Organic Electronics 62 (2018) 95–101

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Efficient organic solar cells based on PTB7/$PC_{71}BM$ blend film with embedded different shapes silver nanoparticles into PEDOT:PSS as hole transporting layers

Chih-Ping Chen[a,*], I-Chan Lee[a], Yao-Yu Tsai[a], Cheng-Liang Huang[b,**], Yung-Chung Chen[c,***], Guan-Wei Huang[c]

[a] Department of Materials Engineering, Ming Chi University of Technology, New Taipei City, 243, Taiwan ROC
[b] Department of Applied Chemistry, National Chiayi University, Chiayi City, 60004, Taiwan ROC
[c] Department of Chemical and Materials Engineering, National Kaohsiung University of Science and Technology, Kaohsiung City, 80778, Taiwan ROC

ARTICLE INFO

Keywords:
PEDOT:PSS/Ag NPs hybrid HTLs
Decahedral and icosahedron Ag nanoparticles
PTB7
Organic photovoltaic

ABSTRACT

In this study, two size-controllable silver nanoparticles, decahedral and icosahedron Ag NPs, were embedded into PEDOT:PSS as hybrid hole transporting layer (HTLs) for organic photovoltaic applications. The Ag-decahedral based nanoparticle exhibited rather red-shifted and larger domain size than Ag-icosahedron one. Due to the plasmonic and light harvesting effects of Ag NPs, the power conversion efficiency (PCE) was increased from 5.8% to 6.5 (decahedral-based) and 6.3% (icosahedron-based) in Poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7):[6,6]-Phenyl C71-butyric acid methyl ester ($PC_{71}BM$) based-OPV upon embedding the Ag NPs. External quantum efficiency (EQE) enhancement was also observed due to the plasmonic scattering effect. The atomic force microscope (AFM) images showed the roughed results of the PEDOT:PSS/Ag NPs hybrid HTL films, i.e. better hole collection efficiency. Furthermore, the active layer did not show any aggregation and morphology change after adopting hybrid HTL films into the devices.

1. Introduction

Organic photovoltaic cells (OPVs) have received much interest because of their characteristics for the solution processability, flexibility, large scale and low cost properties. Power conversion efficiencies (PCEs) enhancement for real applications, the intensive development on active layer structural modifications, device engineering or morphology controlling has been made [1–7]. Recently, a great number of single-junction OPVs with PCEs over 10% and even up to 13% were reported [8]. However, due to the intrinsic narrow absorption of the conjugation polymer, low carrier motilities and limited interfacial charge transported efficiencies, there is still larger room to make high cell performance and ready to market.

The utilization by incorporating functional additives into devices has been shown an effective way for PCE enhancement due to the on sufficient light absorption, better electron transporting, and efficient charge extraction etc [9–12]. Among several kinds of additives, the metallic nanoparticles (NPs) are the most popular materials caused of the efficient optical scattering characteristic and surface plasmon resonance (SPR) effect [13–16]. The additives have been studied and dispersed into the (1) hole transporting layer (HTL), i.e. PEDOT:PSS [16–18], (2) interfacial layer between HTL and active layer [19,20], and (3) active layer [16,21] for OPV devices. In order to maximize the positive effect on NPs, it have to decrease the possibility of transferring non-radiative energy. This means as introducing NPs into active layer, the NPs could become charge recombination centers, leading to exciton quenching and non-radiative energy transfer between organic photoactive layers and metal NPs, i.e. approach 3 [22,23]. Therefore, part of researchers utilized approach (1) or (2), alternatively. However, the SPR effect may decrease as the distance increases between NPs and the active layer [24]. In addition, the OPV film thickness limitations also restricted as the bottleneck for NP particle sizes. Hence, the controlled morphologies and sized of the NPs could be the important factors on this kinds of hybrid devices [18]. Therefore, the two-dimensional

* Corresponding author.
** Corresponding author.
*** Corresponding author.
E-mail addresses: cpchen@mail.mcut.edu.tw (C.-P. Chen), clhuang@mail.ncyu.edu.tw (C.-L. Huang), chenyc@nkust.edu.tw (Y.-C. Chen).

https://doi.org/10.1016/j.orgel.2018.07.024
Received 26 May 2018; Received in revised form 26 July 2018; Accepted 26 July 2018
Available online 27 July 2018
1566-1199/

nanostructures such as nanoplates with high aspect ratios or sized-controllable NPs were the main strategies to overcome this problem [18,25–27].

In addition, the absorption and SPR effect of the NPs strongly depends on the shape, size and distribution [28]. Among these, the shape of NPs is an important factor since it directly affect SPR and scattering of incident light [29]. Previously, Chen et al. synthesized a shape- and size-controlled silver nanoparticles and embedded into HTLs for OPV cells. The triangular Ag NPs (50–60 nm) based cell showed higher cell performance than the circular one (40–50 nm). In addition, the best cell performance (6.4%) was higher than that (6.1%) of a corresponding normal device [18]. Chou et al. prepared different types of gold NPs into OPV device. They concluded that NPs with more corners and proper particle sizes induce more coupling and scattering effect in P3HT:$PC_{61}BM$-based active layers, which potentially increased the light harvesting [29]. Octahedral and decahedral-shaped Au nanoparticles were also synthesized for polymer solar cell systems that developed by Heeger [30] and Yang et al. [31].

Although it had been prepared various shape of Au NPs for photovoltaic but the relevant OPV literature based on shape-dependent polyhedral Ag NPs are very limited. In this work, we try to synthesis size-controlled of decahedral or Icosahedron shape of Ag nanoparticles. Followed by embedded those nanoparticles into HTL layer with Poly [[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b']dithiophene-2,6-diyl] [3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7)/$PC_{71}BM$ (Fig. 1) as an active layer for OPV devices. The commercial electron donor polymer called PTB7 was selected in this work due to due to: (1) a narrower optical band gap and rather red-shifted UV absorption region, (2) good intermolecular π-π stacking when blending with fullerene component; (3) and a well combination with all PSCs (polymer solar cells). Therefore, higher than 10% of PCEs were achieved based on PTB7 under different devices configuration [32–34]. Finally, a configuration of ITO/HTL/active layer/Ca/Al is fabricated and measured. The different compositions of HTLs, i.e. PEDOT:PSS only or PEDOT:PSS/Ag NPs hybrid, were prepared and their photo physical properties, morphologies and cell performance was conducted and compared.

2. Experimental

2.1. Materials

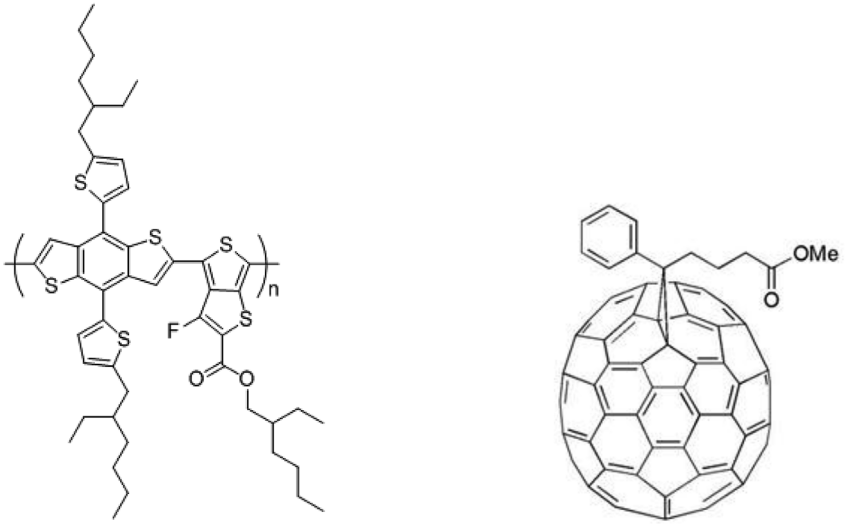
The active layer composition (PTB7 and $PC_{71}BM$) (Fig. 1) unless otherwise specified, were used as received. Solvent such as chlorobenzene (CB), Dimethylformamide (DMF) were used as received. Reagents: silver nitrate, sodium citrate, sodium tartrate were used without further purified. Milli-Q grade water (> 18 MΩ) was used for Ag nanoparticles synthesis part.

2.2. Synthesis of decahedral and icosahedral Ag NPs

The silver nanoparticles were prepared by the seed-free photo-assisted citrate (or tartrate) reduction method under the irradiation of blue LEDs or UV light with a wavelength of 310 ± 12 nm. The procedures described in details in the previous studies [35,36]. Briefly, 1 mL of sodium citrate (4.5×10^{-1} M) or sodium tartrate (4.5×10^{-1} M) and 1 mL of silver nitrate (1.0×10^{-2} M) were mixed with 98.0 mL of pure water. The mixture was subsequently irradiated with 24 blue LEDs (λ_{max} = 460 ± 12 nm, average power ≈100 mW/cm^2, for the preparation of decahedral Ag NPs) or 24 UVB lamps (λ_{max} = 310 ± 12 nm, average power 25 mW/cm^2, for the preparation of icosahedral Ag NPs) assembled on a cylindered reaction pot. Silver nanoparticle colloids with more than 85% nanodecahedra were obtained after 90 min of irradiation under blue LEDs. The decahedral Ag NP colloids exhibited a dipolar LSPR band at about 500 nm. More than 90% of icosahedral Ag NPs can be obtained after 48 h of irradiation under UVB. The icosahedral Ag NP colloids exhibited a dipolar LSPR band at about 435 nm. The prepared decahedral Ag NP colloids were then subjected to centrifugation at 8000 rpm for 60 min. The precipitates were collected and re-dispersed in DMF. The concentration of Ag elements in DMF is about 250 mg/L.

2.3. Devices fabrication

The fabricated BHJ devices were prepared with a configuration of ITO/HTL/active layer/Ca/Al. The corresponding devices were prepared according to the following procedures: (1) Glass–ITO substrates [Sanyo, Japan (8 Ω/square)] were sequentially patterned lithographically, cleaned with detergent, ultrasonicated in acetone and isopropyl



PTB7 **$PC_{71}BM$**

Fig. 1. Structures of active layer components PTB7 and $PC_{71}BM$.