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# Enhanced power conversion efficiency of organic solar cells by embedding Ag nanoparticles in exciton blocking layer

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### ABSTRACT

We demonstrate the power conversion efficiency of bulk heterojunction organic solar cells can be enhanced by introducing Ag nanoparticles into organic exciton blocking layer. The Ag nanoparticles were incorporated into the exciton blocking layer by thermal evaporation. Compared with the conventional cathode contact materials such as Al, LiF/Al, devices with Ag nanoparticles incorporated in the exciton blocking layer showed lower series resistances and higher fill factors, leading to a 3.2% power conversion efficiency with a 60 nm active layer; whereas, the conventional devices have only 2.0–2.3% power conversion efficiency. Localized surface plasmon resonances by the Ag nanoparticles and their contribution to photocurrent were also discussed by simulating optical absorptions using a FDTD (finite-difference-time-domain) method.

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## 1. Introduction

Organic solar cells are a promising alternative to conventional inorganic photovoltaic devices because of their low cost of materials, low processing temperatures and compatibility with flexible form factors. The power conversion efficiency of organic solar cells have improved steadily owing to elaborate morphology control of active materials, development of low bandgap materials with high carrier mobility, interface engineering and light management [1–6]. The efficiency of organic solar cells recently reached over 10% but further improvements are necessary to make organic solar cells commercially viable [7]. In addition to the development of optimal active materials, electrically ohmic contact between active materials and both

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electrodes are required for efficient charge carrier collection [8]. Among the variety of approaches to allow for ohmic contact at both the anode and cathode, the insertion of buffer materials between the active lavers and electrodes is one of the most widely used methods. Conductive polymers and transition metal oxides such as poly(3, 4-ethylenedioxythiophene):poly(styrenesulfonate) (PED-OT:PSS),  $VO_x$ ,  $MOO_x$  and  $NiO_x$  are widely employed at the anode contact [9]. For the cathode contact, inorganic materials such as LiF, and TiO<sub>x</sub> [10,11] or small molecular weight organic materials such as bathocuproine (BCP), Tris-(8-hydroxyquinoline)aluminum (Alq<sub>3</sub>), and Bathophenanthroline (Bphen) have been introduced as cathode buffer materials [12–14]. Although there have been many reports on the use of electron transport layers (ETLs) in polymer based organic solar cells, its effectiveness has been limited and tends to vary from report to report due to a number of morphological or electrical considerations







[15–17]. In this contribution, we demonstrate that the power conversion efficiency of polymer based organic solar cells with BCP as cathode buffer layer can be enhanced with the incorporation of Ag nanoparticles (NPs) in the BCP laver, and its contribution to photocurrent enhancements are also discussed. It was found that the enhanced power conversion efficiency was due to the combined effects of decreased series resistances with the Ag NPs, resulting in improved charge collection at the cathode contact, and enhanced optical absorption due to the localized surface plasmon resonance (LSPR) of Ag NPs. Although the use of plasmonic Ag and Au NPs have been previously considered as a promising method to enhance the efficiency of organic solar cells, they have typically been embedded into active layers or a hole transport layer of PEDOT:PSS in efforts to boost optical absorption [18,19]. In this article, we show that the insertion of plasmonic metal NPs at the back contact between active layers and cathode metal is also effective since the placement of low work function Ag NPs near the cathode contact minimally influences the open circuit voltage.

### 2. Experimentals

Poly(3-hexylthiopene) (P3HT) was purchased from Lumtech Ltd. Co. (Taiwan), PCBM (phenyl-C61-butyric acid methyl ester) was purchased from Solenne B.V. (Netherlands), and BCP was purchased from TCI Co. (Japan) and all were used as received. Patterned ITO (indium tin oxide) substrates for device fabrication were cleaned sequentially with organic solvents of acetone, methanol, and isopropyl alcohol. PEODT:PSS (Clevios P VP AI 4083) was used as an anode buffer layer by spin coating and annealed at 150 °C for 10 min. P3HT and PCBM were mixed in dichlorobenzene at 1:1 weight ratio and concentration of 20 mg/ml and spun on ITO substrate coated with PEDOT:PSS for deposition of active layers at the spinning rate of 800 rpm. The active layers were annealed at 140 °C for 30 min. For the cathode buffer layer, LiF and BCP were deposited by vacuum thermal evaporation. For incorporation of Ag NPs in BCP, Ag of a 1 nm nominal thickness was deposited by thermal evaporation between depositions of two BCP layers. The first layer thickness of BCP was varied from 1 nm to 5 nm; while, the total thickness of the BCP layers was kept at 10 nm as shown in Fig. 1. The devices were capped with an Al cathode deposited through a shadow mask defining a device area of  $0.2 \text{ cm}^2$ . The current density-voltage (I-V) characteristics of the devices were measured in dark and under illumination of AM 1.5G at a light intensity of 100 mW/cm<sup>2</sup>. External quantum efficiency (EQE) and optical reflectance of the devices were measured at the wavelength range of 400-800 nm using a custom-setup (Optoronic Laboratories). Monochromatic light was incident on glass, and the reflected light was measured to determine reflectances using a calibrated Ag mirror as a reference. Using photoluminescence spectroscopy (Fluorolog, Horiba Scientific), PL intensity from P3HT films for the cases with Ag NPs was measured to investigate the effect of BCP on exciton blocking. The wavelength of the excitation light for the PL measurements was 400 nm and incident on the surface of the P3HT films.

Finite-difference-time-domain (FDTD) simulations in three dimensions were performed to investigate the effects of Ag NPs on the optical absorptions of the devices using a commercial software package (Lumerical FDTD solutions). The shape of Ag NPs was assumed to be spherical and their surface density was calculated based on a nominal thickness of 1 nm. The periodic boundary conditions in *x*- and *y*-directions and perfectly matched layer conditions in *z*-direction were used. The optical absorptions in the devices and the active layers were calculated and discussed for the cases of three different locations of Ag NPs: (1) within the active layer and BCP, and (3) within the BCP layer in contact with the active layer.

## 3. Results and discussions

P3HT:PCBM bulk heterojunction solar cells with a 60 nm active layer thickness were fabricated with various contact materials. The J-V characteristics, measured under a standard condition, are shown in Fig. 2(a). For each device an Al (100 nm) cathode was used. Although Al is a





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