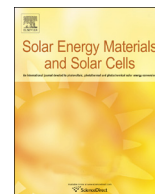




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## Thickness dependent enhanced efficiency of polymer solar cells with gold nanorods embedded in the photoactive layer

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### ABSTRACT

In this work, the dependence of the enhancement in the efficiency of polymer solar cells incorporated with gold nanorods embedded in the photoactive layer on the photoactive layer thickness has been studied in detail. Synthesized toluene-based gold nanorods were introduced to devices by simply blending them with a solution of poly(3-hexylthiophene-2,5-diyl):[6,6]-phenyl-C<sub>61</sub>-butyric-acid-methyl-ester. The photovoltaic parameters for devices made with two different thicknesses, 100 and 40 nm, of polymer:fullerene:nanorods films revealed that while the power conversion efficiency of the thin devices was enhanced by 27% due to the plasmonic effect induced by the presence of the gold nanorods in the film, its value was lowered in devices made with the thicker films. Comparison between thick/thin photoactive films' absorbance, morphologies and shunt resistances related such reduction in the performance to the high leakage current that resulted from quenching energy states in the photoactive film.

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### 1. Introduction

Enhancing the efficiency of bulk heterojunction (BHJ) organic solar cells (OSCs) has become one of the hottest research topics today due to their promising future as a replacement to their inorganic counterparts [1,2,3]. The unique characteristics of OSCs such as solubility in organic solvents, portability, light-weight, and flexibility allow them to be possibly manufactured in large scales with low-cost [4,5]. Yet, the low efficiency of OSC still hinders them from commercialization. Up to now, only 5% of power conversion efficiency (PCE) has been achieved from BHJ-OSCs that were made of the blend poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-phenyl-C<sub>61</sub>-butyric-acid-methyl-ester (PCBM) [6]. Among other factors, the thickness of the photoactive film has a potential significant effect in the device performance. Although thick films absorb a larger fraction of the incident light as compared with the thin ones, the increase in the thickness of the photoactive film, however, enlarges the devices series resistance ( $R_s$ ), and reduces their performance due to the resulting low mobilities of the charge carriers [7,8].

Plasmonic phenomenon in metallic nanoparticles (MNPs) has been used to enhance the light absorption of a constant thickness of photoactive film [9,10]. Localized surface plasmon resonance (LSPR) occurs when oscillations of illuminated electronic clouds

resonate with the incident light, which leads to more light absorption in the visible region of the spectra. Since gold and silver MNPs support the LSPRs, they were widely used in thin-film applications to trap the incident light [3,9,10], and intensify the electromagnetic (EM) field, up to a factor of 100 [11], in their surrounding materials. This indeed opened a wide research area to investigate the effect of incorporating such MNPs into various locations in the photovoltaic (PV) cells. Many reported works showed that the PCE of BHJ-OSCs was noticeably improved by incorporating MNPs into OSC layers either in contact with the front electrode of the cells, indium tin oxide ITO [12–15], or with their back electrode, Al cathode [16], or by blending them with the solution of the anodic buffer layer, poly(3,4-ethyl-enedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) [17–20], or with the solution of the photoactive one, P3HT:PCBM [21,22].

The effect of embedding MNPs into the photoactive layer of BHJ-OSCs is rarely studied experimentally since the MNPs are usually available in aqueous solutions, which hinders them from being directly mixed with the photoactive one. Some reported works [2,3] revealed that the enhancement in the light absorption of OSCs due to embedding of the MNPs in their photoactive films is higher than that associated with placing them in contact with the cells' front/back electrodes. In addition, photoactive layers spin-coated from different concentrations of the polymer:fullerene solutions showed different morphologies in the resulting films, which significantly influences the device performance [23]. Hence, we aimed here to investigate the effect of mixing gold nanorods

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(Au NRs) with two different concentrations of the P3HT:PCBM solutions on the overall performance of the devices. The fact that the plasmonic absorption mode is influenced by the dielectric function of the surrounding medium [24], and the cylindrical particles scatter light more than the spherical ones [1] favor the use of the rod shape of gold nanoparticles in the present work. The resonance peaks of Au NRs are situated around the absorption of P3HT:PCBM, and their longitudinal peak is close to the IR absorption edge of the photoactive film. Hence, we expect that having the rods embedded in the photoactive layer will result in more light absorption in the IR region. The immediate excitation of the adjacent excitons due to the direct effect of the LSPR surrounding them [3] would lead to better device performance since the generation of excitons is expected to increase. In addition, having the rods embedded in the photoactive layer would reduce the devices series resistance ( $R_s$ ) [6] since the distance that charge carriers has to pass through to reach both electrodes will be reduced [21]. The reduction in  $R_s$  would also contribute to the total enhancement of the device performance.

In the current study, we report on the effect of incorporating Au NRs into thick/thin photoactive film of OSCs on their overall performance. The newly synthesized toluene-based Au NRs were directly blended with concentrated/diluted P3HT:PCBM solutions to yield thick/thin photoactive films, respectively. The presence of the rods in the P3HT:PCBM films makes it possible for the intensified EM field surrounding them to directly excite more excitons, thereby improving the film absorption to the incident light. Investigation on the absorption of thick/thin P3HT:PCBM:

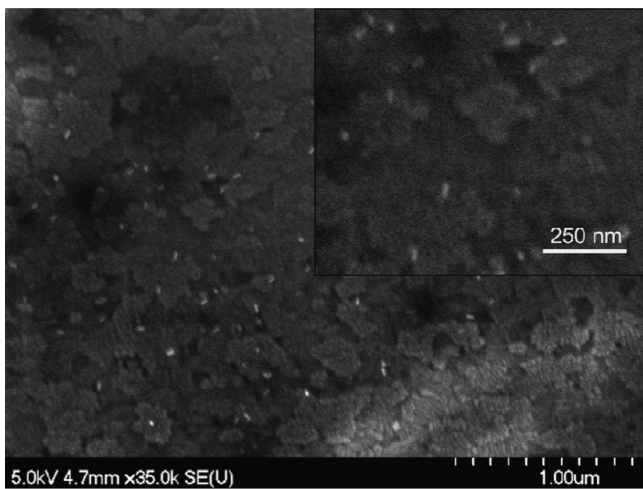


Fig. 1. SEM image showing the toluene-based Au NRs on ITO-coated glass. The white droplet-like structures indicate the rods, with arbitrary alignments.

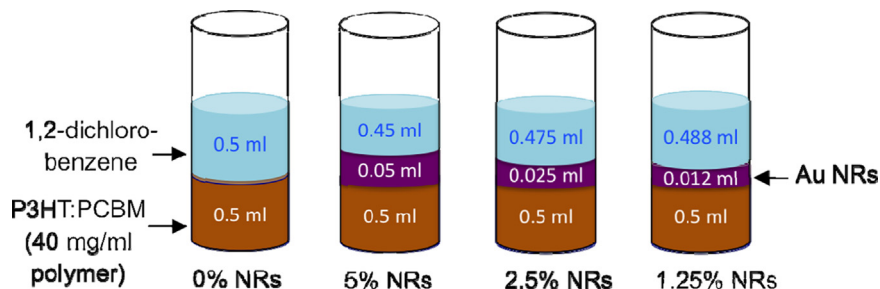


Fig. 2. Schematic representations of the volume percentages of Au NRs, P3HT:PCBM, and 1,2-dichlorobenzene solutions that were used in our experiment. The concentration of P3HT:PCBM blend in the final P3HT:PCBM:AuNRs mixture was kept constant in all cases by adding the required amount of 1,2-dichlorobenzene. The final concentration of the polymer in all cases is 20 mg/ml.

AuNRs films revealed that the effect of the plasmonic particles on the films' absorptivity is not similar, and hence the overall response of the resulted thick/thin devices was different. Investigation on the morphology and shunt resistance of thick/thin devices related the variation in the plasmonic-influence of thick/thin devices to the increase in the leakage current of the thick devices.

## 2. Experimental methods

### 2.1. Synthesis of toluene-based Au NRs rods

Gold nanorods were first synthesized in aqueous solution using the colloidal seed-mediated, cetyltrimethylammonium bromide surfactant-assisted approach following our previously reported method [12]. All chemicals used in the synthesis were purchased from Sigma-Aldrich. The concentration of Au NRs in the aqueous solution was  $\sim 1.593 \times 10^{12}$  rods/ml, and their aspect ratio, as observed by transmission electron microscopy (TEM), was  $\sim 4$ . In order to be able to mix the Au NRs solution with the solvent-based P3HT:PCBM one, Au NRs in the aqueous solution were transferred into a toluene-based solution through the following steps [25,26]: 20 ml of the water-based Au NRs solution was centrifugated at 9000 RPM for 30 min, followed by discarding the clear supernatant, and reloading 20 ml of DI-water. The solution was then sonicated, and the rods were re-dispersed. 30 ml of dodecanethiol (DDT) and 40 ml of acetone were successively added to 20 ml of the re-dispersed rods water solution, and shaken for several minutes to mix the liquid layers. The solution was thereafter allowed to stand for phase transfer. The brown water layer at the bottom became clear, and the top organic layer turned into deep-brown or blue, which indicated the completion of the phase transfer. 20 ml of methanol was added to 10 ml of the above prepared organic solution, mixed, and then centrifugated at 8000 RPM for 20 min. Afterwards, supernatant was discarded and 20 ml of methanol was reloaded to re-disperse the rods. The resulting solution was then centrifugated again at 8000 RPM for 20 min. Supernatant was discarded and toluene was introduced to disperse the rods. According to Ref. [25], the maximum number of thiol molecules attached onto a single gold nanorod (length 40 nm and radius 25 nm) is  $\sim 23844$ . This DDT layer offers the nanorods good stability and dispersion in toluene. Fig. 1 shows a scanning electron microscopy (SEM) image for the synthesized toluene-based Au NRs that were spin-coated on an ITO-coated glass. It is clear that spin-coating of the rods solution produced rods with arbitrary orientation in the layer. It is also worth to mention that the size and shape of the individual rods do not change significantly after the phase transfer process, as observed by TEM (not presented).

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