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Plasmonic nanoparticles based high efficiency organic photovoltaic devices

Final Report

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ESF Organisolar, Exchange Grant number 3088: final report on visit of Barbara Paci to Professor Kymakis Emmanuel at Electrical Engineering Department and Center of Materials Technology & Photonics, Technological Educational Institute (TEI) of Crete, Heraklion, Greece.

Purpose of the visit:

The aim of the visit is to carry out a joint research work focusing on two crucial problems of organic photovoltaic cells: the need of improving cell efficiency and the degradation in working condition.

Indeed, latest advances in the field of organic photovoltaic (OPV) have brought this devices- characterized by low cost, flexibility and the ability to cover large surfaces- to a level at which commercialization is a realistic prospect. In polymer-based photovoltaic cells ultrafast photo-induced electron transfer from a conjugated polymer (P3HT as donor) and a soluble fullerene derivate (PCBM as acceptor) is the basic mechanism exploited [1], providing a molecular approach to high efficiency photovoltaic conversion. Cells based on the P3HT:PCBM bulk heterojunction (BHJ) are among the most studied systems, providing efficiencies exceeding 6% [2,3]. Still, the relatively low absorption of the P3HT:PCBM blend in the near-IR range results in a limited spectral overlap with the solar spectrum. On the other hand the it is not possible to raise absorption by using thicker active layers, due to the low carrier mobility of the organic film [4].

An original approach to elude the mentioned problem is provided by the incorporating, in the photoactive layer of the OPV device, metallic NPs, of size smaller than the light wavelength. In such systems, the basic mechanism is the excitation of Localized Surface Plasmon Resonance (LSPR), resulting from the resonant interaction of the surface electron density of the metallic NPs and the electromagnetic field of light. As a consequence of the excitation of collective electron oscillations a local enhancement of the electromagnetic field is produced and a raise in the system optical properties is expected

Description of the work carried out during the visit:

The possibility of improving both the cell efficiency and its stability via the incorporation of gold (Au) Nanoparticles (NPs) in the photoactive layer was investigated.

The devices under study (see figure 1) combine the good charge carrier separation and transport properties of the poly(3-hexylthiophene-2,5-diyl):C_{61}-butyric acid methyl ester (P3HT:PCBM) bulk heterojunction blend and the capability of the metallic NPs to increase the active layer optical absorption by the excitation of Localized Surface Plasmon Resonance, with respect to pristine cells.

Au NPs generation:

The generation of NPs was performed by ultrafast laser ablation of metallic targets (Au/99.98%). This technique provides the possibility of generating a large variety of NPs that are free of both surface-active substances and counter-ions [5]. The targets were placed into a Pyrex cell and covered by a layer of absolute ethanol. A femtosecond (~100fs@1kHz) laser beam was focused onto the target through the ethanol layer. The cell was mounted on a computer-driven X-Y stage and translated during laser exposure. More experimental details can be found elsewhere [6]. Laser irradiation gives rise to a high temperature gradient in the metal bulk and melts of a thin layer of the target. A fraction of the molten layer of the target is dispersed into the liquid as NPs. The corresponding absorption spectra were measured using a Perkin–Elmer UV-VIS spectrophotometer. The respective colloidal solutions exhibit distinct peaks at about 530nm close to the theoretically predicted enhanced absorption due to plasmon resonance (see figure 2).

Device fabrication:

The PV devices were fabricated on 15 mm x 15 mm pre-patterned indium tin oxide (ITO) glass substrates with a sheet resistance of 10 Ω square $^{-1}$. In all cases, a 50-nm-thick PEDOT:PSS film (Clevios AI 4083, H. C. Starck) was deposited by spin-coating at 4000 rpm for 30s, followed by a 200-nm-thick photoactive layer cast from 2.5 wt% P3HT:PCBM (Rieke Metals, Nano-C) in a 1:1 ratio in dichlorobenzene, spun at 1000 rpm for 20s . This layer was allowed to dry for 45 minutes in a covered Petri dish. The vacuum-deposited cathode of about 60 nm of Al was evaporated at 10^{-6} Torr. Finally annealing was perfomed at 140^{O}C. All device areas were 15 mm^2.

Au NPs were blended into the P3HT:PCBM solution at different weight ratios (wt%), determined from the initial concentration of Ag NPs in ethanol which was $5 \times 10 - 5$ mg mL^{-1} . Composite blends with 2, 5, 7, and 10 wt% Ag NPs were prepared.

Device parameters :

Current–voltage (I–V) measurements were performed at room temperature using an Agilent B1500A Semiconductor Device Analyzer in air. For photovoltaic characterization the devices were illuminated with 100 mW/cm^2 power intensity of white light by an Oriel solar simulator with an AM1.5 filter through the glass/ITO side.

Comparison of IV curves for a pristine and a doped cell is reported in figure 3 and the photovoltaic parameters of the OPV devices are summarised in table I.

Importantly, the use of Au NPs provides a remarkable increment of the initial cell efficiency.

Device stability**:**

Still, improved initial PV efficiencies must be preserved over time. Indeed, the rapid loss in performances under ambient conditions is nowadays the major drawback to overcome for a future commercialization of polymer based devices. A comparison between the pristine and the NPs-doped solar cells can be made reporting the normalized power conversion efficiency, PCE, curves as a function of exposure time (see figure 4) in air. Over the first 12 hours an abrupt aging of the reference cell was detected. On the contrary, in the same time scale, the plasmonic device preserved over 20% of its initial PCE. Therefore, PCE data show that the use of plasmonic NPs enhances the cell performance stability over time.

-Description of the main results obtained:

The joint work addressed the need of improving OPV cell efficiency and mitigating the degradation in working condition. A comparative study is produced, analyzing both reference samples, based on P3HT:PCMB (1:1) blends, and plasmonic samples based on BHJs incorporating Au NPs. We found that the plasmonic devices are characterized by enhanced PV performance. Most importantly, PV aging experiments demonstrate that the Au doped devices are characterized by enhanced PV properties durability.

-Future collaboration with host institution

Future collaboration is planned and will focus on the study of plasmonic systems for OPV devices, their further optimization and the deep investigation of their structural, morphological and photo physical properties, in particular regarding aging effects.

Projected Publication: The results here briefly summarized will be integrated with additional data from undergoing experiments and analysis and will result in a join publication.

Other comments: We require not to publish online this report before the publication of the paper.

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Figures:

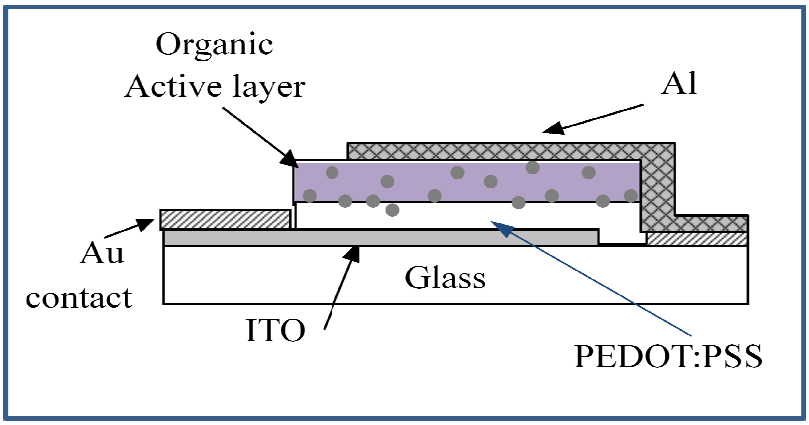

Figure 1

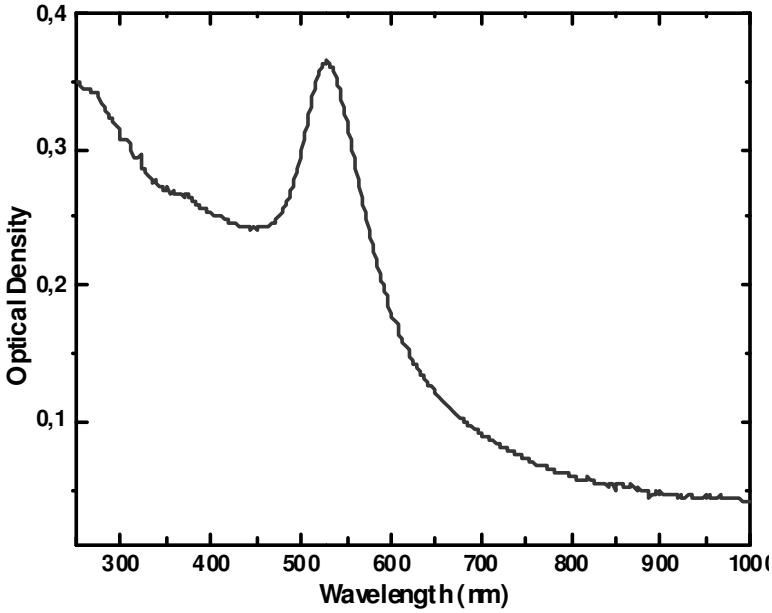

Figure 2

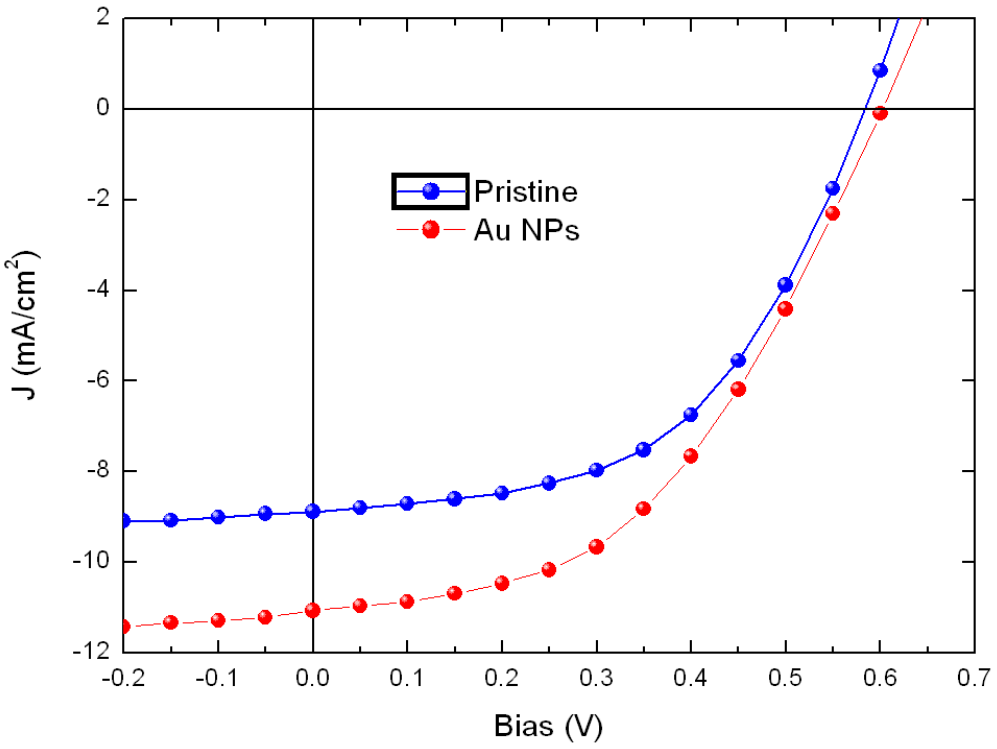

Figure 3

HTL	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
Pristine	0,59	8.87	52	2.7
Au NPs (5% wt)	0.60	11.06	48.2	3.2

Table I

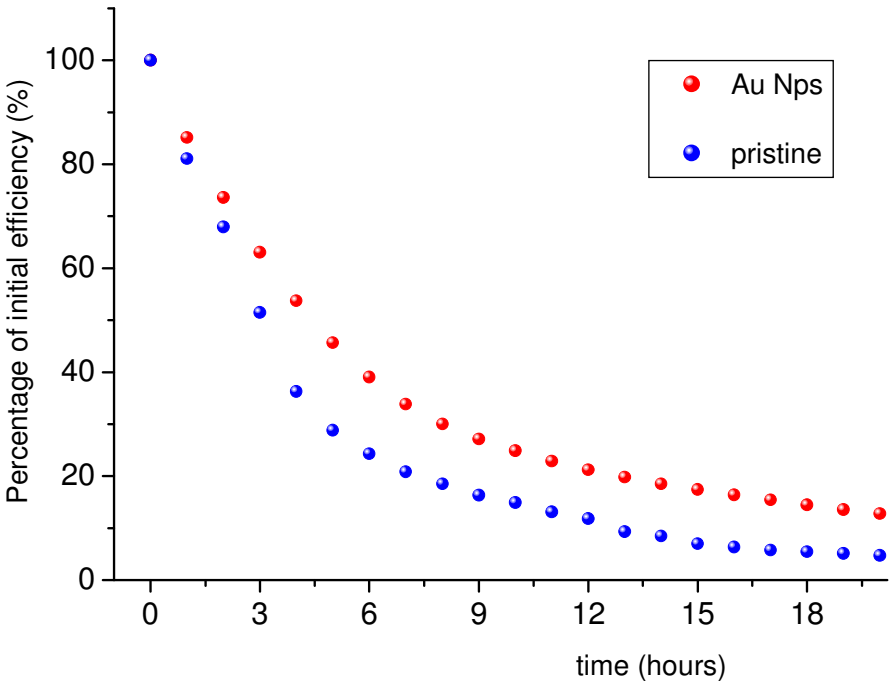
Percentage of initial efficiency (%)
100
80
60
40
20
0
0
3
6
9
12
15
18
time (hours)
Au Nps
pristine

Figure 4