

# DIFFERENT PLASMONIC LIGHT TRAPPING MECHANISMS IN P3HT:PCBM ORGANIC SOLAR CELLS WITH INCORPORATED NANOPARTICLES

*Andrej Vojtko<sup>1</sup>, Monika Benkovičová<sup>1</sup>, Vojtech Nádaždy<sup>1</sup>, Michal Kaiser<sup>1</sup>, Ján Ivančo<sup>1</sup>,  
Matej Jergel<sup>1</sup>, Peter Šiffalovič<sup>1</sup>, Eva Majková<sup>1</sup>*

<sup>1</sup> *Institute of Physics SAS, Dubravská cesta 9, 845 11 Bratislava, Slovakia  
E-mail: andrej.vojtko@savba.sk*

*Received 30 April 2015; accepted 15 May 2015*

## 1. Introduction

Organic (polymer) solar cells are a family of photovoltaic devices where an intense research effort was focused during the last years. Their unique properties such as mechanical flexibility or easy processability allow to produce solar cells on flexible substrates or semi-transparent cells while maintaining low production costs. Despite the progress leading to the current record in power conversion efficiency exceeding 10% [1], there is still need for improvements. The active layer is bulk heterojunction consisting of percolated structure of donor and acceptor with correlation length approaching the exciton diffusion length (~10 nm) [2]. As the phonon light absorption limits the active layer thickness to ~100 nm, a way to increase the photoconversion is to employ plasmonic effects. The noble metal nanoparticles exhibit localized surface plasmon resonance (LSPR) in visible region which matches well the solar cell absorption band.

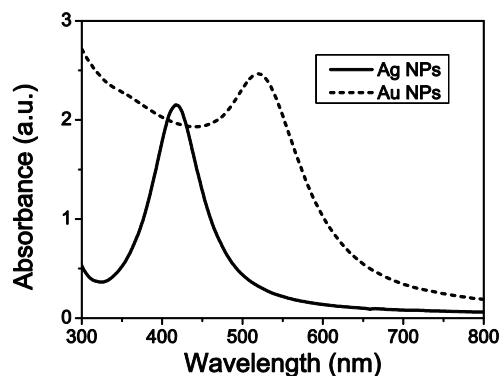


Fig.1: *Plasmonic peaks of colloidal silver and gold nanoparticles.*

The plasmonic nanoparticles incorporated in the organic solar cell active layer provide two mechanisms to trap more light. Firstly, the LSPR is a collective oscillation of electron cloud around the nanoparticle caused by an incoming electromagnetic wave. Therefore, the oscillation results in an enhanced electric field amplitude  $E$  in vicinity of the nanoparticle and thereby enhanced exciton generation that is proportional to  $E^2$ . Secondly, if the nanoparticles are located at the front electrode, the light is scattered predominantly and coupled into the active layer. Moreover, part of the scattered light impinging on the back electrode below the critical angle may experience total reflection and prolong its path inside the active layer [3].

In this study, we explore incorporation of spherical plasmonic nanoparticles into the volume of active layer of the organic solar cell consisting of poly(3-hexylthiophene-2,5-diyl)

(P3HT, donor) and phenyl-C61-butyric acid methyl ester (PCBM, acceptor). This is a well-known prototypic bulk heterojunction that is convenient as a model structure to evaluate plasmonic effect on the power conversion efficiency. Colloidal silver and gold nanoparticles with diameter of 13 nm and 6 nm, respectively, were employed. The former were in-house synthesized with a mixture of oleic acid and oleylamine as a surfactant [4] while the latter were commercial (Plasmachem) with a surfactant being a mixture of mercaptoalkanes with dodecanethiol as the main component. The absorption spectrum of nanoparticles in toluene solution with visible plasmonic peaks is shown in Fig. 1.

## 2. Experimental details

The solar cells with structure glass/ITO/P3HT:PCBM/Ca/Al were studied. The indium tin oxide (ITO) covered glass substrates (PGO, Germany) with typical surface resistivity  $6\Omega/\square$  were used. The substrates were subsequently sonicated in acetone, isopropyl alcohol and deionized water and dried on a hotplate at  $120^\circ\text{C}$ , 10 minutes each. For removing possible debris and adjusting the substrate work function, the substrates were UV/ozone treated for 20 minutes. The prepared substrates were transferred to a glove-box for active layer deposition. After the deposition, the back contact electrode (15 nm Ca + 100 nm Ag) was thermally evaporated.

The active layer was spin-coated (30rps, 37s) from a solution of P3HT:PCBM (1.5:1 wt.%, both Sigma-Aldrich) in dichlorobenzene (anhydrous, Sigma-Aldrich) with 2 wt% concentration. After the spin-coating, the still wet samples were solvent annealed under a Petri dish for 25 minutes and thermally annealed at  $110^\circ\text{C}$  for 5 minutes to ensure the optimal bulk heterojunction morphology.

The samples with nanoparticles were prepared by mixing the active layer solution with the same amount of differently diluted nanoparticle solutions to obtain desired nanoparticle concentration in the resulting solution. The reference cell solution was diluted by the same amount of dichlorobenzene to ensure the same thickness of the active layer.

The silver and gold nanoparticle-enhanced solar cells were produced as separate batches, each batch having its own reference device for an objective evaluation of the plasmonic effect on the power conversion efficiency.

## 3. Results and discussion

As the presence of big amount of nanoparticles can cause phonon light absorption enhancement together with deterioration of the percolated structure, an optimal nanoparticle concentration was determined experimentally.

### 3.1 Gold nanoparticles

The  $J$ - $V$  curves for 0, 0.1 and 3 wt% concentrations of 6 nm gold nanoparticles are shown in Fig. 2. The corresponding device parameters are listed in Tab. 1. No positive effect on the power conversion efficiency ( $PCE$ ) was achieved. However, a short-circuit current density ( $J_{SC}$ ) improvement from 8.1 to 8.6  $\text{mA}\cdot\text{cm}^{-2}$  is observed at 0.1 wt% concentration. The open-circuit voltage ( $V_{OC}$ ) decreased from 0.58 to 0.56 V, together with the fill factor ( $FF$ ). The  $FF$  decrease from 64.5 to 51.6% caused mainly by the shunt resistance ( $R_{SH}$ ) was found to be the most detrimental to the  $PCE$  which decreased from 3.0 to 2.5%. A small increase in series resistance ( $R_S$ ) was also observed.

These results imply increased charge generation due to plasmonic nanoparticles but lower exciton dissociation probability and charge collection at electrodes for any applied voltage when the nanoparticles are incorporated. The changes in  $V_{OC}$  and  $FF$  indicate detrimental changes in the active layer due to the nanoparticles which is supported by  $V_{OC}$  and  $FF$  decrease for higher 3 wt% concentration. The 0.1 wt% concentration is too low to

introduce serious morphology changes, hence, the worsening of  $FF$  may be attributed to the nanoparticle surfactant that provides trap sites for dissociated charge recombination.

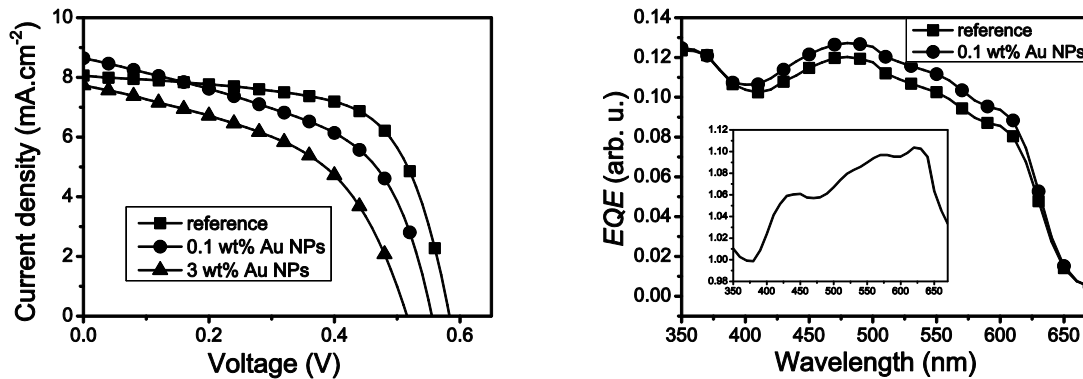


Fig.2: The  $J$ - $V$  curves of solar cells with different concentration (0 % - squares, 0.1 wt% - circles, 3 wt% - triangles) of incorporated plasmonic gold nanoparticles (left) and  $EQE$  enhancement for 0.1 wt% concentration (right). Inset shows ratio between the plasmon-enhanced and reference solar cells.

To better evaluate the positive effect on  $J_{SC}$ , the external quantum efficiency  $EQE$  as a function of the wavelength was measured (Fig. 2). An  $EQE$  enhancement peaking around 550-600 nm is observed that is better visible in the inset. This well corresponds to the plasmonic peak of the gold nanoparticles. Therefore we can assume that the main mechanism causing  $J_{SC}$  improvement is the near-field electric field enhancement around the gold nanoparticles.

Tab. 1. The overview of solar cells parameters with incorporated gold nanoparticles.

	$J_{SC}$ (mA.cm <sup>-2</sup> )	$V_{OC}$ (V)	$FF$ (%)	$PCE$ (%)	$R_{SH}$ ( $\Omega$ .cm <sup>2</sup> )	$R_S$ ( $\Omega$ .cm <sup>2</sup> )
Reference	8.1	0.58	64.5	3.0	590	9
0.1 wt% Au NPs	8.6	0.56	51.6	2.5	213	11
3 wt% Au NPs	7.7	0.52	48.7	1.9	238	15

### 3.2 Silver nanoparticles

The  $J$ - $V$  curves for 0, 0.1 and 1 wt% concentrations of 13 nm silver nanoparticles are depicted in Fig. 3. The overview of solar cell parameters is provided in Tab. 2. For the optimal 0.1 wt% concentration,  $J_{SC}$  enhancement from 8.6 to 9.0 mA.cm<sup>-2</sup> at the same  $V_{OC}$  is observed. The fill factor is improved from 57.6 to 59.9% due to increased  $R_{SH}$  from 389 to 724  $\Omega$ .cm<sup>2</sup>. The series resistance  $R_S$  found to be unchanged. The interplay between all parameters gave rise to the power conversion efficiency increase from initial 2.9 to 3.2% (10% improvement). The higher concentration (1 wt%) shows similar worsening tendencies as it was for the gold nanoparticles which we attribute once more to morphology changes, promoted in this case also by larger silver nanoparticle size of 12 nm that compares well with a typical percolation length of the active layer blend.

The character of  $EQE$  improvement was found to be different from that of gold nanoparticles. Here, we can observe a relatively flat improvement in the interval between 400 and 550 nm with an increase toward 650 nm. This leads to a conclusion that the plasmon-enhanced scattering and prolonged optical path is the dominant mechanism for silver nanoparticles.

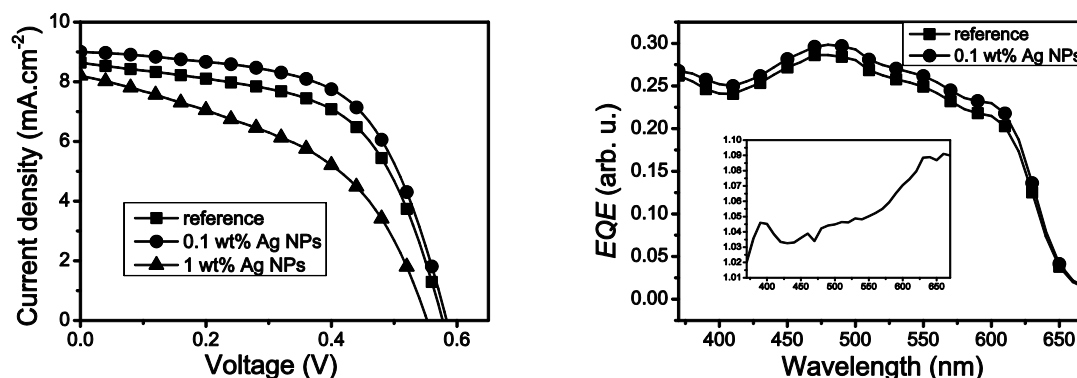


Fig.3: The  $J$ - $V$  curves of solar cells with different concentration (0 % - squares, 0.1 wt% - circles, 1 wt% - triangles) of incorporated plasmonic silver nanoparticles (left) and EQE enhancement for 0.1 wt% concentration (right). Inset shows ratio between the plasmon-enhanced and reference solar cells.

Tab. 2. The overview of solar cells parameters with incorporated silver nanoparticles.

	$J_{sc}$ (mA.cm <sup>-2</sup> )	$V_{oc}$ (V)	$FF$ (%)	$PCE$ (%)	$R_{SH}$ ( $\Omega$ .cm <sup>2</sup> )	$R_s$ ( $\Omega$ .cm <sup>2</sup> )
Reference	8.6	0.58	57.6	2.9	389	14
0.1 wt% Ag NPs	9.0	0.58	59.9	3.2	724	14
1 wt% Ag NPs	7.9	0.55	46.0	2.0	188	19

#### 4 Conclusion

We incorporated two different types of plasmonic nanoparticles into P3HT:PCBM based organic solar cells to investigate their effect on the power conversion efficiency. For 6 nm gold nanoparticles, the near-field plasmon effect results in a short-circuit current density improvement but lower exciton dissociation and recombination of dissociated charges reduce the power conversion efficiency. For 13 nm silver nanoparticles, plasmon-enhanced scattering improves short-circuit current density but also power conversion efficiency from 2.9 to 3.2%, i.e. by 10%. These different effects of different nanoparticle types show crucial role of their surfactant in the recombination processes that controls potential benefit of plasmonic effect on the power conversion efficiency of the organic solar cell.

#### Acknowledgement

The work was supported by the Grant Agency VEGA Bratislava, projects no. 2/0004/15, 2/0010/15 and 1/0501/15, SAS-TUBITAK JRP 2013/6, APVV-0096-11 and M-ERA-Net XOPTICS projects, Centre of Excellence SAS FUNMAT and COST Actions CM1101 and MP1307.

#### References:

- [1] J. You et al.: *Nat. Commun.*, **4**, 1446 (2013).
- [2] N. R. Armstrong et al.: *Macromol. Rapid Commun.*, **30**, 717 (2009).
- [3] H. A. Atwater, A. Polman: *Nature Materials*, **9**, 205 (2010).
- [4] T. Kocsisova et al.: In: *Proceedings of the 38<sup>th</sup> International Conference of Slovak Society of Chemical Engineering*, Bratislava, 1262 (2011).