

# Enhancement efficiency of polymer solar cells by incorporating metal oxide nanoparticles

Abdullah A. Hussein<sup>1</sup>, Waleed A. Hussain<sup>2</sup> Hussein F. Al-luaiby<sup>2</sup> and Assel K. Hassan<sup>3</sup>

1. Department of Material Science, Polymer Research Centre, University of Basrah

2. Department of physics, college of education, Basrah University

3. Materials and Engineering Research Institute, Sheffield Hallam University

\* E-mail of the corresponding author: [amanar\\_2005@yahoo.com](mailto:amanar_2005@yahoo.com)

## Abstract

Gold nanoparticles (AuNPs) deposited at the interface of the hole-collecting buffer layer [poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)(PEDOT:PSS)] and regioregular poly(3-hexylthiophene) : [6,6]-phenylC61-butyric acid methyl ester (rr-P3HT):(PCBM) active layer were found to significantly increase solar cell performance. The photo-physical properties of these devices incorporated with AuNPs with different space distributions in the interface of PEDOT:PSS buffer layer and P3HT:PCBM active layer are investigated. We find that, the optical property is improved as the AuNPs are large enough to penetrate into the active layer and the performance of Photovoltaic solar cells (PSCs) with large AuNPs can benefit from the improved hole collection efficiency. The efficiency enhancement for the device with a PEDOT:PSS: AuNPs film is more significant than for the device with PEDOT:PSS film.

**Keywords:** PEDOT:PSS, Buffer layer, P3HT:PCBM, Gold oxide nanoparticle.

## 1. Introduction

In the past few years, The effective conversion of solar energy into electricity is becoming a very important issue in terms of rising energy costs and needs. Polymer photovoltaic cells offer a great technological potential as renewable energy sources for electrical energy and offer easily manufactured, compatibility with flexible substrates and low-cost alternative to the traditional inorganic-based solar cells [1–6]. Various strategies have been adapted in the fabrication of efficient polymer photovoltaic cells. In the past, bulk-heterojunction photovoltaic cells (BHJ) made by blending p-type (p-conjugated polymer) with n-type (fullerene) materials were studied extensively [7].

To significantly enhance the photovoltaic efficiency is still one of the most important tasks for the polymer photovoltaic cells. The light to electricity conversion process involves four steps: (1) light absorption and exciton formation, (2) exciton dissociation, (3) charge transport, and (4) charge collection. These four steps are affected by the chemical structure of active materials, that is, the donor and the acceptor, and the morphology of the active polymer film [8–12]. P3HT and PCBM become popular polymer donor and organic acceptor for polymer photovoltaic cells due to their easy availability, excellent solubility in common organic solvents, and high mobility. Great progress has recently been made on P3HT:PCBM photovoltaic cells.

Although many reports on the metallic NPs enhanced PSCs the exact understanding on the photovoltaic performance changes remains inconclusive. On one hand, several studies have shown that the absorption of photoactive conjugated polymer in the active layer can be enhanced due to the plasmonic scattering or near-field enhancement caused by localized surface plasmon resonant (LSPR) effect of the metallic NPs (mainly enhance the optical property) [13,14]. On the other hand, many of reports indicated that the strong near field around NPs due to LSPR effect mainly distributes laterally along the PEDOT: PSS layer, leading to minimal enhancement of light absorption in the active layer. Thus they contributed to the improvement of power conversion efficiency (PCE) to the enlarged interfacial area between active layer and PEDOT: PSS buffer layer as well as the improved PEDOT: PSS conductivity (mainly improve the electrical property) [15].

Organic solar cells are very promising because of their high absorption coefficient, their compatibility with flexible substrates and their low manufacturing cost. Some disadvantages such as their short lifetime due to instability in contact with oxygen or humidity [16,17] and their poor efficiency need to be improved. Our work aims to improve efficiency by increasing the absorption inside an organic material. We do so by incorporating metallic nanoparticles inside the absorbing layer, thus generating surface plasmon (SP). These SP produce evanescent waves by a strong coupling between an incident electromagnetic wave and the electrons of the conduction band of a metal occurring when the frequency of an incident wave is equal to the frequency of the plasmon resonance.

This effect leads to a strong increase in the electromagnetic field around metallic particles, which makes it possible to improve absorption in the surrounding medium. It is known that the resonance frequency varies according to the form and the diameter of the nanoparticles (NPs), the period of the considered grating, the

material composing the nanoparticles and the optical constants of the surrounding medium [18]. Gold, silver and metal oxide nanoparticles placed in air have their resonance frequencies in the visible spectra. Here, we used metal oxide nanoparticles. The inclusion of these nanoparticles also enables light to be scattered, which is especially useful in the intermediate layer.

## 2. 2. Experiment

### 2.1. Photovoltaic device fabrication

Each glass substrate was coated with a transparent ITO electrode (120nm thick, 25Ω/sq sheet resistance), washed thoroughly in acetone, isopropyl alcohol, and distilled water, dried under nitrogen gas, heat dried, and finally treated by ozone-ultraviolet cleaner for 10min. The prepared PEDOT:PSS(Sigma-Aldrich) solution was mixed with AuNPs (5 μm). The concentration of AuNPs in PEDOT:PSS 0.5 wt.%. Then this solution was spin coated at 2000rpm on onto ITO substrate (30nm) which was pre-coated on the surface of the active layer. Thermal pre-annealing was conducted at 150 °C for 15min on a dry oven in ambient air. The mixed solutions consisting of rr-P3HT,(10 mg mL<sup>-1</sup>, Sigma-Aldrich) and PCBM (10mgmL<sup>-1</sup>, Sigma-Aldrich) in cosolvent by mixing chlorobenzene and chloroform (CB:CF) solvent in 1:1 weight ratio were then spin-coated at 800rpm on the PEDOT:PSS layer in air. The thickness of the active layer is ~180 nm. After spin-coating photoactive layer, Al (40nm) was thermal evaporated under high vacuum of ~ 2×10<sup>-5</sup>Pa with a rate of 0.1 nm s<sup>-1</sup> onto the polymer layer as a cathode to create a device with an active area of 9mm<sup>2</sup> defined by a shadow mask. The final device structure is ITO/PEDOT:PSS (Au)/P3HT: PCBM/Al, as shown in Fig.1(a,b&c). Finally the post-annealing of the completed photovoltaic cells was carried out at 150 °C for 20 min.

### 2.2 Device characterization

The current density–voltage (J–V) characteristics of devices were measured with a computer-programmed Keithley 2400 source/meter, which simulated the AM1.5 sunlight with energy density of 100mWcm<sup>-2</sup>. Films were prepared by spin coating PEDOT:PSS (Au) and P3HT: PCBM solution on glass substrates for UV–vis absorption spectroscopy and atomic force microscopy (AFM). The UV–vis absorption spectra of the polymer films were taken with a Varian Cary 5000UV–VIS–NIR spectrometer. The light intensity for the solar simulator was calibrated with a standard photovoltaic (PV) reference cell. Incident photon to electron conversion efficiency (IPCE) curves were measured with a Stanford lock-in amplifier 8300unit. The AFM images of the polymer films were acquired using a BRUKER NanoScope IV Multi-Mode Adapter AFM with the tapping mode. The film thickness was measured by spectroscopic ellipsometry(M-2000). The PCE (η) is described by  $\eta = FF \times (V_{oc} \times J_{sc}) / P_{light}$ , where the FF is defined as  $FF = (I_{max} \times V_{max}) / (I_{sc} \times V_{oc})$ ,  $I_{max}$  and  $V_{max}$  are the current and voltage at the maximum power point, and the  $P_{light}$  is the power of incident light. The PCEs of the pristine and hybrid OSCs were estimated to be 5% for AuNPs concentration.

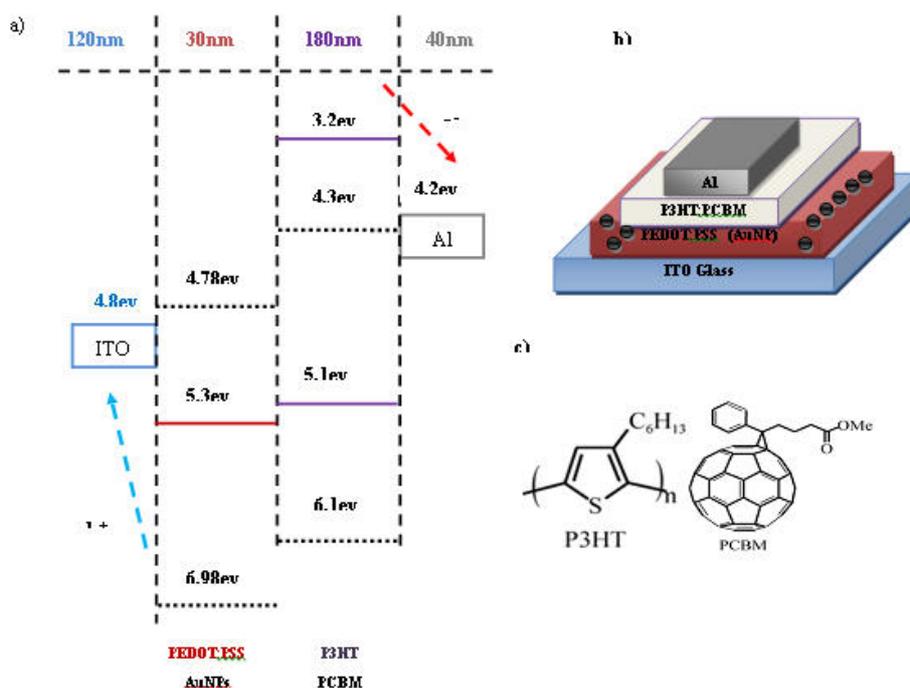


Fig.1. (a) The energy level diagram. (b) Device structure of the organic solar cell. (c) Chemical structure of PH3T and PCBM.

### 3. Results and Discussion

To investigate the plasmonic effects of the AuNPs on the OSCs, the photovoltaic characteristics of OSCs with and without AuNPs were measured and compared. Fig. 1a shows a schematic illustration of the fabricated plasmonic OSCs consisting of a BHJ P3HT:PCBM composite active layer and the PEDOT:PSS with the PSS-coated Au NPs. We investigated the effect of AuNPs on the photovoltaic characteristics of the OSCs. Thin films of ITO/PEDOT:PSS(Au)/P3HT:PCBM/Al and ITO/ PEDOT:PSS/P3HT:PCBM/ Al for UV-vis absorption studies were prepared on ITO coated glass substrate. UV-vis absorption spectrum was presented in Fig. 2(a,b). The net absorbance of the PEDOT:PSS layer with the incorporated AuNPs was obtained as shown in Fig. 2(a). We observed that, No enhanced light absorption was exhibited for the PEDOT:PSS layer after coated by Au NPs. And on the other hand, in fig. 2(b) both films show characteristic peaks for P3HT in 500–600nm range and PCBM at about 330 nm. Obviously, the intensity of the UV-vis absorption peaks slightly increased with Au NPs. First reason for this observation can be attributed to a phenomenon of formation of localized surface plasmon resonance (LSPR) and increase in scattering of light due to the use of metallic NPs, enhancing the light absorption efficiency. The light scattering lengthened the optical path in the active layer, thereby trapping it inside [19–21]. Second reason for the enhancement of the total excitons created in the active layer is that the energy dissipation is proportional to the intensity of the electromagnetic field [22].

The current density (J) versus voltage (V) characteristics of devices were presented in Fig. 3. The device characteristics are summarized in Table 1. The open-circuit voltage ( $V_{oc}$ ) was increased from 0.64 to 0.66 V, whereas the short-circuit current density ( $J_{sc}$ ) and fill factor (FF) were increased from 5.4 to 7.4 mA/cm<sup>2</sup> and 0.63 to 0.64, respectively, for the hybrid photovoltaic cell when compared to the pristine photovoltaic cell. To obtain hybrid photovoltaic cells with higher current density and FF, both electron and hole mobilities must be optimized and most importantly, balanced. Hole is typically the high mobility carrier in regioregular P3HT and thermal annealing will further improve the hole mobility in the photovoltaic cell.

The increased current density in hybrid photovoltaic cell compared to pristine photovoltaic cell may be due to the presence of inorganic NPs through out the active layer of P3HT: PCBM in hybrid film, which could increase the transport of charge-carriers in the hybrid photovoltaic cell. This increases the PCE of the hybrid photovoltaic cell up to 2.17% compared to pristine photovoltaic cell PCE of 3.12%.

To confirm the enhancement in the ( $\eta$ ) of the plasmonic OSCs, the IPCE were measured. The IPCE for the reference and plasmonic OSCs are shown in Fig. 6. We compared the curve of the increase in EQE between PEDOT:PSS and PEDOT:PSS: AuNPs device. The photocurrent within the wavelength range from 400 to 700 nm increased significantly after addition of the Au NPs. The EQE data supports the UV/visible data corresponding to Fig. 3. The device also showed enhanced quantum efficiency in the broad wavelength range due to adequate scattering of light. This indicates a shift in the improvement of optical absorption by the active layer near the PEDOT:PSS (with AuNPs) buffer layer. We suggest that the enhanced  $\eta$  of plasmonic OSCs is mainly caused by the increase of optical absorption, because the incident light on the active layer could be intensified due to the surface plasmons of the Au at resonance frequency and/or the increase of the optical path of incident light by the scattering from AuNPs.

The bulk-heterojunction morphology of pristine (PEDOT:PSS) and hybrid (PEDOT:PSS: AuNPs) films was investigated by AFM. In order to understand the under laying morphology of the devices in the final photovoltaic cells, samples were made by removing the Al cathode from the final photovoltaic cells using sticky tape and the observed AFM images are displayed in Fig. 4. The r.m.s roughness of the pristine (PEDOT:PSS) film is 6.7nm. The surface roughness increased to 8.2nm for the hybrid (PEDOT:PSS: AuNPs) film. The increased roughness and the observed different texture of the hybrid thin film (PEDOT:PSS: AuNPs) could be due to the presence of AuNPs in the PEDOT:PSS layer which has undergone annealing process. The texture of the hybrid film (PEDOT:PSS: AuNPs) is similar through out the surface of the film [23].

### 4. Conclusion

We fabricated the high efficient P3HT: PCBM: AuNPs hybrid photovoltaic cells by generating the Gold nanoparticles in PEDOT:PSS light harvesting system for OSCs of P3HT:PCBM. Light absorption of device differs with AuNPs and showed different  $J_{sc}$  due to much exciton generation. AuNPs contributed in increased light harvesting. The presence of Gold nanoparticles increased the charge-carrier mobility in the hybrid photovoltaic cell. We anticipate that this new concept of making hybrid polymer: fullerene: inorganic photovoltaic cells will be helpful to further improve the PCE of polymer photovoltaic in near future.

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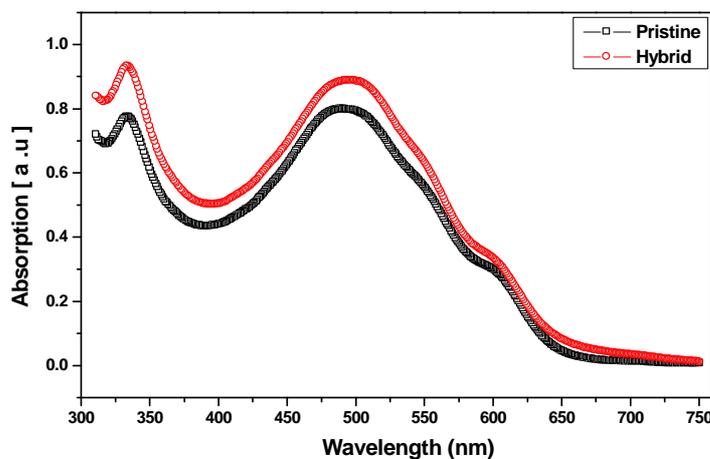


Fig.2. (a) UV–vis absorption spectra of pristine PEDOT:PSS layer and hybrid PEDOT:PSS:(Au) layer and (b) active layer/PEDOT:PSS layer and hybrid active layer/ PEDOT:PSS:(Au) layer thin films.

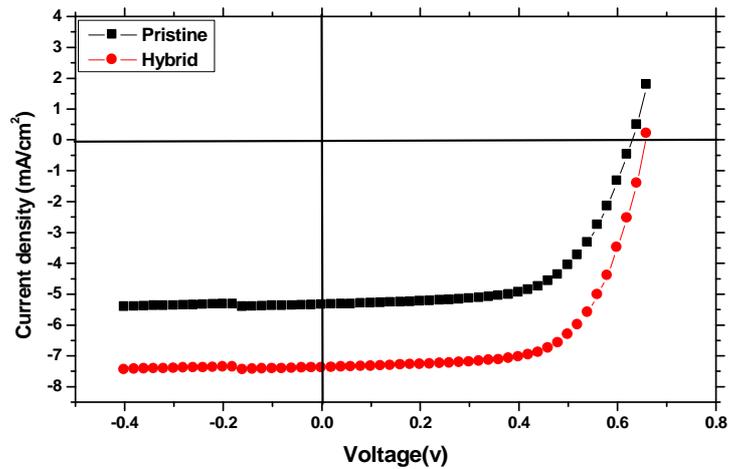


Fig.3. J–V curves of cells fabricated with pristine active layer/PEDOT:PSS layer and hybrid active layer/PEDOT:PSS:(Au) thin films.

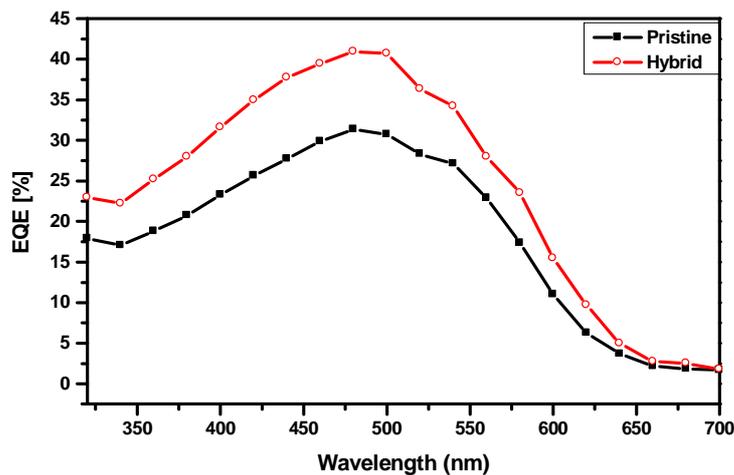


Fig.4. Incident photon-to-current conversion efficiency (IPCE) curves for the pristine and hybrid photovoltaic cells fabricated with PEDOT:PSS.

Table 1. Photovoltaic properties of the devices made with buffer layer and photoactive layer using 1:1ratio of P3HT to PCBM and AuNPs.

Buffer layer	$V_{oc}(v)$	$J_{sc}(mA/ cm^2)$	FF	PCE (%)
PEDOT:PSS	0.64	5.4	0.63	2.17
PEDOT:PSS: AuNPs	0.66	7.4	0.64	3.12

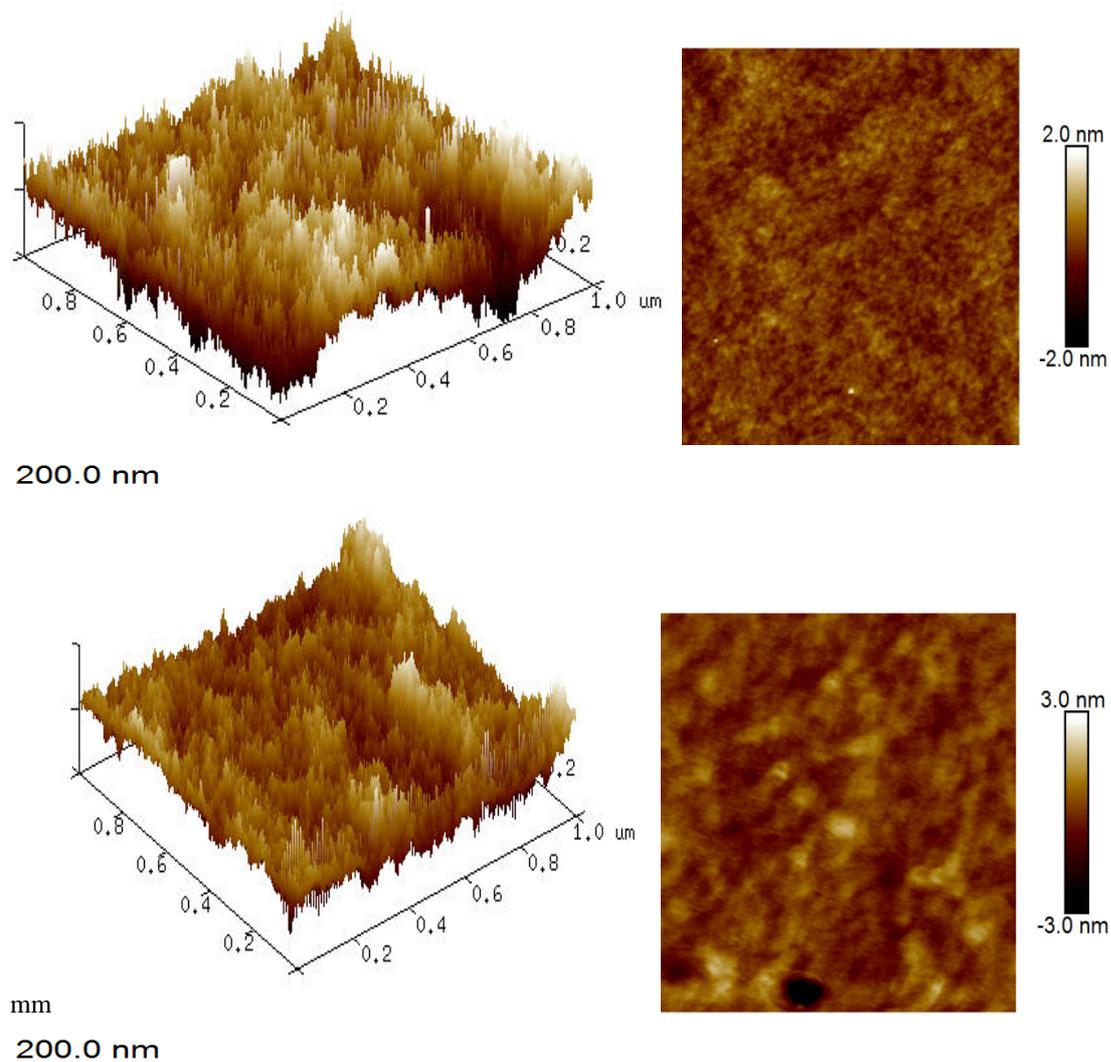


Fig.5. AFM images of the pristine PEDOT:PSS layer and hybrid PEDOT:PSS:(Au) layer thin films .

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