# Charge trapping in organic solar cells with plasmonic silver nanoparticles

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## 1. Introduction

Preparation of sub-wavelength metallic nanostructured materials attracts much attention in material research due to potential applications in electronics, optics or sensors because of the plasmonic effect [1]. Especially, plasmonic nanoparticles are interesting for organic photovoltaic devices because of enhanced light scattering and/or exciton dissociation by local electric field. Physical properties of nanomaterials composed of nanoparticles (NPs) are determined by the size, composition and order of NPs. Structure of ordered NP films has recently been studied by electron microscopy, selected area electron diffraction, or grazing incidence small angle x-ray scattering (GISAXS). It has been found that air-liquid interface provides an ideal way for self-assembling of NP films and especially the Langmuir films [2]. Here, the NP film is created on the air-liquid interface and subsequently deposited onto the solid substrate. However, an organic photovoltaic device with ordered NP Langmuir film has not been analyzed yet.

In this contribution we report on the fabrication and structure investigation of the organic solar cells with plasmonic silver nanoparticles. We show that the charge trapping phenomenon cannot be neglected and suppress the short circuit current density  $I_{sc}$  as well as the open circuit voltage  $V_{oc}$ .

## 2. Experiment

Regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM), both from Sigma-Aldrich, were dissolved in chloroform (spectroscopic grade, Sigma-Aldrich) in the concentration of 2 wt%. The P3HT solution was carefully filtered through a 0.40 µm pore size PTFE membrane syringe filter. Silver nanoparticle (Ag NPs) monolayer was prepared from colloid solution (chloroform as a solvent) by a modified Langmuir-Schäffer method of horizontal lifting at the surface pressure of 5 mN/m. A 100 nm thick P3HT-PCBM blend film (ratio 1:1) was subsequently deposited on clean ITO substrate or covered by Ag NPs monolayer by spin-coating. To obtain Ag NPs localized in the bulk of the organic active layer, a sample with P3HT-PCBM-Ag NPs blend film was deposited as well. To improve organic film crystallinity, the samples were annealed at 120°C for 1 hour. Subsequently, top silver electrodes with a circle area of 1.5 mm<sup>2</sup> were evaporated through a metallic shadow mask. The

GISAXS experiment was performed at the incident angle of 0.5 degree with exposition time of 1000 s. The GISAXS experimental setup is described elsewhere [3].



Fig. 1: (a) GISAXS pattern and the (b) horizontal cut on the ITO critical angle and (c) vertical cut at  $q_v=0 \text{ nm}^{-1}$ .

The devices were investigated by standard current-voltage (I-V) analysis using Keithley 2400 SourceMeter in dark or under illumination (white light of a LED lamp with the irradiation intensity of 25 mW/cm<sup>2</sup>). The frequency dependence of the capacitance using Solartron 1260 impedance/gain-phase analyzer.

#### 3. Analysis

The molecule and NP ordering of all devices was analyzed from the GISAXS pattern as illustrated in Fig.1(a). Its horizontal cross-sections at the critical angle of ITO ( $q_z = 0.5 \text{ nm}^{-1}$ ) and the vertical one at  $q_y = 0 \text{ nm}^{-1}$  are re-plotted in Fig.1(b) and (c), respectively. The horizontal cross-section provides evidence of the lateral ordering of the NP mono-

layer by occurrence of a peak located at  $q_y = 0.66 \text{ nm}^{-1}$  that corresponds to the 9.5 nm period. The ring with well developed peak at  $q_z=3.65 \text{ nm}^{-1}$  is due to the P3HT intermolecular distance of 1.7 nm, that is in agreement with reported values [4], and may be indexed as (100). The lateral ordering of the overcoated NP monolayer is identical with the one of the bare NP monolayer on the ITO surface. Hence, the spin coating of the P3HT-PCBM solution left the Ag NP monolayer untouched Hence, the spin coating of the P3HT-PCBM solution left the Ag NP monolayer untouched. In the P3HT-PCBM-Ag NPs blend, the Ag NPs show strong disorder with aggregation to clusters after annealing (results not shown here). The P3HT order is always conserved, being unaffected by the NPs in the organic film.



Fig. 2: Optical absorbance spectra of P3HT-PCBM film, Ag NPs monolayer, and P3HT-PCBM film deposited on Ag NPs monolayer.

The P3HT-PCBM blend film has a commonly reported optical absorbance spectrum (Fig. 2) while the Ag NPs monolayer exhibits a strong peak at 500nm corresponding to surface plasmons. Even though the optical spectra are strongly sensitive to molecular interactions, the spectrum of the P3HT-PCBM film deposited on the Ag NPs monolayer represents a superposition of both signals only.

Figure 3 depicts the I-V characteristics of fabricated devices under illumination. The overall efficiency of the solar cell without NPs (reference device) reaches value of 0.6% only. This rather low value is associated with presence of the oxygen atmosphere during the organic layer preparation and absence of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) layer on the ITO surface.

Interestingly, Ag NPs in the photovoltaic device in the form of a monolayer or dispersed in the organic blend film always decrease  $I_{sc}$  and  $V_{oc}$  (Table 1). This result is in accordance with the charge trapping observed in organic transistors with Ag NP monolayer on the semiconductor-gate insulator interface [5]. The trapping in our device was confirmed by capacitance measurements (not shown here).



Fig. 3: Current-voltage (I-V) curves for organic solar cell with P3HT-PCBM active layer on bare ITO or ITO covered with Ag NPs monolayer. Inset illustrates device structure in presence of Ag NPs.

Table 1: The short circuit current density  $I_{sc}$ , open circuit voltage  $V_{oc}$ , fill factor *FF*, and the overall efficiency  $\varepsilon$  for various device structures.

Device structure	$I_{sc}$	$V_{oc}$	FF	ε
	$(mA/cm^2)$	(V)		(%)
P3HT-PCBM	0.8	0.4	0.27	0.60
P3HT-PCBM@Ag NPs	0.2	0.2	0.25	0.07
P3HT-PCBM-Ag NPs	0.4	0.2	0.24	0.13

## 4. Conclusion

Organic solar cells with an ordered monolayer of plasmonic Ag NPs on ITO substrate or with Ag NPs incorporated into active organic blend layer were fabricated. The plasmonic effect was observed but did not result in an enhanced overall efficiency. The charge trapping by Ag NPs observed by capacitance measurements is presumably the reason and will require a more detailed study.

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