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IMPROVING THE EFFICIENCY OF POLYMER SOLAR CELLS BY INCORPORATING GOLD NANOPARTICLES AND NANOCLUSTERS DECORATED MULTI-LAYER GRAPHENE

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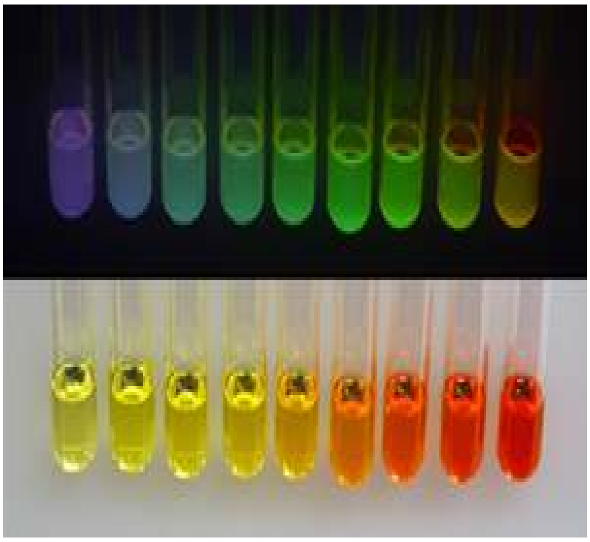


ABSTRACT

We demonstrate efficiency improvement in polymer solar cells (PSCs) by _22% through incorporating Au nanoparticles (NPs) into solar cells. Our theoretical result shows that the absorption enhancement at the active layer is attributed to plasmon resonances with strong near-field distributions penetrated into absorption polymers. These findings can be applied to design high-efficiency metallic NPs-incorporated PSCs.. A thin layer of ultraviolet-ozone (UVO) treated gold (Au) is introduced on multi-layer graphene (MLG) to enable the MLG as an effective anode for polymer solar cells (PSCs). Further analysis shows that UVO treated Au provides favorable band alignment at the MLG/polymer interface. Moreover, the improved interfacial contact and shortened UVO durations reduce the series resistance of PSCs significantly.

KEYWORDS :*solar cells, ultraviolet-ozone, polymer solar cells, multi-layer grapheme, Au, NPs.*

INTRODUCTION :

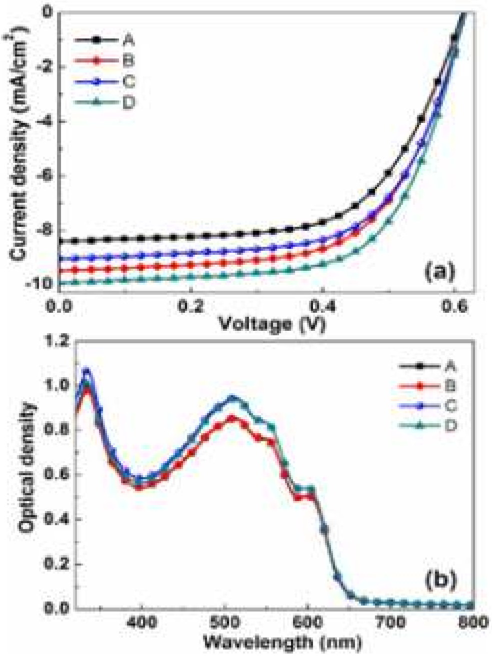
Polymer solar cells (PSCs) have been a highly interesting field in recent years, as they have a strong potential to realize low cost solar cells which are highly portable and deployable due to their flexibility and light weight.1 Compared with inor-ganic solar cells, PSCs usually suffer from the insufficient light absorption due to the thin active layer restricted by the short exciton diffusion length and low carrier mobilities.2–4Polymer solar cells (PSCs) have been considered as a promising candidate for future photovoltaic applications due to the mechanical and chemical flexibility of the organic materials, as well as the low-cost processing methods which enable large area applications 11 . To overcome these limits, metallic (e.g., Au, Ag) nanopar-ticles (NPs) have been incorporated into the polymer layers conveniently in solution processing. Although the power con-version efficiency (PCE) of PSCs has been shown to improve by incorporating metallic NPs in either the buffer layer such as poly-(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) or the active layer,5–10 the understanding on the changes is still not quite clear.

In this work, monofunctional poly(ethylene glycol) (PEG)-capped Au NPs of sizes 18 nm and 35 nm are doped in the PEDOT:PSS and poly(3-hexylthiophene) (P3HT):phenyl-C61-butyric acid methyl ester (PCBM) layers, respectively, leading to an improvement of PCE by _22% compared to the optimized control device. We first identify the impact of NPs in each polymer layer on PSC characteristics by doping Au NPs in either the PEDOT:PSS or P3HT:PCBM layer. Then, we investigate the impact of Au NPs when incorporated in all polymer layers. We demonstrate that the accumulated benefits of incorporating Au NPs in all organic layers of PSCs can achieve larger improvements in PSC performances.

The basic PSC structure in this work is ITO/PEDOT:PSS/ P3HT:PCBM/LiF (1 nm)/Al (100 nm). Device A has no NP doping, while devices B, C, and D have NPs doped into PEDOT:PSS, P3HT:PCBM, and both layers, respectively. For hole-only devices, Au (20 nm)/Al (80 nm) electrode was used in place of the LiF/Al electrode. Detailed information of the optimized conditions for the control device A can be found elsewhere.15 The synthesis of Au NPs with PEG capping aredescribed our previous report.10 The amount of Au NPs doped into the organic layer (0.32 wt. % in PEDOT:PSS and 1.2 wt. % in P3HT:PCBM) had been optimized for the best PCE. De-vice characterization methods including current density (J)-voltage (V) characteristics, optical absorption, atomic force microscopy, (AFM) and scanning electron microscope (SEM) were conducted as stated elsewhere.10–16 The volume integral equation (VIE) method, which is a rigorous solution to Max-well's equations, was adopted to study the optical absorption of PSCs. The coupling between multiple NPs and the interac-tion between NPs and multilayered device structure were fully considered.17

J-V characteristics of the four PSC device structures with Au NPs incorporated into different organic layers are shown in Fig. 1(a), and the photovoltaic parameters are listed in Table I. We observe that the incorporation of Au NPs into either the PEDOT:PSS layer (device B) or the active layer (device C) improves PCE from 3.16% (control device A) to 3.61% and 3.44%, respectively. Interestingly, the simultaneous incorpora-tion of Au NPs into both layers results in a further improve-ment of average PCE to 3.85%. In all cases, the increases in PCE are results of improvements in short-circuit current density (JSC) and fill factor (FF), while the open-circuit voltage (VOC) is unchanged. Notably, when incorporating Au NPs into both PEDOT:PSS and active layer simultaneously, the series resistance (RS) reduces obviously from 3.05 X cm2 (device A) to 1.93 X cm2 (device D), contributing to a remark-able increase of FF from 61.92% to 65.00%.

The effect of NPs doped in a single layer is first studied. For the case of Au NPs doped into the PEDOT:PSS layer only (device B), a study of the physics has been conducted previously.10 In good agreement with our previous results, the absorption spectrum of the active layer does not show any clear change from the control device A as shown in Fig. 1(b). This can be explained by our finding that the strong near field around Au NPs due to the localized surface plas-mon resonance (LSPR) distributes laterally along the PEDOT:PSS layer instead of vertically penetrating into the active layer.10 Meanwhile, the hole mobilities of devices A and B derived from the hole-only devices show negligible changes (Supporting information: Fig. S1),20 indicating that charge transport in the bulk of the active layer is unaffected by NPs incorporated in PEDOT:PSS. The surface morphol-ogy of the PEDOT:PSS þ Au NPs layer (Supporting infor-mation: Fig. S2)20 shows an obvious increase in surface roughness with the root mean square (RMS) roughness increasing from 0.97 nm to 1.55 nm. Therefore, the incorpo-ration of Au NPs only in PEDOT:PSS increases the interfa-cial contact area between the P3HT:PCBM and PEDOT:PSS, allowing more efficient hole collection at the anode and hence improves JSC and FF.18,19 Furthermore, from resistive devices of structure ITO/PEDOT:PSS (with or without Au NPs)/Al, it is found that the resistance of PEDOT:PSS reduces upon addition of NPs (Supporting in-formation: Fig. S3 (Ref. 17)). Both the increased interfacial contact area and conductivity of PEDOT:PSS contribute to the reduction of the series resistance of PSCs from 3.05 X cm2 to 2.11 X cm2 and improvement of FF and PCE.



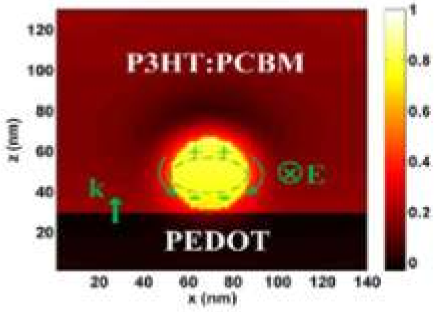


FIG. 2. (Color online) The schematic pattern for the plasmon resonance and charge distribution of a Au NP, as well as the near-field distributions for the vertically incident light with TE polarization in P3HT:PCBM.

FIG.1. (Color online) (a) J-V characteristics of the PSCs with NPs incorpo-rated into different layers under AM 1.5 G illuminations at 100 mW/cm^2. (b) Absorbance of the active layer for different NP doping structures. (device A: No NPs; B: NPs in PEDOT:PSS only; C: NPs in P3HT:PCBM only; and D: NPs in both P3HT:PCBM and PEDOT:PSS).

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Although electrical effects dominantly address the per-formance improvement when incorporating Au NPs only in PEDOT:PSS, the mechanism for PCE improvement is found to be different when NPs are incorporated into the active layer. As shown in Fig. 1(b), when NPs are incorporated into the active layer only (device C), absorption of the active layer increases over a wide wavelength range. From our the-oretical studies, we find that the absorption enhancement can be explained by LSPRs in the Au NPs excited by the TE polarized light. The dipoles generated in the Au NPs and the strong near field by LSPRs by Au NPs in the active layer are shown in Fig. 2. It can be observed that the strong near field distributes into the active layer and directly enhances the light absorption by the blended polymers of the active layer. Together the scattering effects of Au NPs coupled to wave-guide mode, J_{SC}

improves. Regarding electrical properties, hole-only devices indicate that hole mobility increases from 8.94 _ 10_4 cm^2/V s to 1.19 _ 10_^{3} cm^2/V s. Studies have shown that in P3HT:PCBM, electron mobility is higher than hole mobility and this carrier imbalance is detrimental to photovoltaic performan19. The increase in hole mobility allows more balanced charge transport in the active layer, thus improving the JSC and FF of the device. Improvement of efficiency of solar cell we use multijunction cell making by thin films. In this process we adjust many junctions in short thickness and solve problem thickness increased the efficiency comparatively decreases and efficiency higher rate incresed.21.

TABLE I. Photovoltaic parameters of the PSCs with NP incorporated in different layers under AM 1.5G illumination at 100 mW/cm^2. RS is derived from the slope of the current–voltage (J-V) curves under dark at 2 V. (device A: control device without NPs; B: NPs in PEDOT:PSS only; C: NPs in P3HT:PCBM only; D: NPs in both P3HT:PCBM and PEDOT:PSS).

Device	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)	R_S (X cm^2)
A	0.61 60.00	8.35 60.09	61.92 60.33	3.16 60.04	3.05 60.03
B	0.61 60.01	9.41 60.28	62.52 60.66	3.61 60.08	2.11 60.06
C	0.61 60.00	8.85 60.27	63.56 60.53	3.41 60.11	2.92 60.13
D	0.61 60.01	9.74 60.57	65.00 61.02	3.85 60.20	1.93 60.04

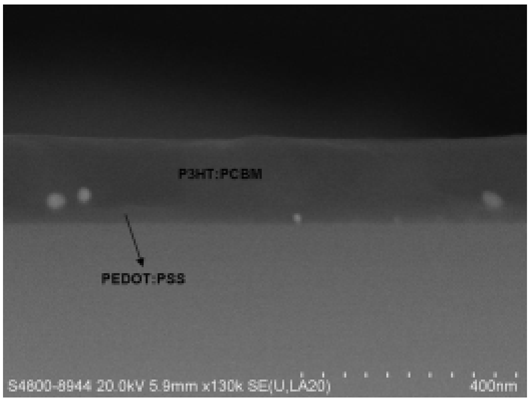


FIG- 3. Representative cross section SEM image of the film structure PEDOT:PSS þ Au NPs/P3HT:PCBM þ Au NPs

When Au NPs are doped into both PEDOT:PSS and P3HT:PCBM, PCE further increases to 3.85%. From hole-only devices, the hole mobility of P3HT:PCBM is determined to be _1.21 _ 10_3 cm^2/V s, which is similar to the case when NP is doped in the active layer only (1.19 _ 10_3 cm2/V s). From the cross section SEM images as shown in Fig. 3, Au NPs doped in the active layer are mostly located at the bottom of P3HT:PCBM (near to the interface with PEDOT:PSS), while the Au NPs doped to PEDOT:PSS are well embedded in the PEDOT:PSS layer. However, despite the fact that the active layer is adjacent to the PEDOT:PSS layer, the highly similar absorption spectra of devices C (Au NPs in P3HT:PCBM only) and D (Au NPs in both P3HT:PCBM and PEDOT:PSS) in Fig. 1(b) show that there is no clear interac-tion between the Au NPs in the active layer and those in the PEDOT:PSS layer. From the principle of optics, the absence of clear couplings between Au NPs in PEDOT and Au NPs in P3HT:PCBM is reasonable because the polarization direction of the electric field of vertically incident light is parallel to each device layer. Furthermore, we have shown that the improvement mechanisms when incorporating NPs in only PEDOT:PSS or P3HT:PCBM mainly originate from interfa-cial or bulk effects, respectively. As interfacial and bulk effects are two separate effects and optical coupling between NPs is not observed, we expect that the improvement of PCE from 3.16% to 3.85% is the accumulated improvements of addition of NPs into the individual layers. One essential aspect of PSCs is the transparent electrode, which must be electrically con-ductive while retaining excellent transparency. More impor-tantly, the work function (WF) of the electrodes should be tuned in accordance with the molecular orbital of the donor or the acceptor in order to minimize injection barrier at an-ode or cathode, respectively. Organic photovoltaics com-monly utilize indium tin oxide (ITO) as bottom anode, which is relatively expensive12 and chemically unstable.13 Moreover, ITO is rather brittle,14 which is not inherently compatible with the flexibility nature of organic materials.

RESULTS AND DISCUSSION

In this work, we focus on introducing an alternative approach to realize transparent graphene anodes. Based on earlier work,22 we report the use of very thin thermally evaporated gold (Au) nanoclusters with proper UVO treat-ments to facilitate efficient hole collection at graphene electrodes, which significantly benefits device performance while avoiding issues arising from PEDOT:PSS. We will investigate the effects of Au thickness and UVO treatments for optimizing device performance. Ultraviolet photoemis-sion spectroscopy (UPS) is conducted to further analyze the WF shift at the graphene/polymer interface modified by UVO-treated Au.

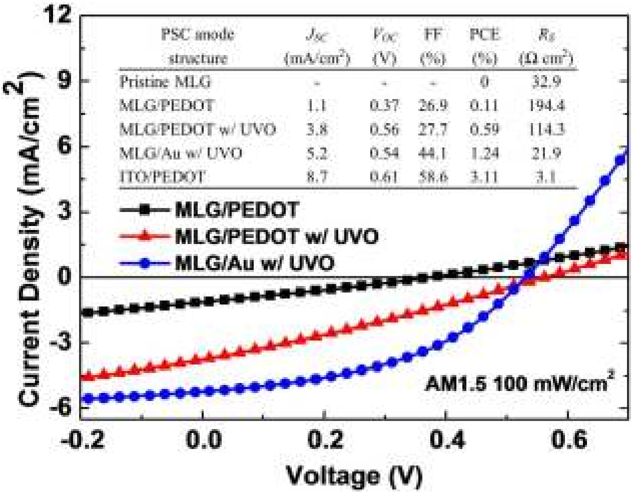
Multi-layer graphene (MLG) films were synthesized on copper foils by a chemical vapor deposition process.23,24 Sheet resistance (SR) of 1.2-2.2 kX sq 1 and average trans-mittance of 75-82% of the MLG were characterized by a four-point probe and spectroscopic ellipsometry, respectively

The MLG samples were treated with UVO (pre-UVO) and then transferred to vacuum chamber immediately for Au evaporation. The MLG/Au samples were treated by another UVO treatment (post-UVO) again. Meanwhile, MLG/ PEDOT samples were prepared for comparison, with PEDOT:PSS (Baytron Al 4083) directly spin-coated on MLG samples, followed by heating at 140 C for 10 min. While for MLG/PEDOT devices with UVO, MLG films were treated by UVO before PEDOT:PSS spin-coating. The prepared MLG samples were then transferred into a nitrogen-filled glove box for spin-coating the blend of P3HT and PCBM with 1:1 weight ratio (20 mg/mL each dissolved in 1,2-dichlorobenzene). Before annealing at 11^{0} C for 10 min on a hotplate, solvent annealing was utilized as described elsewhere.25 LiF (1 nm)/Al was thermally evapo-rated as the top cathode, which defines the device area as 0.03-0.05 cm^{2}. For reference, PEDOT-based ITO device with the structure of ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al was also fabricated. Current density (J)-voltage (V) charac-teristics were measured by using a Keithley 2635 source-meter and ABET AM 1.5 G solar simulator.26

Four samples including A: pristine MLG, B: MLG/pre-UVO (3.5 min)/Au (2 nm) without post-UVO, C: MLG/pre-UVO (3.5 min)/Au (2 nm) with 2 min post-UVO, and D: MLG/pre-UVO (3.5 min)/Au (2 nm) with 6 min post-UVO were prepared for UPS measurement using a He discharged lamp (He I 21.22 eV, Kratos Analytical).

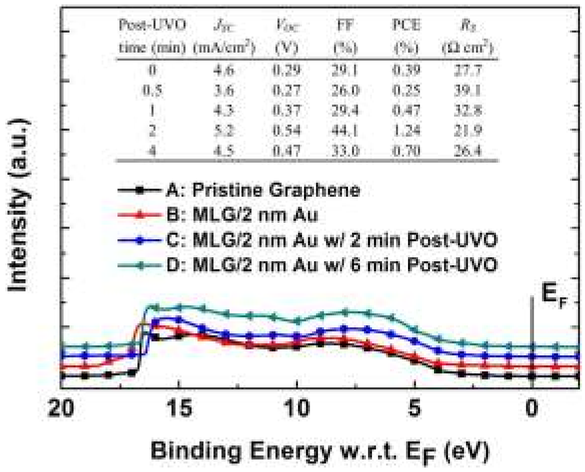
Fig. 4 shows the J-V characteristics and performance of a representative set of PSCs. Conventional ITO/PEDOT:PSS/ P3HT:PCBM/LiF/Al PSC is also listed for reference. RS is calculated from the inverse slope of the illuminated J-V char-acteristics at 1.0 V. For pristine MLG PSCs, no photovoltaic behavior is observed. While the introduction of PEDOT:PSS between MLG and polymer yields limited photovoltaic per-formance, conformal coating of aqueous PEDOT:PSS on the hydrophobic surface of graphene remains a challenging issue. The uniformity of PEDOT:PSS on MLG films is improved by applying UVO treatment in advance to convert the hydropho-bic graphene surfaces into hydrophilic ones.27,28 MLG/ PEDOT:PSS PSC with 8 min of UVO treatment demonstrates the best power conversion efficiency (PCE) (0.59%), with high open-circuit voltage (VOC) and increased short-circuit current density (JSC), yet, fill factor (FF) remains low. As stated such a treatment has negative impact on the conductiv-ity of MLG, which gives rise to RS increasing from 32.9 X cm2 to 114.3 X cm^2. While J_{SC} and VOC are initially enhanced by a short period of UVO treatment, such benefits are outweighed by the loss in conductivity when the treat-ment time is beyond the optimal value.

In this regard, we propose that a thin layer of Au with two separate short UVO treatments (pre-UVO and post- UVO) can enable graphene as an effective anode in PSCs by modifying the interface between graphene and active layer while retaining its conductivity. As a result, FF and J_{SC} are significantly enhanced due to notable reduction in RS, and VOC is largely improved owing



PSC anode structure	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)	R_S (Ω cm^2)
Pristine MLG	-	-	-	0	32.9
MLG/PEDOT	1.1	0.37	26.9	0.11	194.4
MLG/PEDOT w/ UVO	3.8	0.56	27.7	0.59	114.3
MLG/Au w/ UVO	5.2	0.54	44.1	1.24	21.9
ITO/PEDOT	8.7	0.61	58.6	3.11	3.1

FIG. 4. (Color online) Illuminated J-V characteristics of representative MLG PSCs. Inset shows the performance of respective MLG PSCs and ref-erence ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al PSC.



Post-UVO time (min)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)	R_S (Ω cm^2)
0	4.6	0.29	29.1	0.39	27.7
0.5	3.6	0.27	26.0	0.25	39.1
1	4.3	0.37	29.4	0.47	32.8
2	5.2	0.54	44.1	1.24	21.9
4	4.5	0.47	33.0	0.70	26.4

FIG. 5 (Color online) UPS spectra of different MLG samples. A: pristine MLG only, B: MLG/pre-UVO (3.5 min)/Au (2 nm) without post-UVO, C: MLG/pre- UVO (3.5 min)/Au (2 nm) with 2 min post-UVO, D: MLG/pre-UVO (3.5 min)/Au (2 nm) with 6 min post-UVO. Inset shows the perform-ance of MLG/Au PSCs with different post-UVO time and pre-UVO/Au evaporation of 3.5 min/2 nm.

to the WF tuning by UVO-treated Au. When a process of pre-UVO/Au evaporation/ post-UVO of 3.5 min/2 nm/2 min is utilized, the following PSC characteristics are obtained: high VOC of 0.52-0.54 V, increased JSC of 4.5-5.5 mA/cm^2, a greatly enhanced FF of 43-48%, and a best PCE of 1.24%, which is significantly bet-ter than that of MLG devices directly modified with UVO and PEDOT:PSS. In addition, the resistivity of MLG increases only by 40-50% (to 2-3 kX sq 1), achieving smaller increment compared with MLG treated by 8 min UVO for PEDOT:PSS spin-coating (>4 kX sq 1).

Our results show that pre-UVO treatment favors Au adhesiveness on MLG films and greatly benefits RS (see Ta-ble I). Indeed, when no pre-UVO is applied, the device behaves similar to pristine MLG device. When pre-UVO is increased from 1 min to 3.5 min, RS decreases from 67.2 X cm^2 to 21.9 X cm2 indicating improved interfacial contact. As a result, the devices show remarkable improvement over J_{SC} (from 3.4 mA/cm2 to 5.2 mA/cm^2) and FF (from 31.2% to 44.1%). Beyond the peak of performance at a treatment time of 3.5 min, pre-UVO degrades the conductivity of MLG electrode, with the derived RS increased substantially to 66.7 X cm^2 at a treatment time of 8 min, and a drop in J_{SC} and FF is observed.

Devices with different Au thicknesses are also fabri-cated and characterized. Here, an optimal PCE at 2 nm is reached. While thinner Au may not suffice for fully modify-ing graphene surface, Au layer of larger thickness progres-sively reduces J_{SC} since more incoming light is being blocked. We found that for Au layer under 2 nm, the loss in transparency is usually within a reasonable value of 6%. However, this loss goes up rapidly for 3 nm and beyond (>10%). It should be noted that UVO treatment has negligi-ble effect on the transparency of our MLG.

We also investigate WF of MLG samples with Au nano-clusters and UVO treatments. Their UPS spectra are shown in Fig. 2. WF is calculated from the energy difference between secondary electron cut-off and the Fermi level (EF).29 The WF of pristine MLG is found to be 4.4 eV. Evap-oration of Au (2 nm) on MLG has in fact reduced the WF to 4.1 eV attributed to "push-back" effect.30 After treating iden-tical sample with 2 min of post-UVO, the WF increases sig-nificantly to 4.8 eV, i.e., a 0.7 eV upshift in WF is achieved which offers a much more favorable interfacial energymatching with the highest occupied molecular orbital (HOMO) of P3HT (5.0 eV) and is beneficial in two aspects: (i) enhanced VOC due to better ohmic contact formed and (ii) lowered RS due to the reduced injection barrier. The benefits owing to the proper post-UVO are confirmed by the MLG/Au PSCs with different durations of post-UVO as listed in the inset of Fig. 2. Indeed, from no treatment to 2 min of post-UVO, VOC increases notably from 0.29 V to 0.54 V, while RS reduces from 27.7 X cm^2 to 21.9 X cm^2 with improved FF and JSC. Nevertheless, excess post-UVO negatively affects the WF of MLG. As observed from UPS, the WF of MLG/Au sample drops from 4.8 eV to 4.6 eV after 6 min of post-UVO, which may account for the decreased VOC in device treated with 4 min of post-UVO. Besides low-ering WF, excess post-UVO is also detrimental to the con-ductivity of graphene, resulting in performance degradation for post-UVO 4 min.

TABLE II. Performance summary of MLG/Au PSCs with different pre-UVO time and Au evaporation/post-UVO of 2 nm/2 min.

Pre-UVO time (min)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	PCE (%)	R_S (X cm^2)
1	3.4	0.52	31.2	0.55	67.2
2	3.9	0.51	32.0	0.64	63.6
3.5	5.2	0.54	44.1	1.24	21.9
5	4.3	0.52	42.6	0.95	50.5
8	3.6	0.52	32.8	0.61	66.7

While current MLG/Au devices have not yet reached competitive performance with PEDOT-based ITO device, there is clearly much room in making improvement from two notable aspects. In this work, the starting graphene for device study is undoped in order to fully investigate the effect of UVO-treated Au and is of multi-layer to ensure ac-ceptable electrical conductivity, at the cost of performance to a certain extent. Furthermore, chemical doping has been introduced as an effective method to modify the properties of graphene, benefiting both the conductivity31 and WF.32 Therefore, possible approaches for future improvement of MLG/Au PSCs may arise from a combination of employing better fabrication technique, introducing doping to graphene samples, and improving existing method.

In summary, a simple yet effective method of modifying the interfacial properties of graphene by depositing a thin layer of Au assisted by separate UVO processes is proposed and demonstrated as an alternative to conventional PEDOT:PSS for realizing efficient graphene anodes. With proper UVO treatments on MLG/Au (2 nm), PSCs with VOC of 0.52-0.54 V, JSC of 4.5-5.5 mA/cm^2, FF of 43-48%, and PCE up to 1.24% are obtained, exhibiting largely enhanced performance compared with MLG PSCs directly modified by PEDOT:PSS and UVO. With UPS characterization, the per-formance improvement can be understood from two aspects. First, RS is significantly reduced attributed to (i) favorable band alignment at the graphene/polymer interface, (ii) improving interfacial contact by Au layer, and (iii) short UVO durations. As a result, FF and JSC considerably increase. Second, injection barrier is reduced for better ohmic contact and thus a large VOC. Our demonstration of improvement in performance of graphene PSCs can promote further research efforts on realizing efficient and flexible gra-phene PSCs as the next generation organic photovoltaic device.

CONCLUSIONS

In conclusion, we have demonstrated _22% improve-ment in efficiency by incorporating Au NPs into all organic layers in the PSCs. The improvement is attributed to the accu-mulated enhancements in device performance due to addition of NPs into individual layers, while coupling between NPs in different layers is not observed. Our study shows that the advantages of incorporating NPs in individual layers can be utilized together to achieve larger increases of PSC perform-ance and these findings can be applied to the design of high efficiency NP-incorporated PSCs in the future.

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