

# Pulsed laser deposition of a dense and uniform Au nanoparticles layer for surface plasmon enhanced efficiency hybrid solar cells

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Devices based on organic photovoltaic (OPV) materials represent a very intriguing alternative to inorganic solar cells due to their high versatility in mechanical properties, simple process-ability, and cost effectiveness[ 1]. Conjugated polymers have emerged as promising materials, due to their high absorption coefficients in the visible region, allowing capture of suitable solar spectrum intensity with small film thicknesses. Bulk heterojunction (BHJ) configuration with a light absorbing polymer (donor) and a soluble fullerene (acceptor), ensures a better absorption/charge collection due to the intermixing between the two components. However, the thickness of the active layer is often limited by the low charge-carrier mobility and short exciton diffusion lengths of most polymers, resulting in the absorption of a small fraction of the incident sun light[ 2]. The inclusion of metal nanoparticles (NPs) has been proposed as a possible route to improve the light trapping in the active layer without increasing its thickness that would inevitably affect the device resistance[ 3]. Particularly suitable for these applications is Au, most likely because the surface plasmon resonance (SPR) can be tuned from the visible ( $\lambda \geq 500nm$ ) to the near IR range by changing the NPs dimensions, shape, substrate and/or surrounding media of metals in the UV. The control of the shape, dimensions, and number density of the NPs is essential to exploit their optical and electrical properties[ 4]. Pulsed laser deposition (PLD) is well known for its capability of producing a finely tailorable, highly dense and uniform layer of metal NPs on a large variety of substrates[ 5], by controlling the plasma expansion dynamics via the laser parameters and the chamber configuration [4]. In our work, we have studied the effect of the in-

clusion of Au NPs produced by PLD in the active layer of an OPV cell in diffused bilayer geometry, fabricated by a sequential coating of the donor [poly-(3-hexylthiophene), P3HT] and acceptor ([6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester, PCBM) from orthogonal solvents. This solution-based technique gives rise to a graded BHJ, resulting from the diffusion of the PCBM in the P3HT layer [ 6]. The device architecture of the BHJ solar cell is ITO/PEDOT:PSS/(Au NPs)/P3HT:PCBM/LiF/Al. The poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) hole transport layer was spin-coated at 4000rpm for 60s on a indium tin oxide (ITO)-coated glass substrate, with a sheet resistance of  $15\Omega cm^{-2}$ . ITO acts as transparent anode. The NPs have been deposited by PLD in vacuum ( $5 \times 10^{-6}mbar$ ) at room temperature. The deposition was carried out by focusing an ArF laser beam [ $\lambda=193nm, \tau=20ns$  full width half maximum (FWHM)] to a spot of  $1.1 \pm 0.1mm^2$  on a 99.99% Au target at an angle of  $45^\circ$  with respect to the target normal. The laser repetition rate was set at 10Hz, the fluence at the target site was  $\sim 2.5Jcm^{-2}$  and the number of pulses was 300. The ITO/PEDOT:PSS substrates were placed in front of the target. After the deposition of the Au NPs, the P3HT solution in chlorobenzene (CB) was spin-casted onto the PEDOT:PSS layer and dried in the glove box. Then, the PCBM layer was spin-casted from dichloromethane. The P3HT:PCBM layer has an overall thickness of 100nm. The device fabrication was completed by thermal evaporation of 0.6nm LiF and 100nm Al as the cathode. For comparison, the device without Au NPs was fabricated following the same fabrication procedure. Morphological and structural characteriza-

tion of the Au-NPs was performed by AFM, SEM and TEM investigations. SEM image of the sample (Fig. 1a) demonstrates that the nucleation of the NPs has been obtained uniformly in the substrate surface, and that a highly dense coverage has been achieved. The bright field TEM image of the NPs (Fig. 1b) shows a series of rings typical of polycrystalline material, whose lattice spacings are compatible with gold. It can be seen that the Au NPs have mean diameter of  $1.8 \pm 0.4nm$  or  $5.2 \pm 2.2nm$  [7]. AFM analysis on the device without and with Au NPs[7] shows no significant changes in roughness induced by the deposition of the Au NPs. The  $J - V$  characteristics of the device were measured under AM1.5G  $100mWcm^{-2}$  illumination using a calibrated Spectra Physics Oriel 150W Solar Simulator. The photon to current efficiency (IPCE) was measured by using a 300W Xe Arc light source coupled to a monochromator to create the scanning light. A dual-channel Merlin lock-in amplifier was utilized for the sensitive optical power and current measurements. The structure of the hybrid organic-inorganic solar cell is depicted in the inset of Fig. 2. The current density ( $J$ ) versus voltage ( $V$ ) characteristics of the device is shown in Fig. 2. With the Au NPs between the PEDOT:PSS and the P3HT:PCBM layers, the open-circuit voltage ( $V_{OC}$ ) remains unchanged with respect to the undoped cell, the fill factor (FF) slightly increases from 47 to 49%, and the short-circuit current ( $J_{SC}$ ) increases significantly from  $7.57$  to  $8.96mAcm^{-2}$ , resulting in an enhancement of 18%. Consequently, the power conversion efficiency (PCE) improved from 1.98 to 2.41%, where the 22% enhancement was mainly ascribed to the contribution of  $J_{SC}$ . The  $J_{SC}$  improvement results from the absorption enhancement, as it can be seen from the extinction spectrum of a solar cell with and without Au NPs (Fig. 1c and Fig. 1d, respectively). The absorption in the region  $350-650nm$  is enhanced by 20% for the sample with the Au NPs. In conclusion, we can state that the PLD technique allowed to produce a highly dense and uniform layer of small NPs, avoiding post-nucleation functionalization and/or thermal annealing procedures. The tailored morphology of the NPs ensures that the reflection/scattering phenomena are negligible, as well as the roughness introduced at the interface between PEDOT:PSS and P3HT:PCBM layers. The optical absorption and the incident to photon current efficiency of the hybrid device increase with respect the OPV, and fully recover the intensity and the spectral evolution of the SPR band related to the Au NPs, thus suggesting that the higher performance is mostly related to

SPR-induced field enhancement.

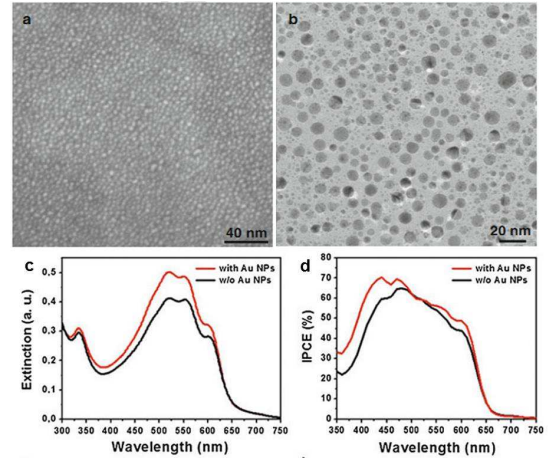


Figure 1. **a** SEM image of the Au NPs layer on PEDOT:PSS. **b** Bright field TEM image of the Au NPs on PEDOT:PSS deposited on a carbon coated grid. **c** Extinction and **d** IPCE measurements on the devices with and without Au NPs.

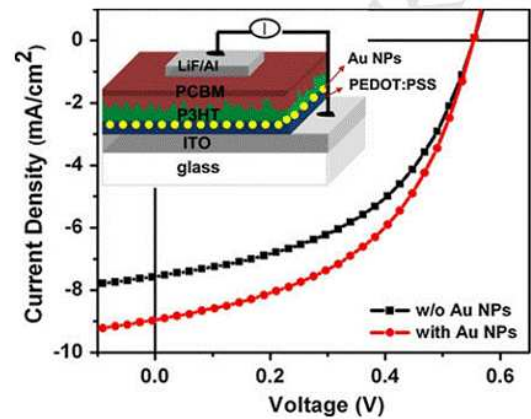


Figure 2. Comparison of I-V curves of the solar cells with and without Au NPs between the PEDOT:PSS and the P3HT:PCBM layers. The inset shows a sketch of the device configuration.

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