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Enhanced organic light emitting diode and solar cell performances using silver nano-clusters

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ABSTRACT

Silver nano-clusters (NCs) were incorporated into organic light emitting diodes (OLED) and solar cells by means of thermal evaporation. Silver NCs enhance the efficiency of both OLEDs and polymer solar cells under tailored device architecture. In tris-(8-hydroxyquinoline) aluminum (Alq_3) based small molecule OLEDs, silver NCs were deposited under the Al cathode. The electron injection from the cathode to organic layer is promoted significantly owing to silver NCs induced lightning rod effect, the Alq_3 OLEDs luminous efficiency is increased up to a factor of 6. In poly(3-hexylthiophene) (P3HT) polymer solar cells, the active layer absorption is enhanced in the presence of silver NCs, which can be ascribed to NCs induced light scattering effect as well as to plasmon enhanced local electric field effect. As a result, photocurrent of the solar cells is increased and the power conversion efficiency (PCE) is improved up to 20%. The comparative study of surface plasmon effects in different organic optoelectronic devices reveals interesting features of the surface plasmon and allows optimization of optoelectronic devices from a novel point of view.

1. Introduction

Surface plasmon enhanced luminescence, both fluorescence and phosphorescence, has attracted intensive interest due to its potential application in biological imaging and single molecule detection [1,2]. Most of the research work so far was limited to surface plasmon enhanced photoluminescence (PL) in which the surface plasmon of noble metals such as gold and silver nanoparticles (NPs) improves the PL quantum efficiency (QE) of a chromophores up to two orders of magnitude [3]. However less attention was paid to surface plasmon enhanced electroluminescence (EL) [4,5], which also shows great potential for improving the EL efficiency of OLEDs [6–10].

OLEDs with the fluorescent small molecule tris-(8-hydroxyquinoline) aluminum (Alq_3) as emitting layer were widely studied. Various methods have been used to date to improve their performance, like balancing the hole/electron injection ratio and reducing the carrier injection barrier [11,12]. The former method relies mainly on doping the hole transport layer (HTL) or inserting a buffer layer between the HTL and the anode to reduce the hole mobility or impede the hole injection. However, this inevitably increases the turn-on voltage and there exists a tradeoff between low driving voltage and high efficiency [13,14]. The latter method requires the development of new materials that match the work functions of both anode and cathode. A few attempts were made to improve Alq_3 OLED efficiency by incorporating silver NPs. For instance Li et al. reported that the silver NPs improved PL QE of Alq_3 more than threefold [15]. However, the EL of their Alq_3 based OLEDs was not enhanced by Ag NPs due to a deep charge trapping effect; the deteriorated performance discourages the extension of the surface plasmon enhanced PL concept to EL.

In the case of solar cells, light harvesting and trapping inside solar cells is an active research topic [16]. For wafer-based solar cells, inverted pyramids of a size around

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10 μm were used for light trapping; however such surface texture is not amenable to thin film solar cells since their thickness is in the range of 1–2 μm. Alternatives were found like the use of surface relief gratings on polymer thin-films [17]. Metal NPs can also be a good alternative to promote light trapping. Pillai et al. reported a sevenfold enhancement of the absorption for a wafer-based cell at λ = 1200 nm, and up to 16-fold enhancement at λ = 1050 nm for a 1.25 μm thin film silicon solar cell using silver NPs [18]. The underlying mechanism is understood as the increase of the optical path length in the silicon thin film due to the large scattering cross section of metal NPs. Therefore this light trapping process can effectively enhance silicon solar cells efficiency.

The application of metal NPs in organic solar cells has been explored recently [19]. However, the incorporation of metal NPs in organic solar cells was not as successful as in silicon solar cells. Yoon et al. reported plasmon enhanced optical absorption in organic bulk heterojunction (BHJ) solar cells using a self-assembled layer of silver NPs, which was deposited between the hole transporting layer and the polymer layer [20]. Although the solar cell incorporating silver NPs presents a slightly larger short circuit current (I_{sc}), it suffers significant decrease of both fill factor and open circuit voltage (V_{oc}), causing a lower PCE. Origin of the reduced cell efficiency was attributed to charge recombination at the surface of silver NPs and delayed charge extraction.

We therefore explored new strategies to incorporate silver NPs into organic optoelectronic devices and investigated the role of silver NPs in enhancing OLED and organic solar cell devices efficiency. Motivation of the research is to improve our insight into metal NPs induced optical and electrical behaviors in organic optoelectronic devices, and to optimize devices performance from a different point of view. In our experiments with OLEDs, we clearly identified the formation of nano-particles; meanwhile they clearly agglomerated into nano-clusters (NCs) in the case of our PV devices.

2. Experiments

2.1. Materials

Tris-(8-hydroxyquinoline) aluminum (Alq_3, 99.995%) and poly(3-hexylthiophene) (P3HT) were purchased from Aldrich, [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM, 99%) was obtained from SES Research, *N*-*N*′-di-[(1-naphthyl)-*N*,*N*′-diphenyl]-(1,1′-biphenyl)-4,4′-diamine (NPB) was obtained from Lumtec, bathocuproine (BCP, 97%) was obtained from Fluka, Poly (3,4-ethylenedioxythiophene) poly (styrenesulfonate) (PEDOT:PSS, PH1000) from Clevios.

2.2. OLED device fabrication

NPB, Alq_3, BCP were used as hole transport layer, emission layer and exciton blocking layer, respectively. OLEDs with the structure ITO/NPB (50 nm)/Alq_3 (*x* nm)/BCP (6 nm)/silver (1 nm)/aluminum (200 nm) were fabricated as follows: organic materials NPB, Alq_3 and BCP were sublimed onto ITO coated slides with sheet resistance 15 Ω/□, in order, under 10^{-6} mbar vacuum at a rate of 0.1 nm/s; subsequently a 1 nm silver NP layer was deposited on top of BCP by thermal evaporation; finally a 200 nm aluminum cathode was deposited. The device structure is presented in Fig. 1.

2.3. Solar cell fabrication

We adopt an inverted solar cell structure [21] with ZnO layer on top of the ITO film as an electron-collecting layer [22], the conductive ITO electrode serves as a cathode as shown in Fig. 6. A ZnO precursor solution containing 0.75 M zinc acetate dihydrate and 0.75 M monoethanolamine in 2-methoxyethanol was stirred overnight and aged another 12 h before using. The precursor solution was spin coated on ITO glass at 2000 rpm, and heated up on a hotplate at 275 °C for 5 min. The transparent ZnO film was then washed with distilled water, acetone and isopropanol to remove residual organic materials from the surface; the resulting ZnO layer thickness is around 70 nm. An active layer around 200 nm thick, consisting of P3HT and PCBM blend (20 mg/ml P3HT in 1,2-dichlorobenzeene, P3HT: PCBM = 1:1 by weight) was then deposited on top of ZnO. The resulting film was annealed in a glove box with N_2 atmosphere at 110 °C for 10 min to crystallize the amorphous P3HT film. A PEDOT:PSS layer (mixed with 5% DMSO and 1 wt.% Triton X-100) around 100 nm-thick was then spin coated on top of the polymer layer, followed by another 10-min thermal treatment at 120 °C to dry PEDOT:PSS film. Finally, silver NPs were evaporated on top of PEDOT under 10^{-6} mbar vacuum. The active area was 1 cm^2. In our solar cells the conductive PEDOT:PSS layer serves as the anode. All solar cells were annealed at 150 °C for 10 min after silver NPs deposition to form silver nano-clusters (NCs) from the regionally continuous silver thin film.

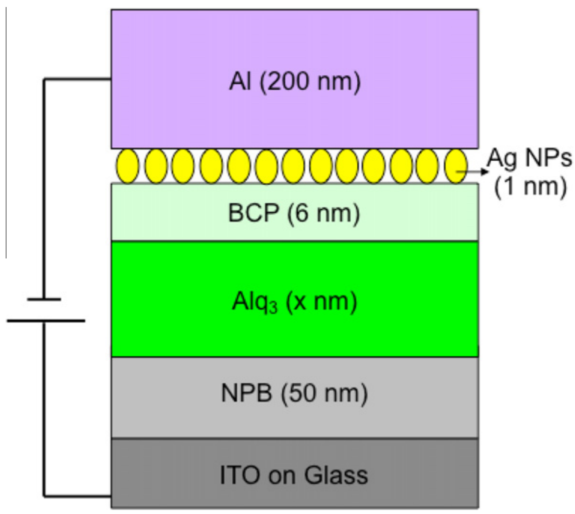

Fig. 1. Schematic diagram of OLED configuration, *x* varies from 20 to 60 nm.