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**Plasmonic Backscattering Effect in High Efficient Organic Photovoltaic Devices**

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**Abstract**

A universal strategy for efficient light trapping through the incorporation of gold nanorods on the electron transport layer (rear) of organic photovoltaic devices is demonstrated. Utilizing the photons that are transmitted through the active layer of a bulk heterojunction photovoltaic device and would otherwise be lost, a significant enhancement in power conversion efficiency (PCE) of PCDTBT:PC71BM and PTB7:PC71BM by ~13% and ~8% respectively. PCEs over 8 % were reported for devices based on the PTB7:PC71BM blend. A comprehensive optical and electrical characterization of our devices to clarify the influence of gold nanorods on exciton generation, dissociation, charge recombination and transport inside the thin film devices is performed. By correlating the experimental data with detailed numerical simulations, we are able to separate the near-field and far-field scattering effects of the Au NRs, and confidently attribute part of the performance enhancement to the enhanced absorption caused by backscattering. While, a secondary contribution from the Au NRs that partially protrude inside the active layer and exhibit strong near-fields due to localized surface plasmon resonance effects is also observed but is minor in magnitude. Furthermore, another important contribution to the enhanced performance is electrical in nature and comes from the increased charge collection probability.

1. **Introduction**

Conventional silicon solar cells can achieve high power conversion efficiencies (PCEs) but are typically fabricated through complicated and cost ineffective processes which hold back the establishment of photovoltaics as the main energy production source. The rapid development of a low cost, large scale and lightweight solar energy conversion technology is thus highly desired. Bulk heterojunction (BHJ) organic photovoltaics (OPVs) fulfill the above requirements and are already showing PCEs exceeding 10% and 11% for single junction[[[1]](#endnote-1)] and multijunction[[[2]](#endnote-2)] devices respectively. Taking also into account that they have presented satisfactory operation lifetimes,[[[3]](#endnote-3)] they can be considered as one of the most promising candidates to replace their counterparts, especially in portable electronics and building integrating applications.

After development of theoretical simulations that predict the optimal characteristics for donor and acceptor materials[[[4]](#endnote-4)] a significant research effort has been focused on the synthesis of conjugated polymers with tailored energy levels[[[5]](#endnote-5)] and on the optimization of the BHJ morphology.[[[6]](#endnote-6)] The maximum theoretical efficiency for a single junction OPV can be derived as a function of the band gap of polymer donor, when electrons lose 1 eV during electron transfer to the fullerene[4a].With this assumption a maximum PCE of ∼15% is calculated with a mid band gap like PTB7 and an offset LUMODonor -LUMOAcceptor of 1.75 eV. Therefore, it is obvious that several limitations are holding the PCE below 11%[1].The most prominent limitation is the fundamental trade-off between light absorption length and exciton diffusion length, which hinders the further increase of exciton generation by an increase in the active layer thickness.[[[7]](#endnote-7)] The dissociated charge carriers have to travel a longer distance in order to reach the respective electrodes, while at the same time the built-in electric field across the BHJ due to the donor-acceptor energy offsets decreases. Therefore, the time of the charge collection from the electrodes is increased, leading to an increase in the recombination probability [[[8]](#endnote-8)]. Owing to this, the optimized active layer thickness of high performance OPVs is around 100 nm, despite the low absorption.

An appealing approach to unblock this bottleneck is the introduction of an efficient light concentration and coupling mechanism to enhance the photon absorption in the thin active layer. In this context various approaches, including tandem structures,[[[9]](#endnote-9)] ternary blends,[[[10]](#endnote-10)] surface texturing,[[[11]](#endnote-11)] metal nanogratings,[[[12]](#endnote-12)] photonic crystals,[[[13]](#endnote-13)] resonance cavity,[[[14]](#endnote-14)] ray-optical light trapping systems[[[15]](#endnote-15)]and plasmonic metal nanoparticles[[[16]](#endnote-16)] have been suggested.

Among these approaches, there has been growing interest in the utilization of metal nanoparticles (NPs) in OPVs[[[17]](#endnote-17)] to boost their absorption. Metal NPs confine resonant photons by an induced coherent surface plasmonic oscillation of their conduction band electrons,[[[18]](#endnote-18)] the so-called localized surface plasmon resonance (LSPR), at which a significant enhancement of light absorption and scattering takes place.[[[19]](#endnote-19)] In addition, the facile tunability of their optical properties by modifying the size,[[[20]](#endnote-20)] shape[[[21]](#endnote-21)] and surrounding materials[[[22]](#endnote-22)] of NPs has shown high potential as an optical engineering tool in thin-film optoelectronic devices. In particular, plasmonic NPs have been recently incorporated either between interfaces,[[[23]](#endnote-23)] inside the front contact buffer layers[[[24]](#endnote-24)] or in the active layers[[[25]](#endnote-25)] and combinations of them of OPV devices in order to promote light absorption and thus enhance the exciton yield. To our knowledge, however, there are no reports in the literature on the use of metal NPs acting as back contact light-concentrators and scatterers in OPV devices.

A significant part of the incident photons are transmitted through the active layer and remain unexploited due to the required low active layer thickness. A theoretical study suggest, that NPs located at the rear part of photovoltaic devices can provide light trapping via scattering while at the same time avoid the optical losses of light back-scattering in a front-type plasmonic devices. [[[26]](#endnote-26)] Furthermore, by placing NPs on the rear, potential absorption losses in the metal are suppressed, as shorter wavelength light is first absorbed in the active layer. Finally, the suppression of absorption due to interference effects can be avoided by using the NPs to tune the standing-wave resonance position over the entire active region. However, there are no reports investigating this geometry in OPVs, except for only in the case of placing an optical spacer on the metal cathode in order to act as a back reflector providing a fair light trapping architecture.[[[27]](#endnote-27)]

In this work, we demonstrate a significant increase on the PCE of OPV devices incorporating high aspect ratio Au nanorods (NRs) inside the titanium suboxide (TiOx) electron transport layer (ETL), and establish a universal light trapping strategy. This mechanism was applied in high efficiency BHJ blends of (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]]:Phenyl - C71-butyric acid methyl ester (PTB7:PC71BM) and Poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)]:Phenyl-C71-butyric acid methyl ester (PCDTBT:PC71BM)) with the champion plasmonic device achieving an efficiency of 8.25%, enhanced by 8.3% compared to the pristine one. Au NRs were used because NRs in general demonstrate superior wide-spectrum scattering efficiency compared to other metallic nanostructures[[[28]](#endnote-28)] and are produced through a complete controllable and facile process.[[[29]](#endnote-29)] A detailed study of processing, characterization, microscopy, and device fabrication, together with detailed optical simulations, is conducted to understand the underlying mechanism for the enhanced device performance. This work provides a simple and generally applicable approach to enhance light harnessing of various low bandgap high efficiency OPVs, which can be easily extended in tandem OPV devices, organic light emitting diodes and many other organic and hybrid optoelectronic devices, establishing a universal photon management technique.

1. **Results and Discussion**

**2.1 Characterization of the Au NRs**

The as-prepared Au NRs, fabricated via a previously described method (**Figure 1**a)36, exhibited relatively uniform diameters (width and length). Figure 1b shows the transmission electron microscopy (TEM) image of the synthesized Au NRs. It is clear that on average the NRs were 30 nm in length and 10 nm in width as also shown in the histograms in Figure S1a,b. The extinction spectrum of the colloidal Au NRs in aqueous solution is shown in Figure 1c with two distinct peaks, at ~510 nm and ~650nm, which correspond to the theoretically predicted enhanced extinction due to transverse and longitudinal surface plasmon resonance.

**Figure 1**

**2.2 Optical and Electrical Characterization of the OPV devices**

Figure S2a,b shows UV-Vis absorption spectra of pristine and Au NRs doped PCDTBT:PC71BM and PTB7:PC71BM based devices. To avoid repetitions within the rest manuscript, the experimental and theoretical analysis was conducted in optimum concentration Au NRs (1.5%) doped devices in comparison with the pristine devices. The addition of Au NRs inside the back contact ETL, results into a broad enhancement of the active layer absorption that we attribute to light scattering by the Au NRs. That is, the Au NRs act as an effective “optical scatterer” for solar light: light scattered at larger angles will have a longer optical path through the active region, and also multiple reflections will cause the light to pass through the BHJ film many times, increasing its contribution to exciton generation. On the other hand, the near-field LSPR effect is not clearly observed because the NRs are mainly located inside the ETL and outside the active layer, whereas near-field effects can only be observed if the metal NPs are embedded inside the photoactive layer.[[[30]](#endnote-30)] Moreover, the AuNRs doped PTB7- PC71BM and PCDTBT: PC71BM OPV devices, exhibit different light absorption enhancement regions. The absorption of the PCDTB: PC71BM device is mainly enhanced below 600 nm, while the absorption of the PTB7- PC71BMis mostly enhanced from 600 to 700 nm. This observed disparity is due to the different absorption coefficients of the phototoactive layers. The PCDTBT:PC71BM photoactive layer has a lower absorption coefficient than the PTB7: PC71BM, which in effect allows more photons to reach the ETL, and scattered by the Au NRs. On the contrary, the PTB7:PC71BM layer has a higher absorption coefficient than PCDTBT:PC71BM, resulting in less photons to reach the ETL and be scattered. Hence, the scattering effect is not as strong as in the PCDTBT:PC71BM case, allowing the LSPR effect to be detected in the absorption spectra.

A series of BHJ photovoltaic devices were fabricated with structure of ITO/PEDOT:PSS(30 nm)/PCDTBT or PTB7:PC71BM/TiOx/Al(100 nm) by using Au NRs as back contact scatterers. Specifically, different volume ratios of Au NRs (0, 1, 1.5 and 2% (v/v)) were incorporated in the TiOx ETL. The device structure is schematically shown in **Figure 2**a, while Figure 2b displays the respective current density-voltage (J-V) characteristics for PCDTBT and PTB7-based devices with and without Au NRs, under illumination with 100 mW cm-2 power intensity. The respective averaged photovoltaic characteristics are summarized in **Table 1**. It is shown that the incorporation of Au NRs inside the TiOx  on top of the active layer induces an enhancement of ~11% and ~6% to the short-circuit current (Jsc) for PCDTBT and PTB7 respectively, and an enhancement of ~2% to the fill factor (FF) for both blends, whereas the open-circuit voltage (Voc) remains constant. As a result, an increase of ~13% and of ~8% for PCDTBT and PTB7 respectively is observed in efficiency after the incorporation of Au NRs. The Au NRs-doped device exhibits a power conversion efficiency (PCE) of 8.25% for PTB7 based devices (Voc=0.76 V, short-circuit current: Jsc=17.46 mA cm-2, fill factor: FF=0.62). The lower enhancement in the case of PTB7 compared to PCDTBT based devices is attributed to the fact that PTB7:PC71BM photoactive blend has higher extinction coefficient compared to PCDTBT:PC71BM,[[[31]](#endnote-31)] and as a result absorbs more incident photons allowing less light to transmit and reach the Au NRs. As noted before, this significant performance enhancement can be attributed to the high scattering efficiency of the Au NRs, which traps the transmitted photons inside the photoactive layer and increases their absorption probability.

**Figure 2 and Table 1**

In order to get an insight for the responsible mechanism of the enhanced device performance, the incident photon-to-electron conversion efficiency (IPCE) curves (**Figure 3**a,b) of the plasmonic device was measured and compared with the pristine one. The pristine device exhibits a maximum IPCE of ~69% and ~75%, while the Au NRs doped devices exhibit an enhanced maximum of ~75% and ~81% for PCDTBT and PTB7 respectively. As shown in DIPCE spectra (insets of Figure 3a,b respectively), the IPCE enhancement is broad and almost uniform ranging from 350 to 600 nm, showing also a distinct peak at ~650 nm which can be directly attributed to the transverse surface plasmon resonance of Au NRs, as evident by the calculations of Figure S8 (optical simulations section). Thus, we can postulate that the NRs protrude inside the active layer, allowing the utilization of surface plasmon resonance effects for enhanced absorption resulted from the local electric field at the vicinity of NRs. The overall increase in IPCE upon the introduction of Au NRs is significant, complying well with the enhanced Jsc observed, and is mainly attributed to scattering effects as the enhancement in the IPCE spectrum is broad and uniform. Therefore, we can claim a dual plasmonic effect: the enhancement caused by Au NRs is a contribution of scattering effects of the NRs inside the ETL and the near-field LSPR of the NRs that penetrate inside the photoactive layer. However, it can be confirmed from integrating the DIPCE spectra of both blends that the IPCE enhancement is mainly caused by scattering effects and that a minor contribution is due to LSPR (~0.7% enhancement). It should also be noted that the integrated Jsc values from the IPCE spectrum as presented in Table 1 for the pristine and the Au NRs based devices are 10.61 and 11.69 mA cm-2 respectively for PCDTBT:PC71BM, while in the PTB7 case are 15.75 and 16.71 mA cm-2. The IPCE calculated values are less than 3% different than the actual measured Jsc values, indicating good accuracy of the OPV measurement. The schematic figure of Au NRs ETL doping explaining the light trapping mechanism and optical reflection by the scattering and excitation of localized surface plasmons resonance is shown in Figure 3c. The cross-section image of the Au NRs doped PTB7:PC71BM device (Fig.S3) was obtained by using scanning electron microscopy images (SEM). It is clear that NRs are well dispersed inside the ETL, while a fraction of them protrude towards the photoactive layer.

**Figure 3**

In order to confirm that the Jsc increase is due to improved light harvesting in the active layer, the total (specular plus diffuse) reflectance of the devices was recorded. Figure S4a,b show the reflectivity spectra of the devices fabricated with and without Au NRs on top of both photoactive blends. The spectrum-wide lower reflectivity of the NR-embedded devices clearly indicates stronger absorption of the incident light due to scattering.

To further support and quantify the proposed mechanisms responsible for the enhanced performance, the photocurrent densities (Jph) of devices with and without Au NRs were measured and plotted (**Figure 4**a,b) versus the effective voltage (Veff), from which the maximum exciton generation rate (Gmax) and charge collection probabilities P(E,T) are calculated. Jph is determined as Jph=JL-JD, where JL and JD are the current densities under illumination and in the dark respectively [24a]. Veff is determined as Veff=V0-Va, where V0 is the voltage at the point of Jph=0 and Va is the applied bias voltage. If we assume that the saturated Jsc,, Jsat, is defined by the total amount of the absorbed photons and all the photogenerated excitons are dissociated into free charge carriers, then Gmax could be calculated by the formula Jsat = qGmaxL, where q is the electron charge and L is the thickness of the active layer. The values of Gmax as calculated from the Figure 4a, are 8.44x1027 s-1m-3 (Jsat = 10.8 mA cm-2) for the pristine and 9.69x1027 s-1m-3 (Jsat = 12.4 mA cm-2) for the Au NRs doped device in the case of PCDTBT:PC71BM and from the Figure 4b, are 1.05x1028 s-1m-3 (17.0 mA cm-2) for the pristine and 1.13x1028 s-1m-3 (18.0 mA cm-2) in the case of PTB7:PC71BM photoactive blend. An impressive enhancement of Gmax occurred after incorporation of Au NRs. Since Gmax is related to maximum absorption of incident photons[[[32]](#endnote-32),[[33]](#endnote-33)], the enhanced Gmax suggests increased light absorption in device with NRs, in good agreement with the increased absorption from UV-vis absorption spectra. The P(E,T) could be obtained from the ratio of Jph/Jsat.[[[34]](#endnote-34)] P(E,T) values under Jsc condition increased from 88% in control device to 93% in device with Au NRs for the PCDTBT based devices and from 91% in control device to 94% in the device with Au NRs for the PTB7 based devices. This indicates that the excitation of LSPR also benefits the dissociation of excitons into free charge carriers,[25] a result that further supports the IPCE measurements. Taking into account the also higher FF of the doped devices, we can conclude that a synergy of optical and electrical effects take place in our devices, leading to the combined effects of enhanced exciton generation, enhanced exciton dissociation and enhanced charge transport.

**Figure 4**

The photoluminescence (PL) spectra of the BHJ devices with and without Au NRs are presented in Figure S5a,b in order to further validate the calculated enhanced exciton generation. The incorporation of the Au NRs, leads to broader PL spectra and an increase of the PL intensity by 15% for PCDTBT and by ~13% for the PTB7 based blends. The broadening and enhancement of the PL intensity can be attributed to the fact that the LSPR excitation of the protruded NRs and the light scattering of the NRs inside the TiOx increases the degree of light collection, thereby, leading to enhanced light excitation rate.[[[35]](#endnote-35)] Moreover, the enhanced PL intensity can arise from the strong coupling between the excitonic state of the polymer and the plasmonic field of the NRs, which is due to the oscillation of the surface plasmon dipole plasmonic field and excitons.[[[36]](#endnote-36)] Thus it can be concluded that the incorporation of Au NRs significantly increases the exciton generation.

Finally, we measured the values of Jsc of the produced OPV devices at various illumination intensities to examine how the plasmonic effects influenced the charge transport process. Figure S6a,b display the dependence of the incident light intensity (Ilight) on the photocurrent. In general, the value of Jsc of an OPV device follows a power-law dependence with respect to Ilight (i.e., Jsc~Ilightn).[[[37]](#endnote-37)] From Figure S6a, the exponential factors (n) for the reference and plasmonic devices were calculated to be 0.987 and 0.983, respectively. The nearly linear dependence of Jsc on the incident light intensity suggests the absence of bimolecular recombination and space-limited charges in either of these devices.[44] A similar trend was observed when using PTB7:PC71BM as photoactive layer (Figure S6b). Therefore, we suspect that the incorporation of Au NRs into the ETL had a negligible influence on the nature of the charge transport process in the device. However, the resulting plasmonic effects led to unique optical properties that improved the OPV devices performance.

**2.3 Optical Simulations and Modeling**

We now turn to optical simulations of plasmonic light trapping in such devices. Our main objective is to understand the two effects of near-field focusing and far-field scattering and quantify their effect on enhanced absorption. We use the finite-difference time-domain (FDTD)[[[38]](#endnote-38),[[39]](#endnote-39),[[40]](#endnote-40)] method and consider for simplicity the PCDTBT:PC71BM active layer, assuming the set of materials and device vertical architecture used in the experiments. For the Au NRs we assumed cylinders of 30 nm in length and 10 nm in width, dispersed inside the 10 nm TiOx ETL at a volume ratio of 1.5%. To separately probe the longitudinal and transverse plasmon effects, the Au NRs were placed either parallel (probing the longitudinal LSPR) or perpendicular (probing the transverse LSPR) to the electric field of a linearly polarized incident light. Also, the NRs were located in three different positions inside the device: (a) inside the TiOx ETL, (b) at the TiOx/BHJ interface, and (c) inside the active layer (just above the TiOx/BHJ interface). Finally, to clearly separate the synergetic effects of LSPR near-field focusing and far-field scattering onto the enhanced optical absorption, we performed simulations on both short-period periodic Au NR arrays (i.e. below the diffraction limit) that inhibit far-field scattering as well as on large disordered Au NR arrays for which far-field scattering is allowed.

The effect of plasmonic near fields in the absorption enhancement is best captured with full 3D FDTD calculations assuming small-period periodic NR arrays. Due to the small periodicity, the system is below the diffraction limit (i.e. *L*<*λ*0/*n*, where *L*=124 nm is our simulated system periodicity, *λ*0 the vacuum wavelength and *n* the refractive index) and thus far-field scattering is inhibited and only the near-field effects are probed. The total ideal current (i.e. assuming carrier recombination is zero) for the cases without Au NRs (pristine) and with Au NRs in different positions and different orientations inside the device was calculated. Results are shown in **Figure 5**, where absorption maps *vs* wavelength and position in the active are plotted, which provide explicit information of where absorption is happening. For both NR orientations relative to the incident electric field, when the NRs were embedded inside the TiOx layer (Figure 5a,d) we find no significant change compared to the pristine case. This is expected, since the field enhancement is localized in the vicinity of the NRs and thus does not really affect the absorption in the BHJ. In contrast, when the Au NRs are embedded inside the BHJ (Figure 5b,e), we obtain a small enhancement in absorption and generated current. This enhancement is localized near the BHJ/TiOx interface, i.e. at <10 nm distances in Figure 5b,e, clearly pointing to a near-field effect. In Figure 5c,f we plot the current generated at each position in the BHJ, where the effect of the Au NRs in the active are clearly shown close to the BHJ/TiOx interface. Interestingly, both NR orientations yield similar enhancements of the order of 1%, with the transverse orientation (Figure 5f) yielding a slightly higher enhancement than the longitudinal one. This is because the longitudinal LSPR is shifted to even higher wavelengths (>800 nm, see Figure S8) compared to that when the NRs are inside an aqueous solution (~650 nm), in which region the BHJ does not absorb light and so the effect of the enhanced near fields is minimized. The transverse LSPR on the other hand is observed in the wavelength region above 600nm, also shifted compared to that in the aqueous solution (~510 nm), but still in the region where the BHJ absorbs light.

**Figure 5**

The next set of calculations was performed to investigate the scattering effect of disordered in the Au NR arrays. Unlike the short-period periodic NR arrangements, the disordered NR arrangements are above the diffraction limit and able to produce off-normal scattering, i.e. they only have both near-field and far-field scattering effects. Off-normal scattering has two effects: (i) increases the optical path inside the active layer and (ii) light can get trapped in the cell by total internal reflection at the glass/air interface. For this purpose, 2D calculations were deemed more suitable given that a large super-cell 3D system is computationally too expensive. We assume a *L*=2 μm cell system with 8 randomly positioned Au NRs, with a statistical sampling of 10 random distributions performed in each case. Similarly to the periodic calculations, the Au NRs was introduced inside the TiOx layer, at the BHJ/TiOx interface and inside the BHJ. Both NR orientations relatively to the incident field were considered, as well as a mixture of them. The average current resulted in each case is plotted in **Figure 6**. For direct comparison in this geometry, periodic Au NR arrangements in these 2D cells were also considered and plotted in Figure 6. We obtain a clear 4-5% enhancement in all disordered cases relatively to the periodic cases, irrespectively of where the NRs are positioned in the device (in TiOx or in BHJ). Needless to stress that this is just a lower limit for scattering: as the super-cell size is increased beyond 2μm, more scattering should be produced, as more diffraction orders become active. Also, all our NRs were assumed to be parallel to the TiOx/BHJ interface. Relaxing this, should add even more to the scattering.

**Figure 6**

To demonstrate the effect on light absorption, we plot in Figure S7 the spectral absorption inside the BHJ (absorption in the Au NRs and rest of materials in the device have been subtracted) for three cases: (a) pristine (no Au NRs), (b) periodic arrangement of Au NRs (average of all 3D calculations), and (c) disordered Au NRs (average of all 2D disordered calculations). A clear wide-spectrum absorption enhancement coming from far-field scattering, very similar to the experimental one is obtained, while the near-field contribution is marginal. Difference between simulation and experiment is attributed to possible small discrepancies between the actual BHJ refractive index in the devices and the one used in the simulations. Our calculations thus clearly point to far-field scattering as being the dominant mechanism for the absorption enhancement in the devices incorporating Au NRs.

**3. Conclusions**

OPV devices with significantly enhanced PCEs (exceeding 8%) have been demonstrated by doping the rear TiOx ETL with Au NRs to enhance light trapping within the BHJ layer. The enhanced light trapping is systematically investigated through detailed processing, characterization, microscopy, and device optimization, as well as detailed numerical simulations. We attributed the recorded PCE enhancement to light trapping by the highly efficient Au NR scattering and secondarily to the near-field LSPR effects by Au NRs partially protruding inside the active layer. An electrical contribution to increased exciton dissociation and charge transport was also evident. The successful demonstration of this novel device architecture provides a very useful design guideline for achieving efficient light harnessing in thin film OPVs and organic/hybrid optoelectronic devices in general.

**4. Experimental Section**

*Chemical Synthesis of Au NRs*:Gold nanorods were prepared by an optimized one step seed mediated growth method. Briefly, a seed solution was prepared by mixing aqueous solutions of hexadecyltrimethylammonium bromide (CTAB, 2 M, 1 mL) and sodium tetrachloroaurate (III) dehydrate (5 mM, 1 ml) at 40°C. Then, an ice-cold solution of sodium borohydride (0.01 M, 0.5 mL) was added drop-wise to the solution under rapid stirring, resulting in a colour change from dark yellow through to colourless and finally light brown. After the addition, the solution was stirred for an additional two minutes and used immediately after.

A growth solution containing aqueous solutions of CTAB (0.2 M, 14.24 ml), sodium tetrachloroaurete (III) dehydrate (5 mM, 2 ml) and silver nitrate (5 mM, 0.21 ml) was prepared with gentle stirring at 40°C. After that, a freshly prepared solution of L-ascorbic acid (0.0788 M, 0.16 ml) was added, resulting in a colour change from deep yellow to colourless. After 30 s, the gold seeds solution (16 µL) was injected to the growth solution. The solution was left unstirred overnight at 40°C. A colour change from colourless to blue/green indicated the formation of AuNRs. Excess of CTAB was subsequently removed by centrifugation (16400 rpm, 15 min, 25°C 2x) and re-dispersion in Milli-Q water.

*TiOx solution preparation*: Titanium (IV) isopropoxide (Ti[OCH(CH3)2]4, 5 ml), 2-methoxyethanol (CH3OCH2CH2OH, 20 ml) and ethanolamine (H2NCH2CH2OH, 2 ml) were added to a three-necked flask under nitrogen atmosphere. The solution was then stirred for 1 h at room temperature, followed by heating at 80 °C for 1 h and 120 °C for additional 1 h. The solution was then cooled to room temperature and 10 ml of methanol was added.

*Device Fabrication*: PCDTBT:PC71BM were dissolved in 1,2-dichlorobenzene:chlorobenzene (3:1) (o-DCB:CB) with a 1:4 (4 mg:16 mg) ratio. A PTB7:PC71BM 1:1.5 (10mg : 15mg) ratio was dissolved in chlorobenzene, followed by the addition of 1,8-diiodooctane (DIO) to give overall DIO amount of 3%. The photovoltaic devices reported were fabricated on 20 mm by 15 mm indium-tin-oxide (ITO) glass substrates with a sheet resistance of ~20 Ω sq-1. The impurities were removed from the ITO glass through a 3-step cleaning process (detergent deionized water, aceton, isopropanol). Before the deposition of the hole transport layer (HTL) the substrates were placed inside a ultraviolet ozone cleaner in order to remove the organic contamination and increase the surface hydrophilicity of ITO coated substrates. Afterwards, poly(ethylene-dioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT:PSS), purchased from Heraeus, was spin-cast from an aqueous solution on the ITO substrate at 6000 rpm for 60 s and the average thickness of the layer was 30 nm, followed by baking for 15 min at 120 °C inside a nitrogen-filled glove box. Both photoactive layers were subsequently deposited by spin-coating the blend solutions at 1000 rpm on top of PEDOT:PSS layer (under inert atmosphene). The thickness for PCDTBT:PC71BM active layer was found to be ~80 nm and for PTB7:PC71BM blend was found to be ~100nm. TiOx interlayer was dissolved in methanol (1:200) and then spin-coated to a thickness of approximately 10 nm (6000 rpm, 40 s) in air[[[41]](#endnote-41)]. Before the mixing of the NRs inside the TiOx the NRs solution was left to settle for 24 h to allow the heavy NRs (with large diameter) to sediment out. Au NRs was subsequently mixed in TiOx solution immediately before the deposition of the ETL. The devices with PCDTBT:PC71BM blend were then heated at 80 °C for 1 min in air, while the PTB7:PC71BM based devices were dried inside a vacuum antichamper with dynamic vacuum for ~15 min. Lastly, 100 nm of aluminum was deposited through a shadow mask by thermal evaporation on the devices to define an active area of 4 mm2 for each device.

*Characterization*:The performances of the devices were measured under inert atmosphere with an Air Mass 1.5 Global (A.M. 1.5 G) solar simulator at an intensity of 100 mW cm-2using an Agilent B1500A Semiconductor Device Analyzer. A reference monocrystalline silicon solar cell from Newport Corp. was used to calibrate the light intensity. The external quantum efficiency measurements were conducted immediately after device fabrication using an integrated system (Enlitech, Taiwan) and a lock-in amplifier with a current preamplifier under short-circuit conditions. The light spectrum was calibrated using a monocrystalline photodetector of known spectral response. The OPV devices were measured using a Xe lamp passing through a monochromator and an optical chopper at low frequencies (~200 Hz) in order to maximize the signal/noise (S/N) ratio. The photoluminescence (PL) measurements of the devices were carried out at room temperature and resolved by using a UV grating and a sensitive, calibrated liquid nitrogen cooled CCD camera, in the wavelength range from 600 to 950 nm using a He-Cd CW laser, at 325 nm with a full power of P0 = 35 mW, as the excitation source. UV-vis absorption and reflectance spectra were recorded using a Shimadzu UV-2401 PC spectrophotometer over the wavelength range of 300-800 nm. The size distribution and the morphology of the as fabricated Au NRs were characterized with High Resolution Transmission Electron Microscopy (JEM 2100 Microscope). The cross-section images were collected by field emission scanning electron microscopy (FESEM JEOL-JSM7000F).

*Modeling and simulations*: Optical calculations were performed by full-vector 2D and 3D finite-difference time domain (FDTD) methods. Normal incidence plane wave excitation was employed in all cases. Input to the simulations is the refractive index of each material and the dimensions of each layer and of the Au NR nanostructure. The boundary conditions of the simulation were periodic boundary conditions along the lateral dimensions and perfectly matched layer (PML) boundary conditions along the normal direction. In the 3D calculations we assume a semi-infinite grass medium and the incident light coming from within it, and post-corrected for reflections at the air/glass interface. For the 2D calculations we assume a finite glass of ~1μm thickness, and repeated calculations for several different glass thicknesses to average-out the artifact Fabry-Perot resonances. Fourier transforms at every point in the active layer provide full spectral information and the detailed absorptionat every point inside the active layer. The exciton generation *G*(r) is found by spectrally integrating the absorption *A*(**r**,*λ*) inside the active , where  is the solar irradiance spectrum AM1.5. For direct comparison with experiments we get by spatial integration the sort-circuit current density, where is the internal quantum efficiency and *V*’ the active volume excluding the plasmonic nanoparticles. In these calculations we quoted the ideal current generated by ignoring recombinations, i.e. by setting=1.

**Supporting Information**

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

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    **Figure 1.** (a) Schematic illustration of Au NRs using the proposed method, (b) Transmission electron microscopy (TEM) image of the synthesized Au NRs, (c) Absorption spectrum of the colloidal Au NRs in aqueous solution

    

    **Figure 2.** (a) Schematic illustration of the fabricated plasmonic BHJ OPV device, (b) Current density-voltage (J-V) curves for PCDTBT and PTB7 based active layer

    **Table 1**. Average photovoltaic characteristics for OPV devices with and without AuNRs as back reflectors with PCDTBT and PTB7 as polymer donor materials.

    |  |  |  |  |  |  |  |  |  |
    | --- | --- | --- | --- | --- | --- | --- | --- | --- |
    | Donor | ETL | Jsc  (mA cm-2)a | Calculated Jsc (EQE) | Voc  (V)a | FF  (%)a | PCE  (%)a | Rs  (Ω cm) | Rsh  (Ω cm) |
    | PCDTBT | TiOx | 10.87±0.21 | 10.61±0.32 | 0.890±0.02 | 61.7±0.4 | 5.96±0.18 | 8.13 | 555 |
    | +1% Au NRs | 11.66±0.20 |  | 0.890±0.02 | 62.7±0.7 | 6.51±0.20 |  |  |
    | +1.5% Au NRs | 12.03±0.26 | 11.69±0.36 | 0.890±0.04 | 62.9±0.5 | 6.75±0.22 | 4.60 | 769 |
    | +2% Au NRs | 11.23±0.19 |  | 0.888±0.03 | 61.9±0.4 | 6.17±0.17 |  |  |
    | PTB7 | TiOx | 16.27±0.22 | 15.75±0.38 | 0.760±0.03 | 60.1±0.5 | 7.43±0.19 | 10.15 | 472 |
    | +1.5% Au NRs | 17.17±0.29 | 16.71±0.41 | 0.760±0.02 | 61.4±0.6 | 8.01±0.24 | 5.71 | 609 |

    aTo account for experimental errors, the reported averages for each case are taken for 10 identical devices, consisting of six photovoltaic cells each.

    

    **Figure 3.** IPCE spectra for the devices with and without Au NRs for (a) PCDTBT and (b) PTB7 based active layer. In the insets are shown the DIPCE spectra for each BHJ system used. (c) The schematic figure of Au NRs ETL doping explaining the light trapping mechanism

    

    **Figure 4.** Photocurrent density (Jph) versus effective voltage (Veff) curvesof the devices fabricated with and without Au NRs for (a) PCDTBT and (b) PTB7 based active layer.

    

    **Figure 5.** Spectral and spatial absorption maps obtained by 3D FDTD calculations of periodic Au NR arrangements (Au cylinders of 10 nm cross section and 30nm length, at 124 nm periodicity and 1.5% volume filling when inside the 10 nm TiOx layer): (a)-(c) for E||NR axis and (d)-(f) for E⊥NR axis. In (a) and (d) the NRs are inside the TiOx layer, while in (b) and (e) they are inside the active layer (PCDTDT:PC71BM). The absorption is measured in %/nm thickness and the height scale is zero at the TiOx/BHJ interface and 80nm at the BHJ/PEDOT:PSS interface. In (c) and (d) is the corresponding current generated as a function of depth inside the active. Black lines are for NR inside TiOx (cases a and d) while dashed red is for NR inside the BHJ (cases b and e). The total current generated is obtained by vertical integration and is noted inside the graphs.

    

    **Figure 6.** Scattering calculations assuming large 2D cells of 2μm width. A statistical sampling of 10 random distributions is performed in each case. The green line is the current obtained for no NRs. [↑](#endnote-ref-41)