

Plasmonic Electrically Functionalized TiO₂ for High-Performance Organic Solar Cells

Di Zhang, Wallace C. H. Choy,* Fengxian Xie, Wei E. I. Sha, Xinchun Li, Baofu Ding, Kai Zhang, Fei Huang, and Yong Cao

Optical effects of the plasmonic structures and the materials effects of the metal nanomaterials have recently been individually studied for enhancing performance of organic solar cells (OSCs). Here, the effects of plasmonically induced carrier generation and enhanced carrier extraction of the carrier transport layer (i.e., plasmonic-electrical effects) in OSCs are investigated. Enhanced charge extraction in TiO₂ as a highly efficient electron transport layer by the incorporation of metal nanoparticles (NPs) is proposed and demonstrated. Efficient device performance is demonstrated by using Au NPs incorporated TiO₂ at a plasmonic wavelength (560–600 nm), which is far longer than the originally necessary UV light. By optimizing the concentration ratio of the Au NPs in the NP-TiO₂ composite, the performances of OSCs with various polymer active layers are enhanced and efficiency of 8.74% is reached. An integrated optical and electrical model, which takes into account plasmonic-induced hot carrier tunneling probability and extraction barrier between TiO₂ and the active layer, is introduced. The enhanced charge extraction under plasmonic illumination is attributed to the strong charge injection of plasmonically excited electrons from NPs into TiO₂. The mechanism favors trap filling in TiO₂, which can lower the effective energy barrier and facilitate carrier transport in OSCs.

1. Introduction

Recently, plasmonic metal nanostructures have been incorporated in active layer made from polymer blend^[1–4] and highly conductive buffer layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)^[5,6] for enhancing light trapping properties of organic solar cells (OSCs). From the literatures, the optical effects of plasmonic metal nanomaterials

on enhancing light absorption have been observed.^[1,4,6,7] Meanwhile, the material effects of the metal nanomaterials (different from the optical plasmonic effects) on the morphologies and electrical conduction of devices have been reported.^[1,3,5] Distinctively, the changes of electrical properties directly induced by the optical plasmonic resonances (hereafter named as the plasmonic-electrical effects) such as plasmon-induced (electrical) carrier generation and changes in carrier extraction of charge transport layers and thus OSCs have not been clearly studied. Here, we propose to investigate the plasmonic-electrical effects of metal nanomaterials incorporated in metal oxides on OSCs and to utilize the plasmonic-electrical effects to enhance the device performance. The metal nanomaterial-metal oxide composites function as very efficient carrier transport layers in OSCs, demonstrating effective device operation enabled by the metal nanomaterials.

Charge transport layers play a crucial role in influencing organic device performance. Because of their wide range of energy-aligning capabilities, inorganic transition metal oxides, such as MoO₃,^[8] V₂O₅,^[9] for p-type metal oxides and TiO₂,^[10] and ZnO^[11] for n-type metal oxide, are newly emerged and regarded as candidates for fulfilling the role of efficient transport layers. It has been demonstrated that OSCs with Cs doped TiO₂ nanocrystals results in one of the highest efficiencies reported (3.9%) for inverted poly(3-hexylthiophene) (P3HT):[6,6]-phenyl C71-butyric acid methyl ester (PC₇₁BM)-based single-junction OSCs.^[10] However, it is a well-known issue that electron states in TiO₂ need to be filled by electrons from carrier excitation (bandgap about 3.0–3.3 eV,^[12] typically by UV irradiation) in order to provide favorable electron transport. Therefore, the devices usually require high-energy UV exposure before becoming fully functional and efficient, which in turn may degrade the organic materials.^[13] In order to facilitate and promote the applications of TiO₂ in organic optoelectronics, improving the poor electron transport of TiO₂ in the absence of UV light, as well as further enhancing the efficiencies of TiO₂ devices, are equally important and should be addressed at the same time.

Here, we propose and demonstrate enhanced charge extraction in TiO₂-based electron transport layer by introducing Au

D. Zhang, Prof. W. C. H. Choy, F. Xie, W. E. I. Sha, X. Li, B. Ding

Department of Electrical and Electronic Engineering
The University of Hong Kong
Pokfulam Road, Hong Kong, China
E-mail: chchoy@eee.hku.hk

K. Zhang, Prof. F. Huang, Prof. Y. Cao
State Key Laboratory of Luminescent Materials and Devices
College of Materials Science and Engineering
South China University of Technology
Guangzhou 510640, China



DOI: 10.1002/adfm.201203776

nanoparticles (NPs) induced plasmonic-electrical effects into thin TiO_2 films. With the Au NP- TiO_2 composite (hereafter named as NP- TiO_2 composite) as the electron transport layer, the performances of OSC with various polymer active layers (with different bandgaps) are studied and the power conversion efficiency (PCE) of 8.74% is reached in inverted single-junction OSCs. Interestingly, the highly efficient OSCs can operate by the optical activation at a plasmonic excitation wavelength far longer than the originally necessary UV light (<400 nm) for pristine TiO_2 and more importantly, the OSCs show better performance than the pristine TiO_2 device. An integrated optical and electrical model (i.e., a multiphysics model), which takes into account plasmonic-induced hot carrier tunneling probability and extraction barrier between TiO_2 and the active layer, is introduced here to illustrate the physics of the improvement. Distinctly, the theoretical and experimental results show that the contributions of metal NPs in the TiO_2 of OSCs are the plasmonically generated hot carriers which can fill the trap states in TiO_2 and lower the effective extraction barrier. As a result, the charge extraction of TiO_2 is significantly enhanced which can activate effective device operation at plasmonic wavelengths far below the bandgap of TiO_2 in UV region. This work provides a new approach to utilize plasmonic nanostructures in OSCs for enhancing device performance with physical understanding. Since TiO_2 can be used as electron transport layer for organic light-emitting diodes and OSCs, the work can also contribute to enabling efficient organic optoelectronic devices with practical applications.

2. Results and Discussion

2.1. Device Performance

The absorption of TiO_2 and Au NP- TiO_2 composite solutions are shown in **Figure 1** (inset shows photographic images of the two solutions). A functional interfacial layer of Au NP- TiO_2 composite nanocrystals is prepared by spin-coating the mixed solution on indium tin oxide (ITO) substrates. The transmission

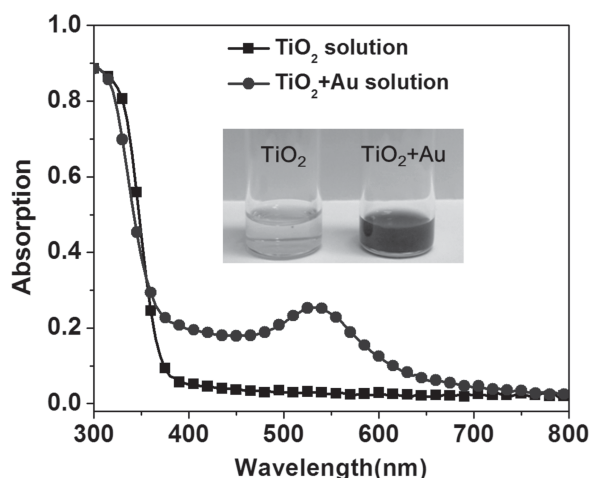


Figure 1. Absorption of TiO_2 and Au NP- TiO_2 composite solutions. Inset shows the photographs of the two solutions.

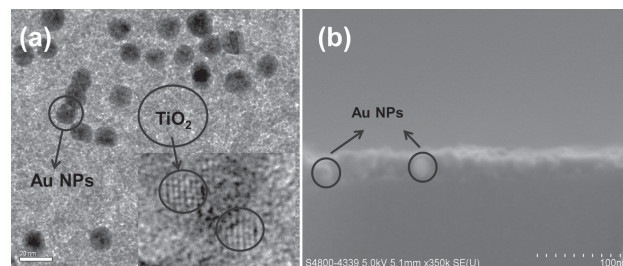


Figure 2. a) TEM image of the Au NP- TiO_2 composite. b) Cross-sectional SEM view of the composite film (bright spots are Au NPs).

electron microscopy (TEM) and scanning electron microscopy (SEM) images of Au NP- TiO_2 composite film can be found in **Figure 2a,b**, respectively. All the TiO_2 layers (with or w/o Au NPs) are ≈ 20 nm thick which are optimized from the pristine TiO_2 -based OSCs.

Current density (J)-voltage (V) characteristics and the device performances of inverted OSCs using TiO_2 as electron transport layer (with or w/o the optimized amount of Au NPs) with two different active layer materials under Air Mass 1.5 Global (AM1.5G) simulated solar illumination are shown in **Figure 3** (device structure schematically shown in **Figure 4**). The details of optimization of P3HT:[6,6]-phenyl-C61-butyric acid methyl ester (PC_{61}BM) and low-bandgap polymer thieno[3,4-b]thiophene/benzodithiophene (PTB7): PC_{71}BM inverted OSC performances with different amount of Au NPs in TiO_2 are shown in Figure S1 (Supporting Information). The corresponding incident photon-to-current conversion efficiency (IPCE) spectra for P3HT: PC_{61}BM OSCs with different amount of Au NPs are shown in Figure S2 (Supporting Information). The results show that the optimized amount of Au NPs in the NP- TiO_2 composite is 4 wt% for P3HT: PC_{61}BM OSCs and 2 wt% for PTB7: PC_{71}BM OSCs. The different optimal concentrations for the two polymer blend systems may be due to the different electron extraction properties of the P3HT: PC_{61}BM and PTB7: PC_{71}BM blends. Under AM1.5G simulated solar illumination, the incorporation of Au NPs into the TiO_2 layer leads to a notable increase in the short-circuit current density (J_{SC}) of inverted P3HT: PC_{61}BM OSCs compared to those without the Au NP incorporation (from $9.38 \text{ mA}/\text{cm}^2$ to $10.15 \text{ mA}/\text{cm}^2$), as well as in fill factor (FF) from 61.7% to 64.8%. This yields an improved average PCE of P3HT: PC_{61}BM OSCs from 3.73% to 4.20%. By adopting the low-bandgap polymer PTB7 into our inverted OSCs, the incorporation of Au NPs in TiO_2 layer results in significantly enhanced device performance of PTB7: PC_{71}BM OSCs, with J_{SC} increased from $17.23 \text{ mA}/\text{cm}^2$ to $18.07 \text{ mA}/\text{cm}^2$ and FF from 65.5% to 68.1%, thus average PCE is improved from 8.02% to 8.74%.

2.2. Plasmonic Electrically Enhanced Charge Extraction

In order to investigate the plasmonically enhanced charge extraction of the TiO_2 electron transport layer, device characterization under light illuminations of different wavelengths is conducted to demonstrate the capability of NP- TiO_2 composite OSC efficiently operating with an initial light illumination at plasmonic resonance wavelength (in the visible region), which

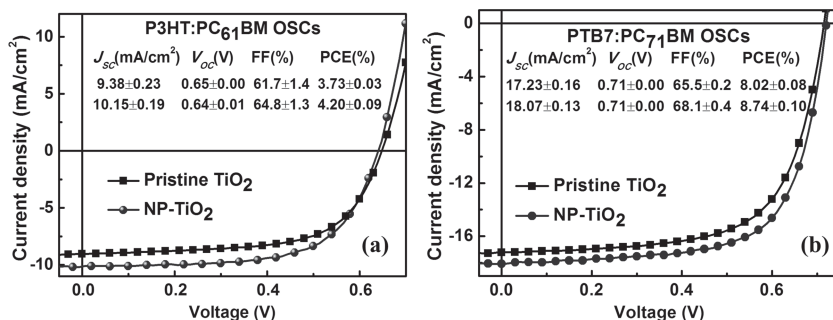


Figure 3. Representative J - V characteristics of inverted single-junction a) P3HT:PC₆₁BM and b) PTB7:PC₇₁BM OSCs with TiO₂ and NP-TiO₂ composite with the optimized NP concentration (4 wt% for P3HT:PC₆₁BM and 2 wt% for PTB7:PC₇₁BM)) as the electron transport layers. The device performances are summarized in the inset of each panel.

is well below the bandgap of pristine TiO₂ (UV region). The J - V characteristics under monochromatic light are hereby referred to as monochromatic J - V measurement. The increased and extended operability of NP-TiO₂ composite OSCs at visible wavelengths well below the UV region is closely related to the injection of plasmonically excited hot carriers (electrons) from metal NPs into TiO₂.

Figure 5 shows the J - V characteristics of TiO₂ OSCs measured by the monochromatic light of 532 nm and 600 nm. Under 532 nm monochromatic illumination, both devices using pristine TiO₂ and NP-TiO₂ composite (Figure 5 triangle and square symbol lines, respectively) show S-shape J - V characteristics, with poor open-circuit voltage (V_{oc} , 0.1–0.3 V) and FF (<30%). In fact, both the pristine TiO₂ and NP-TiO₂ composite OSCs show poor device performance and S-shape J - V characteristics by excitation light sources with wavelength shorter than 560 nm in the visible region. While the S-shape J - V characteristics in OSCs may arise from factors such as unbalanced charge transport in the active layer^[14] or degradation in the electrode interface,^[15] the initial S-shape characteristics in our TiO₂ OSC devices can be eliminated by exposing the OSCs to UV light prior to monochromatic J - V measurement or using other electron transport layers. Hence the S-shape characteristics are from

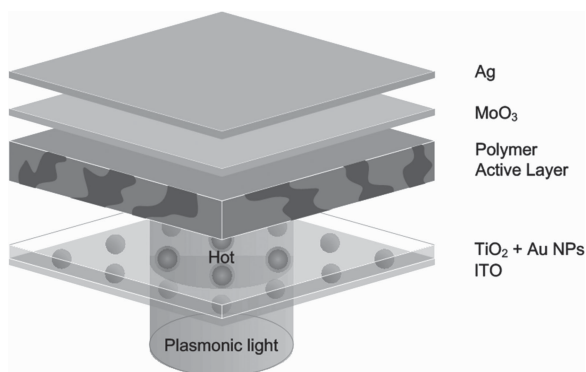


Figure 4. Device structure of inverted OSCs using NP-TiO₂ composite electron transport layer, with the detailed structure of glass/indium tin oxide (ITO)/TiO₂ (with Au NPs, ≈20 nm)/active layer (≈220 nm for P3HT:PC₆₁BM, ≈100 nm for PTB7:PC₇₁BM)/MoO₃ (14 nm)/Ag (100 nm).

the TiO₂ layer. It has been reported that trap states in TiO₂ contribute to the S-shape characteristics.^[16] Upon UV illumination, trap filling occurs by electrons generated in TiO₂, which lowers the effective extraction barrier and the S-shape characteristics are eliminated. Remarkably, the NP-TiO₂ composite OSCs can activate efficient device action and eliminate the undesired S-shape characteristics by monochromatic light ranging from 560 nm to 600 nm outside the UV region. With the illumination at 600 nm, the NP-TiO₂ composite OSC shows significantly enhanced device performance (Figure 5 circle symbol line), with greatly increased V_{oc} from 0.1–0.3 V (as-fabricated) to 0.5–0.6 V and FF from <30% to 40–50%, while the

performance of pristine TiO₂ OSCs remains poor. It should be noted that the plasmonic resonance wavelength of Au NPs in TiO₂ solution is about 532 nm (absorption spectrum shown in Figure 1) and is different from the plasmonic resonance wavelength in devices (red-shifted to 560–600 nm) due to the different optical environment.

The plasmonic activation of the NP-TiO₂ composite OSCs is also confirmed by IPCE measurement performed on as-fabricated pristine TiO₂ and NP-TiO₂ composite OSCs before and after 600 nm light illumination (**Figure 6**). All the OSCs measured are as-fabricated and specifically kept from UV light. The wavelength range of IPCE is from 450 nm to 800 nm to avoid the UV region. Though initially the NP-TiO₂ composite OSC shows smaller IPCE than as-fabricated pristine TiO₂ OSC without any prior illuminations, broad increment in the IPCE of NP-TiO₂ composite device is observed by applying a visible plasmonic illumination of 600 nm before the measurement, resulting in larger IPCE in the NP-TiO₂ composite OSC than that of pristine TiO₂ OSC (which remains almost unchanged by the plasmonic illumination). The broad enhancement in

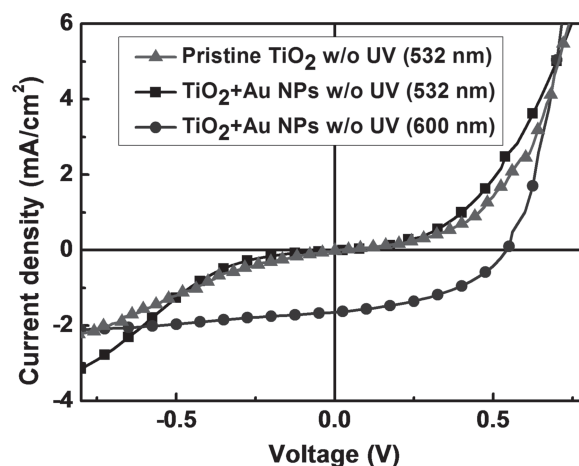


Figure 5. J - V characteristics of P3HT:PC₆₁BM OSCs measured under monochromatic light of 532 nm and 600 nm with pristine TiO₂ and NP-TiO₂ composite (TiO₂+Au NPs) as the electron transport layers. For pristine TiO₂ only J - V characteristics under 532 nm monochromatic light are shown.

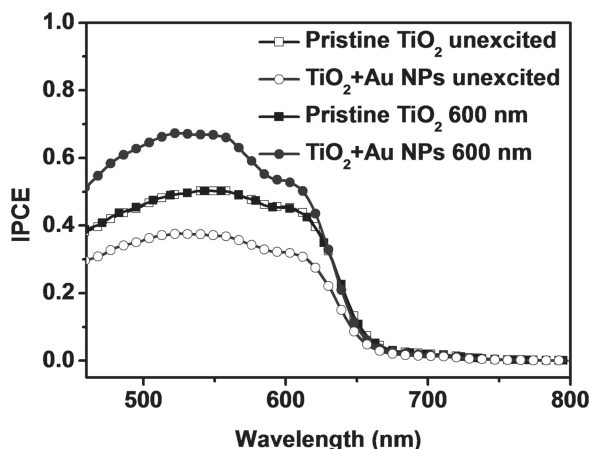


Figure 6. Incident photon-to-current conversion efficiency (IPCE) spectra of pristine TiO_2 and Au NP- TiO_2 composite (TiO_2 +Au NPs) P3HT:PC₆₁BM OSCs before and after plasmonic illumination of 600 nm light and applied voltage bias. All the OSCs are measured from the as-fabricated state and the wavelength range of the IPCE measurement is from 450 nm to 800 nm to avoid the UV region.

IPCE suggests the enhanced device performance of NP- TiO_2 composite OSCs under plasmonic light to be from plasmonically enhanced electrical properties of the NP- TiO_2 composite (plasmonic-electrical effects), rather than from optical effects alone.

Though there are some studies on the effects of plasmonically excited metal NPs in the metal-semiconductor nanostructure, the explanation is still inconclusive. Some studies indicate that the photocatalytic or photocurrent enhancement is induced by hot carrier injection from the plasmonically excited metal NPs into the semiconductor.^[17] However, some other studies report that the improvement of photocatalytic activity in the visible range is caused by the local electric field enhancement near the TiO_2 surface, rather than by the direct transfer of charges between the NPs and TiO_2 .^[18] To examine the origin of effective device operation by visible plasmonic excitation, we perform further transient photo-generated voltage (TPV) measurements on the NP- TiO_2 composite OSCs.

By using laser pulse of 532 nm as TPV excitation source, we obtain very weak signals in both as-fabricated TiO_2 OSCs (pristine TiO_2 and NP- TiO_2 composite) since the 532 nm pulse cannot effectively excite carriers in TiO_2 regardless of the metal NPs. As shown in Figure 7, the NP- TiO_2 composite OSC exhibits a rather small TPV peak of 0.1–0.3 V. The results re-confirm the small V_{OC} of the as-fabricated OSCs in monochromatic J - V measurement by 532 nm illumination, as shown in Figure 5 (black line). Interestingly, prior to TPV measurement, by exposing the Au NP- TiO_2 composite OSCs to a monochromatic light at 600 nm for 15 min, the TPV peak is notably increased to 0.56 V (red line in Figure 7), corresponding to the increased V_{OC} (0.5–0.6 V, circle symbol line in Figure 5) in monochromatic J - V measurement by 600 nm illumination.

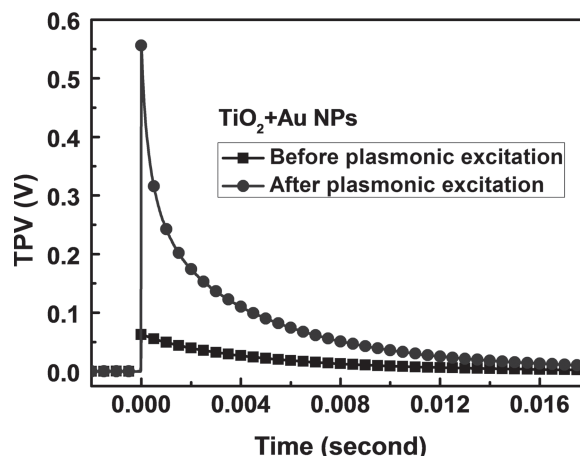


Figure 7. TPV measured by 532 nm laser pulse before and after the plasmonic excitation of monochromatic light at 600 nm. The OSC structure is ITO/Au NP- TiO_2 composite (TiO_2 +Au NPs)/P3HT:PC₆₁BM/MoO₃/Ag.

Meanwhile, TPV measurement also allows us to examine the prerequisites of plasmonic enhanced electron extraction. We find that for the NP- TiO_2 composite devices, the enhancement in electron extraction is not instantaneous upon plasmonic excitation; rather, certain duration of illumination (in our case $\approx 4 \text{ mW/cm}^2$ at 600 nm for 15 min) is required before the TPV peak reaches optimal. However, when we combine the plasmonic illumination with a small externally applied voltage bias (in our case 5 V) shortly before the TPV measurement, the time required for the TPV characteristic reaching optimal and stable is considerably shortened to under 5 min. This observation corroborates to our monochromatic 600 nm illuminated J - V measurement, where the NP- TiO_2 composite is quickly activated by simultaneous plasmonic illumination and voltage sweep during the measurement.

From the above studies, we propose that it is the charge transfer process of plasmonically excited electrons from metal NPs to TiO_2 , rather than the induced field effect near the TiO_2 surface that is responsible for these improvements (schematically shown in Figure 8). Previous studies have indicated Fermi level equilibration in the semiconductor-metal composite under UV irradiation through charge transfer from semiconductor to metal.^[19] For the electron extraction process in OSCs from the

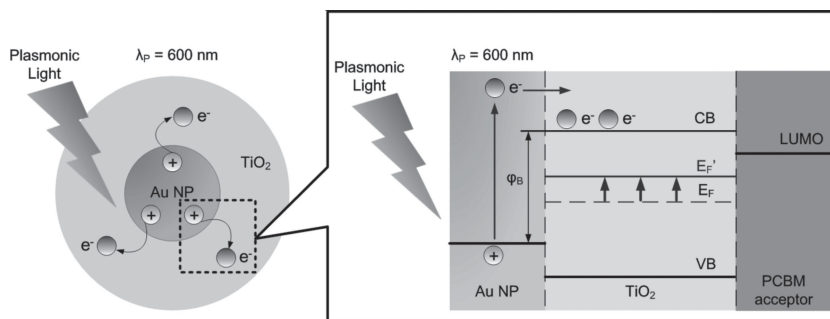


Figure 8. Schematic plasmonic-induced charge injection process. CB and VB denote the conduction band and valence band respectively. ϕ_B is the Schottky barrier height between Au and TiO_2 . LUMO denotes LUMO of the PCBM acceptor in OSCs. Electrons are extracted from PCBM to TiO_2 in OSCs.

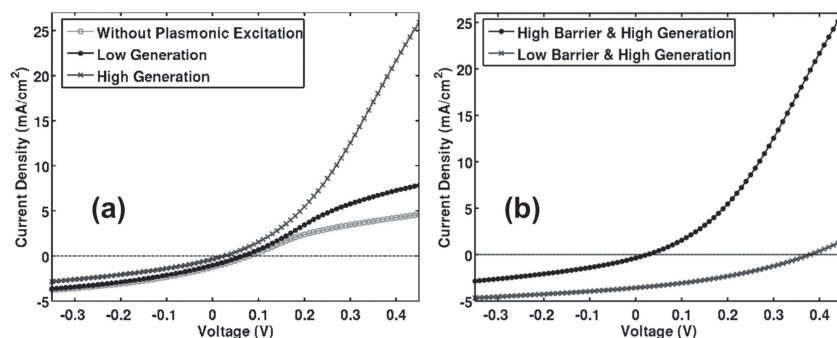


Figure 9. Theoretical J - V characteristics of OSCs using TiO_2 buffer layers. a) J - V characteristics of OSCs using functionalized TiO_2 buffer layer embedded with Au NPs. Free electrons is generated from the conduction band of Au NPs to that of the TiO_2 due to the plasmonic excitation. The S-shaped kink in the J - V curve is eliminated when the electron generation is high enough. The heights of extraction and injection barriers are both 0.7 eV. b) J - V characteristics of OSCs with high electron generation in TiO_2 and different heights of energy barriers at the TiO_2 interface.

PCBM acceptor to TiO_2 , the extraction barrier is generally determined from the conduction band (CB) edge of TiO_2 (≈ 4.0 eV^[20]) and the lowest unoccupied molecular orbital (LUMO) level of PCBM (4.2 eV^[21]), as shown in Figure 8. While the calculated extraction barrier from energy bands seems relatively small, the shallow electron traps in TiO_2 ^[16] can effectively form an extraction barrier between the active layer and TiO_2 , resulting in unfavorable electron extraction and poor S-shape J - V characteristics as observed in Figure 5. UV-generated electrons in TiO_2 were reported to fill the electron traps with enhanced photoconductivity.^[16] Here, the transferred plasmonically excited electrons from Au NPs to TiO_2 can achieve trap filling in the TiO_2 layer, leading to reduced effective extraction barrier, decreased resistance and charge recombination, which can enhance the electron extraction. The ≈ 1.0 eV Schottky barrier (ϕ_B in Figure 8) between bulk Au and TiO_2 is initially unfavorable for plasmonically excited electrons with energy lower than the barrier height.^[22] With the applied voltage bias, the Schottky barrier is lowered and significantly more electrons can be driven into TiO_2 for trap

filling, which enhance the charge extraction process and enable effective device operation. All above are consistent with our observation. To further investigate the detail physics, theoretically optical and electrical studies have been conducted as described below.

2.3. Theoretical Investigation of the Metal NP Enhanced Charge Extraction in TiO_2

We rigorously solve the Maxwell's equations^[23] and organic semiconductor equations simultaneously^[24] to obtain the J - V response of the multilayered OSC structures with the pristine TiO_2 buffer layer. Extraction and injection barriers (each with barrier height of 0.7 eV) are applied to the pristine TiO_2 interface to simulate the effects from the trap states in TiO_2 . As shown in

Figure 9a, the presence of energy barriers at the unexcited TiO_2 (w/o plasmonic excitation) interface hinders efficient electron extraction and injection in both the reverse bias and forward bias regimes. The transition between the reverse bias (extraction) and forward bias (injection) regimes forms an S-shaped kink in the J - V characteristics of OSCs. Our experimental results show that Au NPs plasmonically generate free electrons (i.e., so-called "hot carriers") from the conduction band of the metal which are injected to that of the TiO_2 by plasmonic excitation. The S-shaped kink in the J - V characteristics of OSCs is eliminated through the plasmonic-electrical effects (Figure 5). To fully understand the origin of the improvement, free electron generation is imposed at the TiO_2 layer through our theoretical modeling, as shown in Figure 9a. At low electron generation, the S-shape feature still largely exists. However, the unwanted S-shape feature in J - V characteristics disappears with high electron generation in TiO_2 , which corresponds to the injected hot carriers from Au NPs. The energy barriers at the interface are also manifested by the unbalanced distributions of electrons at both reverse and forward bias regimes, which are typical phenomena of the S-shaped kink (Figure 10a). After enough electrons are generated in the TiO_2 buffer layer, the charge distribution becomes more balanced at both reverse bias and forward bias regimes, which can be observed in Figure 10b. The more balanced electron distribution, which effectively lowers barrier height, can facilitate carrier extraction and injection, of which the J - V characteristics no longer exhibit poor S-shaped kink, as demonstrated in Figure 9a. Since the electron traps in TiO_2 are filled by the injected hot electrons from Au NPs, the effective barrier will be considerably reduced. As a result, we observe significantly enhanced V_{OC} in device simulation with high electron generation and lowered barriers as shown in Figure 9b. Consequently, the simulated J - V characteristics of OSCs show enhanced V_{OC}

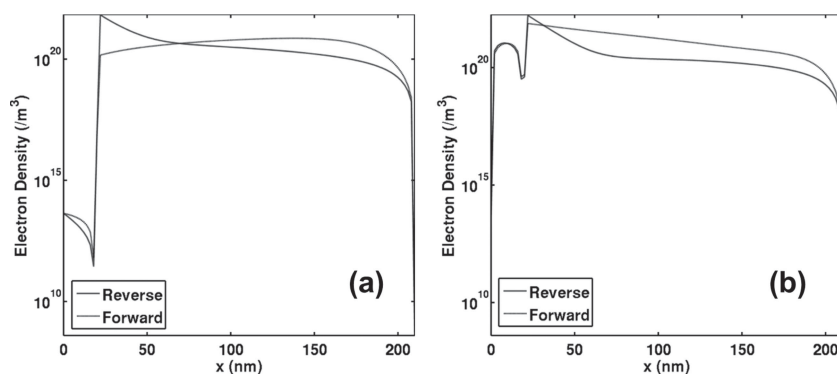


Figure 10. The electron distributions of the OSC at reverse bias and forward bias regimes. The OSC structure is cathode/ TiO_2 /active layer/anode. Cathode is located at $x = 0$. The thickness of the device is 210 nm. TiO_2 is adopted as an electron transport (buffer) layer with thickness of 20 nm. Both the extraction and injection barrier (0.7 eV) are formed at the two interfaces of TiO_2 . a) The pristine TiO_2 is employed as the buffer layer without plasmonic excitation. The electron density in the buffer layer (0–20 nm) is very low. b) The plasmonic-functionalized TiO_2 is employed as the buffer layer. The electron density in the buffer layer is significantly increased.

and FF, which are consistent with our experimental results as shown in Figure 5.

3. Conclusions

In conclusion, we propose and demonstrate enhanced charge extraction by plasmonic-electrical effects in TiO_2 as a highly efficient electron transport layer for improving the OSC performance by the incorporation of metal NPs. By using the Au NP- TiO_2 composite, PCE of OSCs can reach 8.74%. Moreover, the highly efficient OSCs using NP- TiO_2 composite can operate at a plasmonic wavelength (560–600 nm) far longer than the originally necessary UV light (<400 nm) for pristine TiO_2 . Our experimental and theoretical results show that the improved charge extraction in TiO_2 under plasmonic wavelength illumination is attributed to the enhanced charge injection of plasmonically excited electrons in metal NPs into TiO_2 . The mechanism favors trap filling in TiO_2 , and thus improving the carrier extraction of OSC devices. Consequently, the NP- TiO_2 composite transport layer exhibits excellent charge extraction for efficient organic devices.

4. Experimental Section

Material Synthesis and Device Fabrication: Anatase phase TiO_2 nanocrystals were prepared and mixed them with Au NPs. The TiO_2 nanocrystals were synthesized by a nonaqueous method detailed in reference,^[25] and were dispersed in ethanol. Au NPs (15 nm in size) were synthesized by the reduction of HAuCl_4 by sodium citrate. The two solutions (TiO_2 and NPs) could be mixed by any proportions and remain stable. The absorption of TiO_2 and Au NP- TiO_2 composite solutions are shown in Figure 1. A functional interfacial layer of Au NP- TiO_2 composite nanocrystals was prepared by spin-coating the mixed solution on ITO substrates. After the spin-coating process, all TiO_2 films were annealed at 150 °C for 10 min on a hot plate in ambient. The TEM and SEM images of Au NP- TiO_2 composite film can be found in Figure 2a,b, respectively. All the TiO_2 layers (with or w/o NP doping) were ≈ 20 nm thick, which was optimized from the pristine TiO_2 -based OSCs. The prepared samples were then transferred into a nitrogen-filled glove box for spin-coating the blend of P3HT and PC₆₁BM with 1:1 weight ratio (20 mg/mL each dissolved in 1,2-dichlorobenzene), or the low-bandgap semiconducting PTB7:PC₇₁BM with 11.0 mg/mL (PTB7):16.5 mg/mL (PC₇₁BM) dissolved in chlorobenzene.^[26] For P3HT:PC₆₁BM OSCs, solvent annealing was utilized, as described elsewhere,^[27] after which the samples were annealed at 130 °C for 10 min on a hotplate. MoO_3 (14 nm)/Ag (100 nm) were thermally evaporated through a shadow mask as the top anode, which defined the device area as 0.045 cm². The final device structure was glass/ITO/ TiO_2 (with or w/o Au NPs, ≈ 20 nm)/active layer (≈ 220 nm for P3HT:PC₆₁BM, ≈ 100 nm for PTB7:PC₇₁BM)/ MoO_3 (thermally evaporated, 14 nm)/Ag (thermally evaporated, 100 nm). AM1.5G Current density J – V characteristics were measured using a Keithley 2635 sourcemeter and ABET AM1.5G solar simulator.

Optical and Electrical Models: The multiphysics of plasmonic OSCs are governed by Maxwell's equations and semiconductor equations (Poisson, continuity, and drift-diffusion equations). The unified finite-difference (FD) approach was adopted to model both the optical and electrical properties of OSCs. Although the multiphysics solver has been developed previously,^[24] the treatment of extraction barrier was developed in this work. The internal electric fields, which strongly affect the drift current and V_{OC} , are given by

$$E_n = -\nabla\varphi - \frac{\nabla\chi}{e} - \frac{k_B T}{e} \nabla[\ln(N_c)]$$

$$E_p = -\nabla\varphi - \frac{\nabla\chi}{e} - \frac{\nabla E_g}{e} + \frac{k_B T}{e} \nabla[\ln(N_v)]$$

where E_n and E_p are internal E-fields for electrons and holes, χ is the electron affinity, and E_g is the band gap. Moreover, N_c and N_v are effective density of states (DOS) for electrons and holes, respectively. The extraction barrier can be formed by the jumping of the electron affinity and effective DOS at the interface between buffer and active layers.

The generation of electron at the TiO_2 buffer layer should take into account both the metal absorption (obtained by solving Maxwell's equation^[23]) and internal quantum efficiency (IQE) of the hot-carrier effect. Hot electrons in the metal nanoparticles by plasmonic excitation should have sufficient energy to overcome the potential (Schottky) barrier between metal/ TiO_2 . According to the Fowler-Nordheim field emission theory, the IQE can be written as

$$\eta = \frac{H}{8E_F} \frac{(h\nu - \phi_B)^2}{h\nu}$$

Where H is the device-specific Fowler emission coefficient, $h\nu$ is the incident photon energy, and ϕ_B is the Schottky barrier energy.

Supporting Information

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

Acknowledgements

This work was supported by University Grant Council of the University of Hong Kong (grants #10401466 and #201111159062), and the General Research Fund (grants: HKU#712010E and HKU711612E) from the Research Grants Council (RGC) of Hong Kong Special Administrative Region, China. This work was also supported by a grant from the SRFDP and RGC ERG Joint Research Scheme sponsored by the RGC of Hong Kong and the Ministry of Education (M-HKU703/12). F.H. thanks the Natural Science Foundation of China (NSFC) (No.21125419) and Research Fund for the Doctoral Program of Higher Education of China (20120172140001) for financial support. W.E.I.S. would also like to acknowledge the financial support in part from NSFC (No. 61201122).

Received: December 20, 2012

Revised: February 5, 2013

Published online:

- [1] a) D. H. Wang, D. Y. Kim, K. W. Choi, J. H. Seo, S. H. Im, J. H. Park, O. O. Park, A. J. Heeger, *Angew. Chem. Int. Ed.* **2011**, *50*, 5519; b) D. H. Wang, K. H. Park, J. H. Seo, J. Seifter, J. H. Jeon, J. K. Kim, J. H. Park, O. O. Park, A. J. Heeger, *Adv. Energy Mater.* **2011**, *1*, 766.
- [2] A. P. Kulkarni, K. M. Noone, K. Munechika, S. R. Guyer, D. S. Ginger, *Nano Lett.* **2010**, *10*, 1501.
- [3] a) C.-H. Kim, S.-H. Cha, S. C. Kim, M. Song, J. Lee, W. S. Shin, S.-J. Moon, J. H. Bahng, N. A. Kotov, S.-H. Jin, *ACS Nano* **2011**, *5*, 3319; b) K. Kim, D. L. Carroll, *Appl. Phys. Lett.* **2005**, *87*, 203113.
- [4] a) F. X. Xie, W. C. H. Choy, C. C. D. Wang, E. Wei, D. D. S. Fung, *Appl. Phys. Lett.* **2011**, *99*, 153304; b) X. Li, W. C. H. Choy, L. Huo, F. Xie, W. E. I. Sha, B. Ding, X. Guo, Y. Li, J. Hou, J. You, Y. Yang, *Adv. Mater.* **2012**, *24*, 3046.
- [5] D. D. S. Fung, L. Qiao, W. C. H. Choy, C. Wang, E. Wei, F. Xie, S. He, *J. Mater. Chem.* **2011**, *21*, 16349.
- [6] a) J. Yang, J. You, C.-C. Chen, W.-C. Hsu, H.-r. Tan, X. W. Zhang, Z. Hong, Y. Yang, *ACS Nano* **2011**, *5*, 6210; b) J.-L. Wu, F.-C. Chen, Y.-S. Hsiao, F.-C. Chien, P. Chen, C.-H. Kuo, M. H. Huang, C.-S. Hsu, *ACS Nano* **2011**, *5*, 959.
- [7] H. Chen, T. Ming, L. Zhao, F. Wang, L. D. Sun, J. Wang, C. H. Yan, *Nano Today* **2010**, *5*, 494.

- [8] C. Tao, S. Ruan, X. Zhang, G. Xie, L. Shen, X. Kong, W. Dong, C. Liu, W. Chen, *Appl. Phys. Lett.* **2008**, 93, 193307.
- [9] J.-S. Huang, C.-Y. Chou, M.-Y. Liu, K.-H. Tsai, W.-H. Lin, C.-F. Lin, *Org. Electron.* **2009**, 10, 1060.
- [10] M.-H. Park, J.-H. Li, A. Kumar, G. Li, Y. Yang, *Adv. Funct. Mater.* **2009**, 19, 1241.
- [11] S. K. Hau, H.-L. Yip, N. S. Baek, J. Zou, K. O'Malley, A. K. Y. Jen, *Appl. Phys. Lett.* **2008**, 92, 253301.
- [12] H. Luo, T. Takata, Y. Lee, J. Zhao, K. Domen, Yushan, *Chem. Mater.* **2004**, 16, 846.
- [13] S. Chambon, A. Rivaton, J.-L. Gardette, M. Firon, *Sol. Energy Mater. Sol. Cells* **2007**, 91, 394.
- [14] W. Tress, A. Petrich, M. Hummert, M. Hein, K. Leo, M. Riede, *Appl. Phys. Lett.* **2011**, 98, 063301.
- [15] H. Jin, M. Tuomikoski, J. Hiltunen, P. I. Kopola, A. Maaninen, F. Pino, *J. Phys. Chem. C* **2009**, 113, 16807.
- [16] C. S. Kim, S. S. Lee, E. D. Gomez, J. B. Kim, Y.-L. Loo, *Appl. Phys. Lett.* **2009**, 94, 113302.
- [17] a) A. Furube, L. Du, K. Hara, R. Katoh, M. Tachiya, *J. Am. Chem. Soc.* **2007**, 129, 14852; b) Y. Tian, T. Tatsuma, *J. Am. Chem. Soc.* **2005**, 127, 7632; c) Y. Nishijima, K. Ueno, Y. Yokota, K. Murakoshi, H. Misawa, *J. Phys. Chem. Lett.* **2010**, 1, 2031; d) M. W. Knight, H. Sobhani, P. Nordlander, N. J. Halas, *Science* **2011**, 332, 702.
- [18] Z. Liu, W. Hou, P. Pavaskar, M. Aykol, S. B. Cronin, *Nano Lett.* **2011**, 11, 1111.
- [19] a) M. Jakob, H. Levanon, P. V. Kamat, *Nano Lett.* **2003**, 3, 353; b) V. Subramanian, E. E. Wolf, P. V. Kamat, *J. Phys. Chem. B* **2003**, 107, 7479.
- [20] Z.-X. Li, Y.-L. Xie, H. Xu, T.-M. Wang, Z.-G. Xu, H.-L. Zhang, *J. Photochem. Photobiol. A: Chem.* **2011**, 224, 25.
- [21] J. You, C.-C. Chen, L. Dou, S. Murase, H.-S. Duan, S. A. Hawks, T. Xu, H. J. Son, L. Yu, G. Li, Y. Yang, *Adv. Mater.* **2012**, 24, 5267.
- [22] a) J. Y. Park, H. Lee, J. R. Renzas, Y. Zhang, G. A. Somorjai, *Nano Lett.* **2008**, 8, 2388; b) E. W. McFarland, J. Tang, *Nature* **2003**, 421, 616.
- [23] a) W. E. I. Sha, W. C. H. Choy, Y. G. Liu, W. C. Chew, *Appl. Phys. Lett.* **2011**, 99, 113304; b) W. E. I. Sha, W. C. H. Choy, W. C. Chew, *Opt. Express* **2010**, 18, 5993.
- [24] W. E. I. Sha, W. C. H. Choy, Y. Wu, W. C. Chew, *Opt. Express* **2012**, 20, 2572.
- [25] G. V. Jensen, M. Bremholm, N. Lock, G. R. Deen, T. R. Jensen, B. B. Iversen, M. Niederberger, J. S. Pedersen, H. Birkedal, *Chem. Mater.* **2010**, 22, 6044.
- [26] Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray, L. Yu, *Adv. Mater.* **2010**, 22, E135.
- [27] G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, Y. Yang, *Nat. Mater.* **2005**, 4, 864.