Organic Solar Cells with Plasmonic Layers Formed by Laser Nanofabrication

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ABSTRACT

A method for the synthesis of metal nanoparticles coatings for plasmonic solar cells which can meet large scale industrial demands is demonstrated. A UV pulsed laser is utilized to fabricate Au and Ag nanoparticles on the surface of polymer materials which forms the substrates for plasmonic organic photovoltaic devices. Control of the particles' size and density is demonstrated. The optical and electrical effects of these embedded particles on the power

conversion efficiency are examined rigorously. Gold nanoparticles of particular size and spatial distribution enhance the device efficiency. Based on our findings, we propose design considerations for utilizing the entire AM1.5 spectrum using plasmonic structures towards enhancing the efficiency of polymer solar cells using broad spectrum plasmonics.

Organic photovoltaics (OPVs) are attracting significant interest, mainly due to the perceived lower cost, ease of manufacture based on roll-to-roll processing, mechanical flexibility, light weight suitable for portability, low cost materials and relatively high power conversion efficiencies comparable with a-Si:H. Despite these advantages, OPV devices suffer from inefficient light absorption due to the smaller thickness of the active layer, a fundamental requirement in OPVs to mitigate for low mobility and thereby lower extraction and transportation efficacies of the generated charges. Another performance bottleneck is the limited utilization of the entire AM1.5 spectrum, a limitation which arises from the physical properties of the materials, such as band gap of the photo-active layer. It has been demonstrated that structuring the front surface of a material with refractive index n with small micron sized pyramids can enhance efficiency by up to a factor of $4n^2$ by scattering light into different angles and thus increasing the absorption path.¹ However, this approach is difficult to implement in thin film OPVs, where the total active layer thickness is only a few hundreds of nanometers. In addition, structuring the surface does not allow one to utilize wavelengths which are not directly absorbed in the active material. These unabsorbed wavelengths can cause thermal effects at the back and front contact by exciting phonons. This thermal effect may lead to a further decrease in efficiency and life time, if careful precautions are not taken. Incorporation of metal nanoparticles (MNPs) with sizes smaller than the wavelengths of light in the AM1.5G solar spectrum to create and utilize surface plasmons for trapping the light into the photonic devices^{2, 3} is a promising

alternative solution.^{4, 5} It has been shown that the high contrast between the refractive index of metal and the surrounding medium works much like a very fine waveguide coupling efficiently the light (forward scattering) into the absorber.^{6, 7} The strong local electric field due to surface plasmons can enhance the exciton dissociation in OPVs contributing positively to power conversion.^{8, 9} Furthermore recent studies demonstrated that the NPs can lead to an enhancement of the OPV device structural stability as well.¹⁰⁻¹²

Methods to synthesize and incorporate MNPs are in abundance. Chemical synthesis can give precise control of size, however, it produces a lot of hazardous wastes,^{13, 14} with a requirement of an additional process step for deposition. Photo-reduction is similar to chemical synthesis although light is used to decompose the precursor and create metal nanoparticles.¹⁵ Thermal annealing of thin metal films inside ovens within an inert atmosphere requires extended time periods and the processing area is limited to the oven's dimensions, while the process is incompatible with plastic flexible substrates.¹⁶ e-Beam lithography allows for superior control over the minimum feature size but can only be used for small areas in practice due to severe time demand for processing. Herein, we present a method for fabricating metal nanoparticles of various sizes directly on polymers by rapid laser annealing of thin metal coatings. The method features rapid processing times in air or vacuum, allowing the raster scanning of large areas very fast, favorable for industrial production of OPVs on flexible substrates such as in roll-to-roll processes.¹⁷ The ability to control the metal nanoparticle dimensions,¹⁸ and the possibility to create alloy nanoparticles¹⁹ for tuning the surface plasmon resonance, linked with no chemical wastes, are distinct advantages of the process. Finally, nano-growth processes involving lasers are known for the excellent quality of produced nanostructures.²⁰

When a thin metal film is laser irradiated at adequate fluence, metal nanoparticles can be formed if the molten film is unstable on the substrate surface.²¹⁻²⁴ For very short light pulses in the order of nanoseconds (ns) the heating and cooling transient periods are extremely short.^{23, 25} This short time scale implies, that the laser-induced thermal effects are localized and heat diffusion is limited within an epidermic layer only on the surface of the irradiated area. Therefore this method allows fabrication of metal nanoparticles directly onto substrates made of temperature sensitive materials such as polymers without damaging their physical properties.

OPVs were fabricated on indium tin oxide (ITO) coated glass substrates with the following device structure: glass / ITO / Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) / metal nanoparticles / PEDOT:PSS / poly(3-hexylthiophene) (P3HT) : phenyl-c61-butyric acid methyl ester (PCBM) / bathocuproine (BCP) / Al as shown in Figure 1. All substrates were initially cleaned by ultrasonication in water, acetone, isopropyl alcohol for 10min respectively, and subsequently blow dried with nitrogen. Oxygen plasma treatment was applied for 5 mins to further clean the samples and enhance the ITO electrical properties.²⁶ PEDOT:PSS from Baytron was spin cast on top to form the first layer with an average thickness of 35nm. The substrates were annealed for 10min at 150 °C in air and transferred into a thermal evaporator for Au deposition. A thin gold layer was deposited on four substrates at different thickness ranging from 0.6, 1, 3 and 5nm at a deposition rate of 0.2Å/sec. Thereafter all substrates were placed on a translation stage set to move at a speed of 60mm/min where they were laser annealed in air with a 248 nm KrF Excimer pulsed laser at the fluence of 53mJ/cm² and repetition rate of 20Hz to fabricate metal nanoparticles. A second PEDOT:PSS layer was applied subsequently by drop casting and spinning at 8500rpm each substrate to create a thin film of ~8nm followed by thermal treatment for 10min at 150 °C in air. The substrates was then transferred into a nitrogen

filled glove box and solution with a blend of P3HT:PCBM (20mg:20mg) in 1ml of o-dichlorobenzene was spin cast on top of the second PEDOT:PSS layer. The stratified structure was dried at 120 °C for 10min and films of BCP (7nm) and Al (90nm) evaporated through a shadow mask to form the back contact (Figure 1g). The current density-voltage (J-V) characteristics were measured with a Keithley 2400 source-meter under AM 1.5 G using an Oriel solar simulator and with an irradiation intensity 1000W/m^2 . A calibration cell from Newport was used to calibrate the solar simulator intensity. The external quantum efficiencies of the devices were acquired with a Bentham PVE300 photovoltaic characterization system. The Hall mobility of the PEDOT:PSS with Au nanoparticles were measured using a PCB SPCB-01 Hall effect probe from ECOPIA. The scanning electron microscopy (SEM) images and energy dispersion X-ray (EDX) spectrum were acquired with a Quanta 200 F microscope from FEI. The photoluminescence (PL) of the samples was measured with a Cary Eclipse spectrometer from Varian exciting them with a beam at 570nm wavelength. For the Raman measurements, a Renishaw micro-Raman 2000 system with a 782 nm laser at 4mW was used. A (50X) optical lens was used to focus the laser down to approximately $1\mu\text{m}$ diameter spot. The detector integration time was set at 1sec and 50 accumulations at the same location were acquired to improve the signal-to-noise ratio.

Figure 2 a-e shows SEM images of MNPs formed on top of PEDOT:PSS layer after laser annealed at 53mJ/cm^2 for all Au films with thickness 0.6, 1, 3, and 5nm, respectively. An EDX study on a representative film with the initial Au thickness of 1nm revealed that Au particles exist on the substrates (Figure 2 inset).

Analyzing the NMP layers one can observe that, the irradiated thin Au films with 0.6 and 1nm thickness produced large particles with wide separations, while for thicker Au films of 3 and

5nm, dense nanoparticle films with smaller size particles were produced. For thick metal films, the energy is mainly absorbed in the metal, breaking the initial film to small droplets. Due to the very short solidification time small particles are formed without any aggregation between them. Conversely, in 0.6 and 1nm thin films, the lower metal thicknesses allow higher transparency. Hence, extra energy is absorbed into the PEDOT:PSS layer underneath raising its temperature. That accumulation of extra thermal energy in the substrate subsequently decreases the cooling rate, allowing extra time for aggregation of small particles into bigger ones and consequently particles with longer separation distances are formed.

The PEDOT:PSS layer serves a dual functionality. First, it serves as an electron blocking layer for organic solar cells in the active layer and secondly, as a buffer layer to prevent ITO being thermally damaged from UV laser irradiation and lowering its conductivity. Furthermore, the second PEDOT:PSS thin layer (~8nm) spin coated on top of the metal nanoparticle films (MNFs) was used to minimize the film roughness and prevent recombination of electron-hole pairs on the surface of metal nanoparticles. This extra film was kept very thin to minimize the degradation of surface plasmon induced localized electric field.²⁷

Figure 3 displays the optical surface plasmon resonance (SPR) signature for all substrates with different Au particle sizes, as well as the current-voltage curves and the external quantum efficiency (EQE) of solar cells made with them. For large particle MNFs in Figure 2 b, c with 65nm and 45nm diameters, respectively, and wide spatial separation, the absorption is relatively low (Figure 3 a). The lower values at long wavelengths, which were recorded for MNF with 45nm particle diameters compared to the reference substrate (ITO coated glass with spin coated and laser annealed two PEDOT:PSS layers), can be attributed to forward scattering, which dominates in the extinction of particles with big diameters. Vice versa for dense MNFs with

small diameter particles of 22nm and 15nm (Figure 2 d, e), the absorption component in the particles' extinction is prominent. The characteristic peak near 370nm observed at all absorption curves (Figure 3 a) and can be attributed to the PEDOT:PSS.²⁸

The hypothesis that forward scattering at long wavelengths is stronger for MNFs with big particles while absorption is dominant at small particles was verified by a theoretical model (Figure 3 b, c). The scattering and absorption components of extinction were calculated with a simulation tool²⁹ by considering a single Au particle with diameter equal to the real ones acquired from the SEM images for each different substrate. The model simulated the particles embedded in a dielectric medium with refractive index 1.53 similar to that of PEDOT:PSS,³⁰ and is shown in Figure 3 b, c.

The fabricated plasmonic cells and the reference one were characterized under AM1.5G at 1000W/m^2 to determine their performance. Figure 3 d, e shows the current density-voltage (J-V) and the EQE for each cell.

The samples with the relatively larger particles 65nm and 45nm diameter, show an enhancement in the short circuit current density, compared to the reference cell (Figure 3 d). An analysis of the EQE measurements is displayed in Figure 3 e, and shows the photocurrents for the films with big particles (65, 45nm) to be higher compared to reference for almost the entire active spectrum of the photoactive film. The photocurrent reaches its maximum near 600nm ~ 650nm, the region where the scattering is maximum in agreement with the simulations (Figure 3 b, c). For the samples with small particles (22, 15nm) the generated photocurrent is reduced below the recorded response of the reference cell for wavelengths between (400nm and 650nm). This effect could be due to strong absorption of light occurring at nanoparticles, a hypothesis which agrees well with our simulations. Thus, a lower number of photons interact with the

photoactive layer. Intriguingly, enhanced photocurrent is observed for all films with metal nanoparticle in the region 300nm ~ 400nm in comparison with the reference. That enhancement could indicate that the charges are extracted more efficiently from the films with metal nanoparticles, an assumption which is verified by the mobility measurements for the PEDOT:PSS films. Indeed as shown at Table 1 the enhanced charge extraction in the PEDOT:PSS films doped with the relatively big particles is prominent, attributed to the lower sheet resistance, as opposed to the small particles where they exhibit higher sheet resistance⁴ with concomitant decrease in the film's mobility.

Thus, the current density enhancement can be attributed at two parameters. First, the improved extraction and collection of charges as a result of the higher mobility of nanoparticle containing PEDOT:PSS films. This can be seen in the EQE as a photo-current enhancement through the entire photoactive spectrum of the P3HT:PCBM blend. Second, for samples with big particles (65, 45nm) the increased number of photons penetrate into the active layer, due to enhanced forward scattering components agreeing with previous studies.³¹ This increases the number of photo-generated electrons and induces a characteristic EQE peak near the surface plasmon resonance (630nm) of particles.

Table 1 Electrical characteristics for each different cell and the mobility of the Au doped PEDOT:PSS layers for all substrates prior to the active layer deposition. For all samples the active area is 0.73cm².

<i>Particle diameter / Film thickness(Au)</i>	<i>Effic. (%)</i>	<i>V_{oc} (V)</i>	<i>J_{sc} (mA/cm²)</i>	<i>FF (%)</i>	<i>PEDOT:PSS film mobility (cm²/V s) prior to active layer deposition</i>
65 nm / 0.6 nm	2.42	0.54	8.30	54.08	2.070E+01
45 nm / 1 nm	2.61	0.54	7.76	62.31	2.376E+01
22 nm / 3 nm	2.21	0.52	7.17	59.88	2.041E+01
15 nm / 5 nm	2.37	0.52	7.37	62.30	1.913E+01
Ref / 0 nm	2.40	0.530	7.60	59.00	1.856E+01

The difference in refractive index between the Au particles and PEDOT:PSS forms a planar wave guide⁶ managing efficiently the incoming light. In addition, the strong local electric field can enhance the exciton dissociation in the active layer, a concept which has been proven experimentally at other studies.³²⁻³⁴ On the contrary, in dense particle films the absorption of light at metal nanoparticles near the surface plasmon resonance (SPR) dominates. This results in reduced number of photons in the active layer (Figure 3 e), affecting the total performance of the solar cells. The exciton dissociation in dense films with small nanoparticles (22, 15nm) is better than that of the reference, as the PL indicates lower quenching (Figure 4 a) in agreement with previous studies.^{35, 36} The lower PL quenching can be attributed to the strong local electric field at the particles' vicinity which promotes the exciton dissociation.³²⁻³⁴ Furthermore, the high density of particles with small separation distances causes an extra shadowing effect, undesirable for high efficiency photovoltaics.

The PL study verified that extra quenching occurring in all films with particles compared to the reference, which is a desirable effect for enhancing the short circuit current. The lower quenching in films with big particles strengthens the assumption that the power conversion enhancement is mainly due to the dominant scattering effect for the large particles (Figures 3, 4)

and with only a small contribution of the SPR generated E-field for those substrates. Furthermore, the higher mobility at PEDOT:PSS films doped with big Au particles (Table1) provides a better charge transportation mechanism minimizing the current losses.

The higher quenching for dense NMFs of relatively small (15nm) Au particles and the relatively higher generated current compared to the film with slightly bigger particles (22nm), is a consequence of the stronger SPR E-field at small particles where the absorption is dominating. However, the reduced photon flux which reaches the active layer due to the SPR absorption and shadowing effect from nanoparticles leads to reduced efficiencies.

A Raman study (Figure 4 b) was performed to determine the crystallization levels in the active layer.³⁷ A higher crystallization may be expected in the devices with higher metal quantities in PEDOT:PSS due to the higher heat capacity and thermal-conductivity. This could result in higher heat transfer rates during the cell annealing process enabling enhancement of the phase separation in the blended active layer with consequently higher performances. A 782nm laser was used as a probe light for the measurements. The wavelength of the probe light was chosen carefully to be as far away from the SPR to eliminate signal distortion from effects such as surface enhanced Raman spectroscopy.

The Raman signal for different metal thickness indicates that the crystallization and phase separation were similar for all substrates, independent of the metal nanoparticles size and density in the PEDOT:PSS film. Thus, it is suggested that the variations in power conversion efficiencies are purely due to the optical and electromagnetic modes which metal nanoparticles exhibit, as well as the improved charge extraction consequences of the enhanced mobility at the PEDOT:PSS films containing metal nanoparticle, other than any physical change in the PEDOT:PSS.

Having demonstrated that metal nanoparticles can enhance or suppress the power conversion by interacting with the impinging light, a further study was performed to determine their role in the electron-hole recombination process, critical to achieve the optimum power conversion. It has been reported by different groups that plain metal particles on the front contact³⁸ or inside the active layer³⁹ of photovoltaic cells can degrade their efficiency. This is an effect which is debated in the plasmonic solar cells community. Considering that the local field from SPR rapidly dissipates with distance, one would expect the shorter the distance between the nanoparticles and the active layer, the stronger the expected effect due to the SPR electric field would be.

To investigate this hypothesis, a series of plasmonic substrates were prepared as described previously with identical initial metal film thickness of 5nm Ag. After laser annealing, metal nanoparticles with an average size of 17nm were produced. The substrates were coated with a second PEDOT:PSS layer using different spin coating speeds of 5500, 6500, 7500 and 8500 rpm to achieve different thicknesses. One substrate was left without a second PEDOT:PSS layer. Ag particles were used instead of Au, in this case, because they exhibit a stronger SPR field.⁶ Hence the effect should be stronger. The corresponding absorption spectra are presented in the supporting information online at Figure S1. As expected, the absorption in the substrate without the second PEDOT:PSS layer is lower compared to the films with the additional layer. Interestingly, for the device with no second layer of PEDOT:PSS, the efficiency was lower compared with those that have the thin PEDOT:PSS second layer (Figure S1, Table T1).

The film with the thinnest PEDOT:PSS (~8nm) for second layer spun at 8500rpm gave the highest performance. This sample had the best fill factor among the samples with the additional layer. Indeed, the particles in that sample were closer to the active layer, compared to those formed with thicker second PEDOT:PSS layer. Thus one should expect that in this sample the

SPR E-field is stronger at the active layer, thus the effect from particles SPR should be stronger and higher efficiency should be observed. Increasing the thickness of the second PEDOT:PSS layer damps the efficiency, indicating that the thickness of PEDOT:PSS is affecting both the fill factor of the solar cell as well as the effect of surface plasmon induced E-field at the active layer, since the E-field degrades very fast with distance.²⁷

Analyzing more carefully the device structure, the active layer is a blend of two semiconducting materials, therefore for the front contact surface it is expected that both donor and acceptor materials coexist in the same layer (Figure 4 d). For a device without a second PEDOT:PSS layer, although the surface plasmon field can enhance the exciton dissociation, the areas where a metal nanoparticle is at the boundary between donor and acceptor region, it can act as an ohmic link between the two semiconducting materials. Vice versa at devices with the second layer, the PEDOT:PSS acts as an electron block layer reducing the probability of electron - hole recombination to occur on MNP's surface.

Thus, the decrease in cell's performance which observed in some study cases by incorporating metal nanoparticles it is expected to be due to holes and electrons recombining at the metal nanoparticle, reducing the output current. Furthermore from the strong light absorption into small particles, at wavelengths where the photoactive layer is active, leading to reduces photocurrent.

Summarizing, it has been demonstrated experimentally and verified theoretically that metal nanoparticles produced by in-situ laser annealing of metal thin films deposited on the front contact of a polymer heterojunction solar cell can enhance or suppress the efficiency of the solar cell depending on the NMPs size, spacing, density in the film, and their distance from the photoactive layer. Intuitively, we can note some key features for designing broadband polymer plasmonic solar cells.

Metal nanoparticles independent of their position (front-back electrode, photoactive layer) into the solar cell structure should be isolated from the active material with a very thin layer such as PEDOT:PSS or by encapsulating the MNPs with a dielectric coating to facilitate strong local surface plasmon electric field but prevent recombination of dissociated electron-hole pairs at their surface.

Metal nanoparticles placed at the front contact (before the active layer) should generally be large where the scattering component dominates to minimize losses from absorption of light in particles (Figure 4 c, d). Generally, Au nanoparticles have stronger scattering mode than absorption.⁶ In addition, the Fermi level of Au align well with PEDOT:PSS 4.7-5.5 eV, favorable for the front contacts minimizing the probability for charge trapping. Calculations performed to optimize particle size for the specified surrounding material allows efficient waveguide modes (45-65nm for PEDOT:PSS based on our experimental data) as well as wide space distributions to minimize possible shadowing effects.

Nanoparticle in the active layer have to be small in order the absorption mode to dominate and stronger electric dipole to have effect from theirs SPR enhancing the efficiency of exciton dissociation and consequently the current intensity. The optimum size of nanoparticles should be calculated in accordance with the type of encapsulating dielectric for optimum results. Generally, Ag metal nanoparticles have stronger absorption and local SPR. Although Ag it is good material for particles with SPR, the ideal particles for exciton dissociation enhancement should exhibit strong surface plasmon resonance at wavelengths away from the useful absorption spectrum for the active layer (Indicated with blue in Figure 4 d). That can allow the entire AM1.5 G spectrum to be utilized and to minimize the undesirable thermal effects from wavelengths which are not

absorbed in the active layer. Such particles with SPR in the infrared spectrum have been reported before with ITO.⁴⁰

Nanostuctures at the back contact should be a combination of both big and small sizes, carefully designed to achieve the desired effects. For small features, the absorption mode dominates, enhancing the surface plasmon waves developed across the boundary of the back metal contact and the photoactive layer,⁴¹ enhancing the exciton dissociation with the strong E-field. Large particles would increase the scattering and redistribution of the unabsorbed photons in the active layer at different angles, increasing the active path and therefore the probability that photons are absorbed. Assuming that these particles are all part of the back contact, careful consideration must also be taken regarding the materials used, to avoid misalignment of the electronic band level, which can introduce charge trapping states and therefore reduction in the I_{sc} and degradation in the V_{oc} .

ASSOCIATED CONTENT

Supporting Information

Optical and electrical characterization curves for the devices with Ag nanoparticles are supplied as supporting information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ABBREVIATIONS

Organic photovoltaics (OPVs), metal nanoparticles (MNPs), indium tin oxide (ITO), Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS), poly(3-hexylthiophene) (P3HT), phenyl-c61-butyric acid methyl ester (PCBM), bathocuproine (BCP), current density-voltage (J-V), photoluminescence (PL), scanning electron microscopy (SEM) images and energy dispersion X-ray (EDX), surface plasmon resonance (SPR), external quantum efficiency (EQE)

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Figure 1:

Figure 2:

Figure 3:

Figure 4: