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# High-efficiency solution-processed smallmolecule solar cells featuring gold nanoparticles†

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The effect of gold nanoparticles embedded in a hole transport layer, poly(3,4-ethylene-dioxythiophene):poly(styrenesulphonate) (PEDOT:PSS), was successfully studied based on small-molecule organic solar cells. The incorporation of nanoparticles results in a power conversion efficiency enhancement of 4.96%. This improvement was attributed to enhanced light harvesting because of the localized surface plasmon resonance (LSPR) effect.

Solution-processed small-molecule solar cells are attracting attention to be a competing substitute as the most popular investigated organic solar cell.1 Solution-processed smallmolecule solar cells have power conversion efficiency (PCE) higher than 10%. It has been demonstrated to be successful when coordinating chromophores within single molecules and when applied to oligothiophenes with dye units as end caps.<sup>2</sup> Moreover, small molecules are easily synthesized, have high charge carrier mobility, high open-circuit voltage  $(V_{OC})$ , better reproducibility and monodispersity (similarly sized particles), compared to its counterpart, polymer materials.<sup>3-8</sup> In contrast to polymer solar cells, the designing and optimization of the solution-processed small-molecule solar cell is demanding due to the mismatch between optical absorption length and charge transport scale.9 Therefore, it is imperative to improve light absorption without sacrificing the thickness of the active layer. One simple technique to improve light absorption in organic solar cells is the integration of metallic nanoparticles (NPs) to trigger a so-called plasmonic effect.<sup>10</sup> Numerous studies have reported the use of plasmonic organic solar cells with metallic NPs embedded into the (i) hole transport layer (HTL),<sup>11-15</sup> and (ii) active layer.<sup>16-20</sup> Moreover, various types and shapes of metallic NPs have also been used in organic solar cells.<sup>21-25</sup> Although device advancements have demonstrated remarkable improvements in efficiency, there is still limited work on the plasmonic effect of solution-processed small-molecule solar cells. The incorporation of metallic NPs into the HTL, active layer, or ETL, leads to a better hole, electron transports, and improved light absorption.<sup>11–25</sup> Simultaneously, the integration of metallic NPs with various types and shapes is embedded in the active layer, which causes enhancement in the broadband absorption.<sup>14,21-24</sup>

In this letter, we study a high-performance, solutionprocessable small-molecule solar cells with the incorporation of 30 wt% of Au NPs into the poly(3,4-ethylene-dioxythiophene):poly(styrenesulphonate) (PEDOT:PSS) hole transport layer featuring large band gap, small-molecule DR3TBDTT with a benzo[1,2-*b*:4,5-*b'*]dithiophene (BDT) building block (1.74 eV).<sup>25</sup> By incorporating Au NPs into the PEDOT:PSS layer, significant increases are documented in both  $J_{SC}$  and FF, resulting in higher conversion efficiency.

Fig. 1a–c show the molecular structure of solution-processed small-molecule DR3TBDTT, the transmission electron microscopy (TEM) image of Au NPs, and the normalized UV-vis absorption spectrum of Au NPs in chloroform solution, respectively. Au NPs were synthesized using the seed-mediated method.<sup>26,27</sup> Au NPs have an average diameter of about 15 nm with the maximum absorption peak of Au NPs located at 521 nm. In this study, two different small-molecule solar cells were fabricated (Device A: control device without the presence of Au NPs; and B: Au NPs in PEDOT:PSS solution).

To confirm the presence of Au NPs in the PEDOT:PSS layer, the atomic force microscopy (AFM) images of the pristine PEDOT:PSS and Au NPs in the PEDOT:PSS layer are shown in Fig. 2. The root-mean-square (RMS) roughness of PEDOT:PSS films slightly increased from 0.87 to 0.90 nm upon introduction of Au NPs. It can be observed that the RMS roughness is almost constant, and it is noteworthy that Au NPs are safely embedded into the PEDOT:PSS layer without any significant effect on the surface morphology.

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Fig. 1 (a) Molecular structures of solution-processed small-molecule DR3TBDTT, (b) the transmission electron microscopy (TEM) images of Au NPs, and (c) the normalized UV-vis absorption spectrum of Au NPs in chloroform solution.

Fig. 3a depicts the current density-voltage (I-V) characteristics of the small-molecule solar cells without (red curve) and with Au NPs (blue curve) embedded into the PEDOT:PSS hole transport layer. The average photovoltaic parameters from ten identical photovoltaic cells are tabulated in Table 1. In brief, we also investigated various concentration effects of Au NPs integrated into the PEDOT:PSS layer. Their respective J-V characteristics are tabulated in Table S1,† which shows the statistical data for photovoltaic parameters collected from conventional solution-processed small-molecule solar cells under AM1.5 sunlight at 100 mW cm<sup>-2</sup>. The PCE was substantially enhanced from 7.58 to 8.92% (from 10 to 40 wt%), resulting mainly from the significant  $J_{SC}$  improvement of approximately 4.04%, from 13.86 to 14.42 mA cm<sup>-2</sup>. The FF was also improved, and the V<sub>OC</sub> was unchanged, suggesting that the PCE improvement fundamentally resulted from optical engineering through the integrated Au NPs. It is worth noting that the incorporation of such high amounts of NPs in the device could potentially harm the overall device performance. However, several studies have demonstrated that the incorporation of high amounts of NPs could still be beneficial to the device.28-30

The control device demonstrates an average PCE of 8.66% with an open-circuit voltage ( $V_{\rm OC}$ ) of 0.92 V, a short-circuit current density ( $J_{\rm SC}$ ) of 13.29 mA cm<sup>-2</sup>, and a fill factor (FF) of 70.79%. However, upon the integration of Au NPs into the PEDOT:PSS layer, the  $V_{\rm OC}$  remained unchanged, while the  $J_{\rm SC}$  increased from 13.29 to 14.50 mA cm<sup>-2</sup>, and FF decreased from 70.79 to 67.93%, leading to an average PCE of 9.06%. The decrement of FF can be attributed to the increase in series resistance ( $R_{\rm S}$ ). The  $R_{\rm S}$  increases from 2.14 to 2.66  $\Omega$  cm<sup>2</sup>. On the other hand,  $J_{\rm SC}$  improved more (14.50 mA cm<sup>-2</sup>) than the control device (13.29 mA cm<sup>-2</sup>).

To find the origin of the improved  $J_{SC}$  because of the optical effect of Au NPs, we carried out external quantum efficiency (EQE) measurements. Fig. 3b demonstrates that the



Fig. 2 AFM images of (a) PEDOT:PSS and (b) Au NPs:PEDOT:PSS layers.

enhancement in the EQE spectra are well matched with the plasmonic resonance region of Au NPs. Integrated  $J_{SC}$  from the EQE spectra of the control and plasmonic devices are 12.96 and 14.47 mA cm<sup>-2</sup>, respectively. These values are indeed in agreement with the experimental results of  $J_{SC}$  of 13.29 and 14.50 mA cm<sup>-2</sup>, respectively. Please note that throughout this work the error between the experimental  $J_{SC}$  and integrated  $J_{SC}$  from spectral response was less than 4%.<sup>31</sup> These values are tabulated in Table 1 for a clearer comparison, and the slight differences are a consequence of the spectral mismatch of the xenon lamp, which exhibits a higher photon flux in the UV region than the sun.<sup>32</sup>

To explain the influences of Au NPs on exciton generation and dissociation behaviors, we evaluated the maximum exciton generation rate ( $G_{max}$ ) and exciton dissociation probabilities P(E,T) of the control and plasmonic devices. The devices were biased, sweeping from +1 to -1 V. Fig. 4a shows the dependency



Fig. 3 (a) J-V characteristics and (b) EQE spectra of control and plasmonic devices.

of the photocurrent density  $(J_{\rm ph})$  on the effective voltage  $(V_{\rm eff})$  for control and plasmonic devices, measured under AM1.5G illumination at 100 mW cm<sup>-2</sup>.  $J_{\rm ph}$  is defined as follows:

$$J_{\rm ph} = J_{\rm L} - J_{\rm D},\tag{1}$$

where  $J_{\rm L}$  and  $J_{\rm D}$  are the current densities under illumination and under the dark, respectively.  $V_{\rm eff}$  is determined as follows:

$$V_{\rm eff} = V_0 - V_{\rm a},\tag{2}$$

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where  $V_0$  is the voltage, when  $J_{\rm ph}$  equals 0 (*i.e.*  $J_{\rm L} = J_{\rm D}$ ), and  $V_{\rm a}$  is the applied voltage.<sup>33</sup>

Fig. 4a illustrates two distinctive regimes: (i)  $J_{\rm ph}$  linearly increases at a low  $V_{\rm eff}$ , and (ii)  $J_{\rm ph}$  saturates at a high  $V_{\rm eff}$ , in which the internal field is large enough to dissociate all the photogenerated excitons into free charge carriers and sweep out all the carriers to the electrodes. Thus, at a high  $V_{\rm eff}$ , the saturation current density ( $J_{\rm ph,sat}$ ) is limited by the total number of absorbed photons, and assuming that  $J_{\rm ph,sat}$  is independent of bias and temperature, we determined the  $G_{\rm max}$  as follows:

$$J_{\rm ph,sat} = qLG_{\rm max},\tag{3}$$

where q is an electronic charge, and L is the thickness of the active layer.<sup>34</sup> The  $G_{\text{max}}$  for the control and the plasmonic devices are  $5.17 \times 10^{27}$  m<sup>-3</sup> s<sup>-1</sup> ( $J_{\text{sat}} = 135$  A m<sup>-2</sup>) and  $5.41 \times 10^{28}$  m<sup>-3</sup> s<sup>-1</sup> ( $J_{\text{sat}} = 140$  A m<sup>-2</sup>), respectively. The  $G_{\text{max}}$  values exhibit considerable improvement after the integration of Au NPs. It is worth noting that  $G_{\text{max}}$  is the maximum number of absorbed photons, and such enhancement corresponds to increased light absorption in the plasmonic device.

The mechanisms of enhanced light absorption by Au NPs are studied by the finite-difference time-domain (FDTD) method.<sup>35</sup> Fig. 4b shows the distribution of field intensity around the Au NPs at 680 nm. It is found that the field intensity increased by a factor of 2 relative to the incident light outside the Au NPs shell, which increases the absorption of the PEDOT:PSS layer. Fig. 4b also illustrates the increase in field intensity upon incorporating the Au NPs, demonstrating that Au NPs scatter more light to increase the optical path. Both plasmonic and scattering effects excited by the NPs contribute to light absorption in small-molecule plasmonic solar cells.

For deeper insight into the exciton dissociation probabilities [P(E,T)], Fig. 4c compares the control and plasmonic devices, which are related to the electrical field (*E*) and temperature (*T*). In brief, only a fraction of photogenerated excitons can be dissociated into free carriers. Therefore, the  $J_{\rm ph}$  of solar cell can be written as follows:<sup>34,36</sup>

$$J_{\rm ph} = qG_{\rm max}P(E,T)L.$$
(4)

The P(E,T) at any bias can be extracted from the curves of the normalized photocurrent density ( $J_{\rm ph}/J_{\rm sat}$ ) with respect to  $V_{\rm eff}$ .<sup>37</sup> Fig. 4c illustrates the increment of the P(E,T) under short-circuit conditions ( $V_{\rm a} = 0$  V) from 75% for the control device to 90% for the plasmonic device, implying that the excitation of the LSPR induced the photogenerated excitons to dissociate into free carriers. Therefore, it can be concluded that the excitation of the LSPR not only improved the exciton generation rate but also the dissociation probability, thus improving the  $J_{\rm SC}$  of the OPVs. To

Table T	Photovoltale parameters of control and plasmonic devices						
Device	$J_{ m sc}~({ m mA~cm}^{-2})$	$J_{\rm sc}^{\ a}$ (mA cm <sup>-2</sup> )	$V_{\rm oc}$ (V)	FF (%)	PCE (%)	$R_{\rm s} \left(\Omega \ {\rm cm}^2\right)$	$R_{\rm sh} \left(\Omega \ {\rm cm}^2 \right)$
Control	13.29	12.96	0.92	70.79	8.66	2.16	935
Plasmoni	c 14.50	14.27	0.92	67.93	9.06	2.66	898

<sup>a</sup> Integrated value from EQE spectra.



**Fig. 4** (a) Photocurrent density *versus* effective voltage, (b) the distribution of field intensity around the Au NPs at 680 nm, and (c) exciton dissociation probability *versus* effective voltage for control and plasmonic devices.

further understand the origin of the improvement in the absorption of Au NPs embedded in a PEDOT:PSS layer, we carried out near scattering optical microscope (NSOM) measurements<sup>38</sup> by evaluating the NSOM signal of the PEDOT:PSS without (Device A) and with Au NP (Device B) layers. The transmission mode with a green laser light ( $\lambda = 532$  nm,



**Fig. 5** Scattering optical microscopy (NSOM) image for (a) PEDOT:PSS and (b) Au NPs embedded in PEDOT:PSS layer.

 $\sim$ 20 mW) was selected. The incident light passes through either PEDOT:PSS or Au NPs:PEDOT:PSS, and the evanescent wave is captured by the tip, which is close to the hole transport layer.

Fig. 5a and b show the NSOM images of PEDOT:PSS and Au NPs:PEDOT:PSS, respectively. As shown in Fig. 5b, bright spots were observed along with a slightly rougher scattering profile compared to that of the PEDOT:PSS (Fig. 5a). The bright spots can be attributed to the strong local forward scattering region.<sup>39</sup> The RMS values (*i.e.*, the degree of scattering) of the PEDOT:PSS and Au NPs:PEDOT:PSS were 0.52 and 0.75, respectively. The improvement is approximately 44.23% for the Au NPs:PEDOT:PSS layer compared to that of PEDOT:PSS layer. These observations demonstrate that the scattering is further improved by the enhancing plasmonic forward scattering effects of the Au NPs.<sup>38</sup>

### Conclusions

In conclusion, we demonstrate that maximum PCE is 9.06% with a relative performance increase of 4.96% in solution-processed small-molecule solar cells with the integration of Au NPs into PEDOT:PSS. Absorption spectra, EQE spectra,  $G_{max}$ , and P(E,T), FDTD simulation, and NSOM confirm that the Au NPs produced this improvement in the small-molecule solar cells. The enhanced light absorption is the result of both plasmonic and scattering effects by the Au NPs. Enhanced carrier collection and carrier transport properties ensure good performance in plasmonic devices. Therefore, in addition to contributing to light absorption in the active layer, the Au NPs:PEDOT:PSS layer can facilitate hole collection.

## **Experimental section**

### **Device fabrication**

Indium tin oxide (ITO)-coated glass substrates ( $10 \Omega \text{ sq.}^{-1}$ ) were sequentially cleaned in detergent, deionized water, acetone and isopropyl alcohol under sonication for 15 min each. The substrates were then dried under a flow of nitrogen and treated with UV ozone for 10 min. To prepare a buffer layer, Au NPs solution was doped into PEDOT:PSS (Baytron P 4083). The diameter of Au NPs is around 15 nm. The PEDOT:PSS solutions with weight ratios of 10, 20, 30, and 40 wt% Au NPs were spincoated at 5000 rpm for 30 s on ITO substrates and annealed at 150 °C in air for 25 min. The thickness of both PEDOT:PSS films were around 30 nm, as determined by a surface profiler, indicating that the incorporation of Au NPs does not change the PEDOT:PSS film thickness. The optimum weight ratio of DR3TBDTT with PC<sub>71</sub>BM was 1 : 0.8 in chloroform, with 0.2 mg mL<sup>-1</sup> of polydimethylsiloxane (PDMS) processing additive, which was spin-coated at 1000 rpm for 35 s and later baked at 120 °C for 10 min. Finally, 0.5 nm of LiF and 100 nm of Al were thermally evaporated on the active layer under vacuum condition of  $1 \times 10^{-7}$  torr. All devices had an active area of 0.04 cm<sup>2</sup>, and were encapsulated before any measurements were performed.

### Device characterization

For small-molecule plasmonic solar cells, the layers comprising PEDOT:PSS/DR3TBDTT:PC71BM were electrically isolated using toluene and methanol along the perimeter, defined by the area on top of the electrode. This isolation avoids fringing effects and also prevents overestimation of the photocurrents generated by the device. During the measurements, a shadow mask  $(0.04 \text{ cm}^2)$  with a single aperture was placed onto the SM solar cells to define its photoactive area. The current density-voltage (J-V) characteristics were recorded with a Keithley 2410 source unit. The EQE measurements were performed using an EQE system (Model 74000) obtained from Newport Oriel Instruments USA, and a HAMAMATSU-calibrated silicon cell photodiode was used as a reference diode. The wavelength was controlled with a monochromator of 200-1600 nm. The absorption spectrum of Au NPs thin films was measured using a SCINCO S4100. The surface morphology of the thin films was obtained by tapping mode using an atomic force microscope (AFM, Digital Instrument Multimode equipped with a nanoscope IIIa controller). Transmission electron microscopy (TEM) of the Au NPs was performed using a JEOL 1400 TEM with an acceleration voltage of 100 kV. FDTD simulation was performed using Lumerical Simulation.

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