NPs_{Interlayer} device) exhibit clear improvement in the IPCE spectra, particularly around 350–500 nm and 600–800 nm for the grating device, 600–750 nm for the NPs_{ActiveLayer} device, and 500–600 nm for

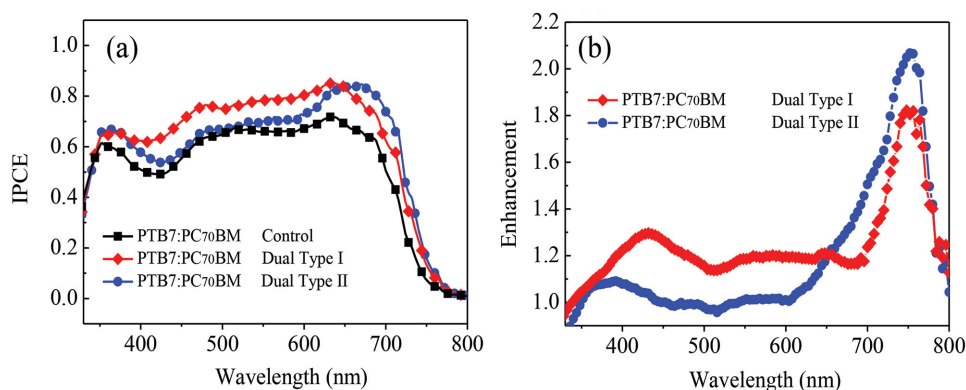


Figure 8. a) Experimental IPCE of different PTB7:PC₇₀BM devices and b) their corresponding enhancements.

the NPs_{Interlayer} device, respectively. By comparing the IPCE spectra of the two types of dual plasmonic devices (Figure 7e,f), not only does the Dual Type I device show a higher IPCE than that of the Dual Type II device, but more importantly, the IPCE enhancement of the Dual Type I device can cover a broadband wavelength of 350–800 nm. In addition, the IPCE spectra from the PTB7:PC₇₀BM devices also clarify that the Dual Type I device shows a broader IPCE enhancement from 350 to 800 nm than that of the Dual Type II device (see Figure 8), matching well with the results of the P3HT:PC₆₀BM device (see Figure 7). By comparing the absorption in Figure 3 with the IPCE spectra in Figure 7 for the P3HT:PC₆₀BM device to the absorption in Figure 4 with the IPCE spectra in Figure 8 for the PTB7:PC₇₀BM device, the trend of the IPCE enhancement is coincident with the absorption enhancement. Comparison of absorption enhancement, the large IPCE enhancement is mainly due to the electrical effect including better charge extraction (NPs incorporated ZnO) and charge collection (grating electrode).

3. Conclusion

In conclusion, we have developed a novel dual plasmonic structure, called Dual Type I device, by simultaneously incorporating Au NPs into the ZnO interlayer and fabricating the nanopatterned Ag back electrode with the 600 nm period using the nanoimprinted method. By strategically leveraging two types of metal nanostructures experimentally and theoretically, a broadband plasmon-induced absorption enhancement ranging from 350 to 800 nm wavelengths has been achieved. As a result, significant enhancement of OSC performance is improved from 7.7% PCE up to the maximum 9.62% PCE and an average 9.34% PCE, which is one of the highest plasmonic OSC PCEs reported thus far for single junction OSCs. Importantly, compared with the dual device composed of Ag NPs embedded into the active layer and Ag grating electrodes as a back reflector, called Dual Type II device, the as-proposed Dual Type I device shows an excellent reliability and reproducibility, which is more applicable for the practical application.

4. Experimental Section

Device Fabrication: The concentration of the P3HT/PC₆₀BM (27 mg mL⁻¹, 1:0.8, weight ratio) blend solution was used to form active layer by spin-coating. The chlorobenzene was used as a solvent. The concentration of the PTB7/PC₇₀BM (25 mg mL⁻¹, 1:1.5, weight ratio) blend solution was used to form active layer by spin-coating. The chlorobenzene was used as a solvent and 3% (v/v) DIO (1,8-diiodooctane) was used as an additive to improve photovoltaic performance.

Devices were fabricated with the structure of ITO/ZnO (40 nm) with or without Au NPs/active layer with or without Au NPs/MoO₃ (10 nm)/Ag (with or without grating) (80 nm). ITO glasses were cleaned based on a standard procedure. A thin layer (40 nm) of ZnO was prepared on the ITO by spin-coating.^[32] These samples were then dried at 150 °C for 30 min. Subsequently, the polymer solution was spin-coated at 900 rpm for 60 s on the top of the ZnO layer for both of the two types of devices. The optimized active layer thickness is about 100 nm for P3HT:PC₆₀BM and PTB7:PC₇₀BM devices. The PDMS nanoimprinted method was applied to form grating features on the active layer. After the removal of the PDMS mold, MoO₃ (10 nm) and silver (100 nm) layers were thermally evaporated onto the active layer with a pattern at a pressure of 10⁻⁶ Torr. The synthesis of Au NPs with 35 nm size followed the sodium citrate reduction method.^[30,59] The optimized concentration of Au NPs is about 1.5%, 1.2 wt% weight ratio of the active layer for the Dual Type I device and Dual Type II device, respectively.

Characterization of Solar Cells and Thin Films: The thickness of the polymer sample was measured using a Dektak alpha-step profiler. The morphology of the sample was characterized using SEM (Sirion 200) and TEM (Hitachi 800). The diffused reflection and transmission spectra were measured by using a goniometer integrated with CCD spectrometer and integrating sphere. J–V characteristics were performed using a Keithley 4200 under 1.5 illumination condition at an intensity of 100 mW cm⁻². An NREL certified silicon photodiode with a KG5 filter was used for calibration. Device IPCE was measured in air by comparison to a known AM1.5 reference spectrum for a calibrated silicon photodiode.

Theoretical Modeling: To rigorously solve Maxwell's equations, the finite-difference time-domain (FDTD) method with discretization of Yee lattice was adopted to model the dual plasmonic system. The perfectly matched layer-absorbing boundary conditions were imposed at the top and bottom of the device structure. Together with the Floquet theorem, the periodic boundary conditions were implemented at the transverse sides (front, back, left, and right sides) of OSC devices.^[40,50,60–63] The optical properties of LSP mode and SPP mode together with the hybridization of quasi-guided and plasmonic modes were fully taken into account in this model. For a metallic grating structure with periodicity P , the momentum matching condition was

$$k_x = k_0 \sin \theta + \frac{2\pi}{P} n = k_0 \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}} = k_{\text{spp}} \quad (1)$$

where ϵ_d , ϵ_m are permittivities of dielectric and metal, respectively, k_{spp} is the dispersion relation of SPP wave propagating in the semi metal-dielectric interface. The modification of SPP resonance by grating period and surrounding material can be well understood by the momentum matching condition and the relevant results are shown in Figure 1a,b.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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