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# Gold Nanorods on the Cathode Electrode for Enhancing the Efficiency of Polymer Solar Cells

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## ABSTRACT

Different densities of gold nanorods (GNRs) were incorporated on the back electrode of bulk heterojunction organic solar cell (OSC). GNRs layers (1, 3, and 5) were deposited on top of the poly(3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) layer using spin-casting technique. According to the optical and structural characterizations, the solar cell devices incorporated with one layer of gold nanorods showed an enhancement in both power conversion efficiency and short-circuit current by up to 14% and 22% respectively as compared to the devices without gold nanorods. This result suggests that GNRs in the back electrode of polymer solar cells act as backscattering elements. They not only increase the optical path length in the active layer but also store energy in localized surface plasmon resonance mode. Both mechanisms lead to enhancement of light absorption and in turn contribute to photocurrent generation and the overall power conversion efficiency. On the other hand, the solar cells with high density GNRs on the back electrode showed inferior performance compared to that of low density integrated ones. The decrease in PCE would stem from enhanced charge recombination induced by high density GNRs. Furthermore, generation of intense local electric fields named hotspots, would reduce the charge transportation and exciton dissociation probability. In such cases, the power conversion efficiency of the device is observed to be less than that for one layer GNRs or even the control device.

**Keywords:** Organic bulk heterojunction, solar cell, gold nanorods, plasmonic effect

## 1. INTRODUCTION

The ongoing environmental problems of fossil fuels stimulated scientific research to develop inexpensive, renewable, and efficient energy sources. Solar energy is one of the thoroughly green energy sources without any supply limit. Therefore, converting the energy of light directly into electricity by means of solar cells is one of the most pertinent research topics nowadays.<sup>[1]</sup>

The organic, polymer-based photovoltaics (OPV) has the potential to contribute significantly to the solar energy market, due to their many favourable properties including ease of processing, the possibility of improving the properties of polymer materials by facile chemical manipulation, low-cost, low temperature fabrication, light-weight, portability and flexibility.<sup>[2]</sup> The main difference versus traditional inorganic semiconductors is that OPVs create excitons instead of free charge carriers when the device absorbs photons.

The short diffusion length of photogenerated excitons is an important limiting factor of organic solar cells which has a negative effect on the power conversion efficiency (PCE) of the device. On the other hand, these excitons could just be dissociated to free charge carriers at the interface of donor (D) and acceptor (A) materials, where the electronic potential has a significant increase. In order to eliminate this limitation, the concept of bulk heterojunction (BHJ) active layer was introduced, which is a composite film created by mixing the donor and acceptor phases.<sup>[3]</sup>

BHJ increases the interfacial area between the polymer (donor) and fullerene (acceptor), and consequently enhances the exciton dissociation regions. Therefore, it contributes significantly to the performance of OSCs.<sup>[4]</sup> So far, the most high-performance OPVs using polymer/ fullerene BHJ active layer have reached the PCE up to 6-8%.<sup>[5]</sup>

In order to reach higher efficiencies, the device thickness should be kept thin enough to reduce the device resistance, which results from low carrier mobility as well as short excitons diffusion lengths of organic semiconductors. On the

other hand, the thickness of polymer/ fullerene active layer should be adjusted thick enough to absorb most of the incoming light. Therefore, there is a crucial need to develop an efficient light trapping technique.<sup>[5]</sup>

It has been reported that incorporation of metal nanoparticles (MNP) in OSCs increased the optical absorption, photocurrent generation and subsequently the PCE of the device.<sup>[6]-[9]</sup> The most exceptional specification of MNPs is surface plasmons (SP). It is defined as the collective oscillations of conduction electrons in the interface of metal and dielectric, which occurs upon light illumination. The plasmonic effect contributes to more light trapping inside the active layer which results in enhancement of light absorption by the device. Various plasmonic structures of deposited MNPs would offer different ways to increase the efficiency of the OSC including localized surface plasmon resonance (LSPR), surface plasmon polaritons propagating along the metal/dielectric interface, and acting as scatterer elements.<sup>[10], [11]</sup>

To our knowledge, no previous investigations were done on the effect of the density of GNRs on the overall PCE and performance of the OSCs. In this study, the impact of incorporating multi-layers of GNRs, with different densities, on top of the active layer was explored.

## 2. EXPERIMENTAL DETAILS<sup>[12]</sup>

Each control device includes a transparent positive anode (ITO coated on glass substrate), a negative metallic cathode (Al), and there is a 0.16 Cm<sup>2</sup> area in-between which is the polymer bulk heterojunction active layer (P3HT: PCBM). The control and experimental devices have respectively the following configurations: ITO/PEDOT:PSS/P3HT:PCBM/LiF/Al and ITO/PEDOT:PSS/P3HT:PCBM/GNRs/LiF/Al (Fig 1).



Figure 1. Schematic structure of BHJ OSC (the GNRs are represented by yellow ellipsoids).

### 2.1 Chemicals and Materials

#### 2.1.1 Organic Solar Cells

High regioregularity (98%) P3HT with average molecular weight of <50,000 MW was purchased from Rieke Metals. PCBM (>99.5%) and 1, 2-dichlorobenzene (anhydrous, 99%) were purchased from Sigma-Aldrich. Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) (CLEVIOS™ P VP AI 4083) was purchased from HC Stark. Aluminium (Al) wire and lithium fluoride (LiF) were purchased from Alfa Aesar. The materials were used as received without further purification.

#### 2.1.2 Gold Nanorods

The gold nanorods have been graciously supplied by Professor Dongling Ma of the Institut de la Recherche Scientifique (INRS). All materials needed for gold nanorods preparation including hydrogen tetrachloroauric acid (HAuCl<sub>4</sub>·3H<sub>2</sub>O), cetyltrimethylammonium bromide (CTAB), sodium borohydride (NaBH<sub>4</sub>), silver nitrate (AgNO<sub>3</sub>) and ascorbic acid (AA) were purchased from Sigma-Aldrich. The method for preparing these nanorods was described in detail in refs. 12 and 13.

## 2.2 Fabrication of Organic Solar Cells<sup>[14]</sup>

The indium tin oxide (ITO) coated glass substrates (2.6 cm × 3.7 cm) were etched in the manner that each patterned substrate includes 8 devices. Both control (without GNR) and experimental (with GNR) devices were synthesized and tested under the same processing conditions. The patterned ITO-coated glasses were cleaned with detergent, rinsed with deionized (DI) water, and then successively ultrasonicated in acetone, isopropanol and DI water for 20 min each. The substrates were then dried with a nitrogen flow and baked at 150 °C for 20 min.

The substrates were subjected to an oxygen plasma treatment for 35s before PEDOT:PSS deposition. Afterwards, the PEDOT:PSS was passed through a 0.45 μm PVDF membrane filter and spun-cast on the top of ITO-coated glass under an ambient environment. The substrates were baked at 120°C for 1h for dehydration. Then, in order to deposit the polymer bulk heterojunction active layer the substrates were transferred to a nitrogen glove box with a pressure of 3 mbar and humidity level less than 0.1 ppm. The blend of P3HT:PCBM with a ratio of 1:0.8 and a concentration of 20 mg/ml (P3HT) was first dissolved in 1, 2-dichlorobenzene then passed through a 0.45 μm PTFE membrane filter and finally spun-cast at 1000 rpm on top of the ITO/PEDOT:PSS modified anode. The substrates were then left to dry in covered Petri dishes for 30 min before the deposition of GNRs layer.

In this step, GNRs were deposited directly on top of the active layer by spin-casting technique. The whole process was done inside the nitrogen glove box. Spin-casting was performed in two steps, 200 rpm for 3s and 1000 rpm for 10s. In each set of experiment, four samples were synthesized and characterized. Each sample is a glass substrate that includes eight devices. The first sample is the control device, in which no GNRs were deposited. The second one is the one-layer deposited GNRs sample. The third one contains three layers of GNRs, and the active layer of the last sample were covered with five layers of GNRs.

Afterwards, they were transferred to the evaporator system in which the LiF/Al cathode would be deposited. As the final step, a bilayer LiF/Al cathode was thermally evaporated using a shadow mask under a pressure of 10<sup>-5</sup> torr. The thickness of the evaporated layer and the evaporation rate for LiF were ~1 nm and ~1Å/s respectively, and the same specifications for Al layer were measured as ~90nm and ~2.5-5 Å/s. The material thicknesses were determined with a mechanical profilometer (Veeco Dektak150). To increase the performance of the devices a post-production annealing was performed inside the glove box using a digital hotplate. The devices were placed in direct contact with the heater at 160 °C for 30 min, then they left to cool-down before characterization.

## 2.3 Characterization

### 2.3.1 Organic Solar Cells

For device characterization purposes, no device encapsulation was applied and all tests were done under ambient conditions. To do the current-voltage measurements a solar simulator made of Zenon lamp (Oriel instruments), which was equipped with AM 1.5 filter, was utilized. Using a light meter (LI-250 Bioscience) equipped with silicon photodiode (LI-200 Pyranometer), the output density of the lamp was adjusted to 100 mW/cm<sup>2</sup>. The final current-voltage measurements were accomplished by a source meter (Keithley 2400). The PV parameters including the short-circuit current (J<sub>sc</sub>), the open-circuit voltage (V<sub>oc</sub>), the fill factor (FF) and the power conversion efficiency (PCE) were measured for both control and experimental devices under the same conditions.

The absorbance spectra were also measured using a UV-Vis spectrophotometer (PerkinElmer LAMBDA 650 spectrophotometer). In all cases, a comparison among samples with different GNRs densities including devices with none, single, and multilayer (3 and 5 layers) GNRS was made.

### 2.3.2 Gold Nanorods

The concentration of GNRs in aqueous solution was measured using transmission electron microscopy (TEM). (Fig 2a). The calculated concentration is  $\sim 1.593 \times 10^{12}$  rods/ml relies upon the average aspect ratio carried out by TEM image, which was  $\sim 4$ . For determination of absorption maxima the UV-Vis spectrum of GNRs colloidal solution was also measured. As it is presented in Fig. 2b, the maximum of both longitudinal and transverse modes were 715nm and 520nm respectively.

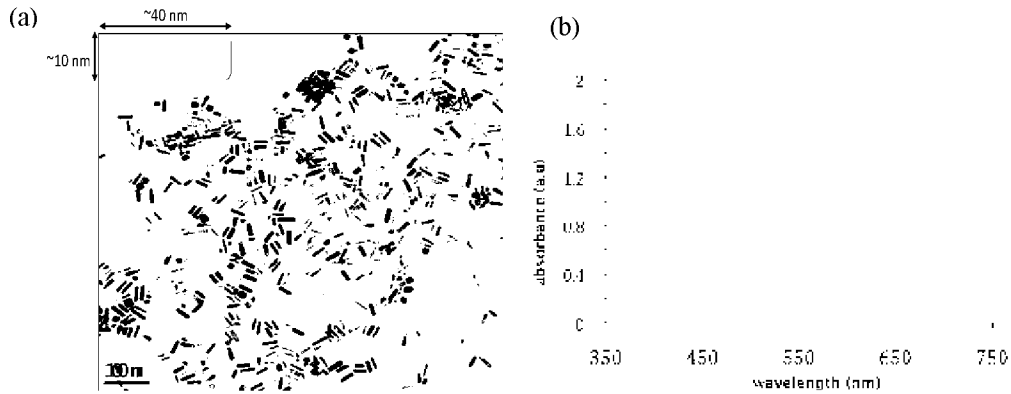


Figure 2. (a) TEM image of GNRs on glass; included is a schematic image of a single nanorod. (c) UV-Vis spectrum for the GNRs colloidal solution. (The image and spectrum were provided by INRS)

## 3. RESULTS AND DISCUSSIONS

Fig. 3 clearly shows the difference in the absorption spectra of pristine polymer/fullerene blend (control sample) with experimental samples in which multi-layers of GNRs are deposited directly on top of the P3HT:PCBM. In other words, the absorption of P3HT:PCBM intensifies with the GNRs density because the plasmon region of GNRs (500-700nm) matches with the absorption peak of P3HT:PCBM which is extended from 350nm to 660nm. Due to the enhancement of optical density over the entire excitation spectral region, the absorption profile of GNRs deposited P3HT:PCBM kept the same shape of that for a pristine sample.<sup>[12], [15]</sup>

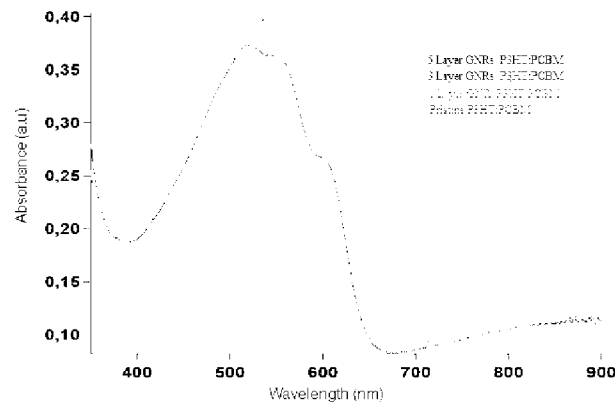


Figure 3. A comparison between the optical density of P3HT:PCBM with and without gold nanorods on the ITO-coated glass.

Fig. 4 exhibits the J-V characteristics of solar cells fabricated with (multi-layers) and without GNRs under illumination (4a) and in the dark (4b). Moreover, a summary of their performance is given in Table 1.

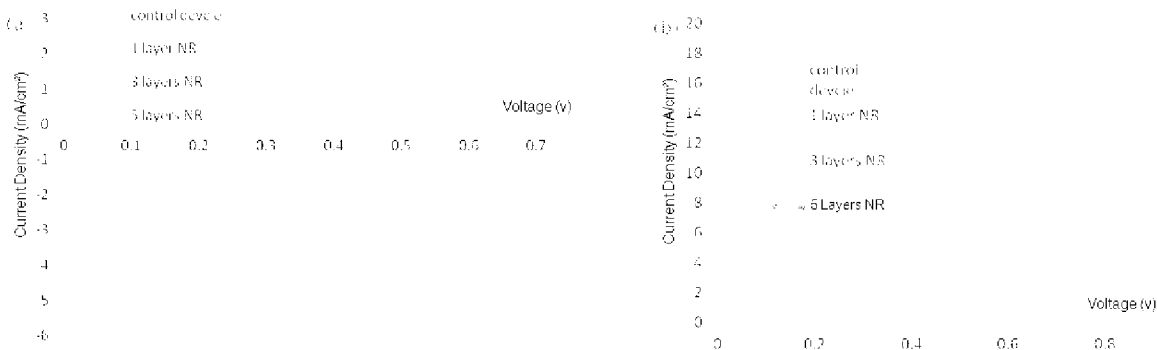


Figure 4. IV curves for both control (ITO/P3HT:PCBM/LiF/Al) and experimental (ITO/P3HT:PCBM/GNRs/LiF/Al) devices. (a) under illumination. (b) in the dark.

As it was expected, an increased efficiency was observed for the devices with GNRs incorporated on the back electrode. According to Table 1, the highest PCE of 1.779% achieved for the one layer GNR (low density), with a short-circuit current density ( $J_{sc}$ ) of 4.78 mA/cm<sup>2</sup>, an open-circuit voltage ( $V_{oc}$ ) of 0.595 V, and a fill factor (FF) of 0.625. The 14% increase of PCE resulted from an enhancement in FF, which suggests that the presence of surface plasmons would lead to an efficient charge transfer of excitons inside the active layer.<sup>[8]</sup>

Table 1. The PV parameters for control device (without gold nanorods) and experimental one (with gold nanorods) under AM 1.5G spectral illumination.

<b>control device</b>	0.570	-4.618	0.418	59.39	1.562	
<b>3 Layers NR device</b>	0.595	-4.134	0.418	58.40	1.436	-8%

The backscattering effect causes an increase in the optical path length of incident light inside the active layer which results in higher possibility of light absorption which in turn generates more excitons.<sup>[11]</sup> Moreover, optical electric field concentration because of excitation of LSPR contributes to the improvement of the FF and consequently the PCE.<sup>[16]</sup>

Based on Fermi golden rule, there is a correlation between the electron transition probability and the electric field strength that molecules experience. This is the reason behind the enhancement of photocurrent generation while the excited particles' near-field increases.<sup>[15]</sup> In addition, the intense local field causes a significant increase in the strong coupling between surface plasmons and excitons which multiplies the population of hot-excitons. These excitons possess extra thermal energy to overcome the coulombic attraction of their initial pairs. Hence, they could contribute to exciton dissociation and charge transfer via reducing the level of exciton loss by geminate recombination.<sup>[16], [5]</sup>

On the other hand, deposition of higher densities of GNRs (3 and 5 layer) lowered the performance of the solar cell. The 3-layer incorporated GNRs device with PCE of 1.43% and FF of 0.584 showed a slight decrease compared to the control device with PCE and FF of 1.562% and 0.594 respectively.

In the case of high density GNRs on the back electrode, not only the near-field around nanorods would be strong but also the near-fields in the gap between GNRs could be enlarged due to the dipole-dipole interaction between GNRs. The

arisen local intense electric field is named 'hot-spot'.<sup>[17]</sup> The result is the creation of new hybridized plasmons with frequency lower than that of the surface plasmons. Accordingly, the electromagnetic profile inside the active layer is disturbed which complicates the plasmon-exciton coupling and in turn would decrease the exciton dissociation probability. As a consequence, the photocurrent generation, the FF, and the PCE would be reduced.

Moreover, the effective scattering cross section at the plasmon resonance is much larger than the geometrical cross section.<sup>[1]</sup> This suggests that increasing the GNRs density would not necessarily enhance the scattering effect by nanoparticles. The optimum particle density should be inversely proportional to the effective particle cross section at the plasmon resonance.<sup>[18]</sup> On the other hand, GNRs in direct contact with the active layer materials are assumed to be efficient charge recombination sites. Thereby, the exciton quenching effect overwhelms the light absorption enhancement induced by the backscattering effect of GNPs. In conclusion, a high density of GNRs reduces the photocurrent, FF, and in turn the PCE because of an enhanced biomolecular recombination without any remarkable increase in the back scattered light inside the active layer.

#### 4. CONCLUSION

Our experiments demonstrate that there is an optimum density for incorporation of GNRs on top of the active layer in which the power conversion efficiency of the device is highest. An increase in PCE of bulk heterojunction organic solar cell by up to 14% is observed which is promoted by spin-casting of one layer GNRs in the back electrode of the device. Integration of low density GNRs results in the improvement of the device performance by both backscattering effect and near-field enhancement induced by excitation of LSPR. A high density of GNRs (3 and 5 layers), however, reduces the exciton generation and charge transport probability due to geminate charge recombination along with the creation of hot-excitons. In these cases, the measured FF and PCE are less than the corresponding values for the solar cell with one layer of deposited GNRs as well as the control device.

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