Chinese Chemical Letters 26 (2015) 419–425

Contents lists available at ScienceDirect

Chinese Chemical Letters

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

Review

Optical enhancement effects of plasmonic nanostructures on organic photovoltaic cells

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ARTICLE INFO

Article history:
Received 13 November 2014
Received in revised form 29 December 2014
Accepted 7 January 2015
Available online 25 February 2015

Keywords:
Organic photovoltaic
Plasmonic nanostructure
Nanoparticle
Nanograting
Nanoimprint lithography

ABSTRACT

In this article, the optical enhancement effects of plasmonic nanostructures on OPV cells were reviewed as an effective way to resolve the mismatch problems between the short exciton diffusion length in organic semiconductors (around 10 nm) and the large thickness required to fully absorb sunlight (*e.g.* hundreds of nanometers). Especially, the performances of OPVs with plasmonic nanoparticles in photoactive and buffer layers and with periodic nanostructures were investigated. Furthermore, nanoimprint lithography-based nanofabrication processes that can easily control the dimension and uniformity of structures for large-area and uniform plasmonic nanostructures were demonstrated.

1. Introduction

Surface plasmons (SPs) are surface waves whose electromagnetic field is confined to the vicinity of the metal/dielectric interface. When the condition of the resonance is fulfilled, this confinement leads to an enhancement of the electromagnetic field at the interface [1–3], therefore, this aspect has been utilized in many photonic applications such as optical devices, sensors and optoelectronics [4–7]. Among them, their effects on organic photovoltaic (OPV) cells have been highlighted [8–12], because the field enhancement associated with such nanostructures can be potentially effective means to improve the efficiency of OPVs by enhancing the absorption of light even in a very thin organic semiconductor layer. Because exciton generated in organic semiconductor upon light absorption has limited diffusion distance around 10 nm, which is mismatched to the thickness of photoactive layer for efficient light absorption (*e.g.* hundreds of nanometers scale), there is inevitably trade-off between photo-generated charge collection and light absorption, which should be resolved to achieve high performance OPV devices [13–15]. Therefore, the approaches utilizing surface plasmon resonance (SPR) that can improve the optical field in OPV without increasing the thickness of photoactive layer, in principle, can be an effective way to address the mismatch problems between the short exciton diffusion length in organic semiconductors and the large thickness required to fully absorb sunlight [16–18].

Metal nanoparticle system has been extensively studied to apply SPR effect to OPV cells due to the simple preparation steps. Those plasmonic metal nanoparticles can be fabricated by electrodeposition [19], chemical synthesis [20–22], nanoimprint lithography (NIL) [7], thermal annealing [23], pulse-laser ablation [24] and vapor phase deposition [25]. In general, the effects of those plasmonic nanoparticles on OPV cells are classified by the size of the particles. It has been known that small nanoparticles (<20 nm) can enhance near-field due to the excitation of localized surface plasmon resonance (LSPR), increasing effective absorption, and relatively larger nanoparticles (>40–50 nm) can be sub-wavelength scattering sites that can trap propagating plane waves of incident light, consequently increasing optical path length in photoactive layer [1,26–28]. Those nanoparticles affect the absorption of light in buffer layer or photoactive layer. Besides, periodic metal nanostructures such as nanogratings are also promising candidate as plasmonic light-trapping structure, because geometrical parameters can be easily controlled for the efficient light absorption [1,7,11,12,29,30].

In this article, we summarize recent works to improve the performances of OPV cells by enhancing the absorption of light without increasing the thickness of photo-absorber using light

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http://dx.doi.org/10.1016/j.cclet.2015.02.001

trapping structures, especially plasmonic metal nanostructures, in OPV devices, including the works demonstrated in our research group.

2. Metal nanoparticles in buffer layer

There have been many works that have reported improved PCE by embedding metal nanoparticles in buffer layer such as poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), widely utilized hole transport layer (HTL) in OPV structure. A benefit of this approach is to prevent the quenching of excitons by the metal nanoparticles. By adding Ag or Au nanoparticles into PEDOT:PSS, increased photocurrent by SPR was shown in various BHJ blends systems such as poly(3-hexylthiophene-2,5-diyl) (P3HT):phenyl-C_{61}-butyric acid methyl ester (PCBM) [19,22,31,32], poly[*N*-9″-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT): [6,6]-phenyl C_{71}-butyric acid methyl ester ($PC_{71}BM$) [9], 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):$PC_{71}BM$ [9], and poly-(2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV):PCBM [33], as shown in Fig. 1. Furthermore, the cooperative plasmonic effect from dual resonance enhancement of mixture of Ag and Au nanoparticles was also demonstrated showing 20% improvement of PCE in PTB7:$PC_{71}BM$ blend system [10], and more broadband absorption enhancement by mixture of different shapes of nanoparticles such as nanorod and nanosphere was shown [34]. To achieve broad light absorption, carbon-dot-Ag (CD-Ag) nanoparticle scheme was also developed. CD-Ag nanoparticle in PEDOT: PSS layer gave 10% improved PCE of PTB7:$PC_{71}BM$ blend PV cell [35]. In addition, it has been shown that plasmonic metal nanoparticles embedded in interconnecting buffer layer of tandem cells can be utilized to enhance the absorption of both top and bottom sub-cells [36]. Meanwhile, there are several reports that nanoparticles can induce other effects instead of plasmonic optical enhancement. Fung *et al.* [37], showed that optical enhancement from their nanoparticles in PEDOT:PSS is minimal due to the lateral distribution of strong near field LSPR along PEDOT:PSS layer, not vertical direction into active

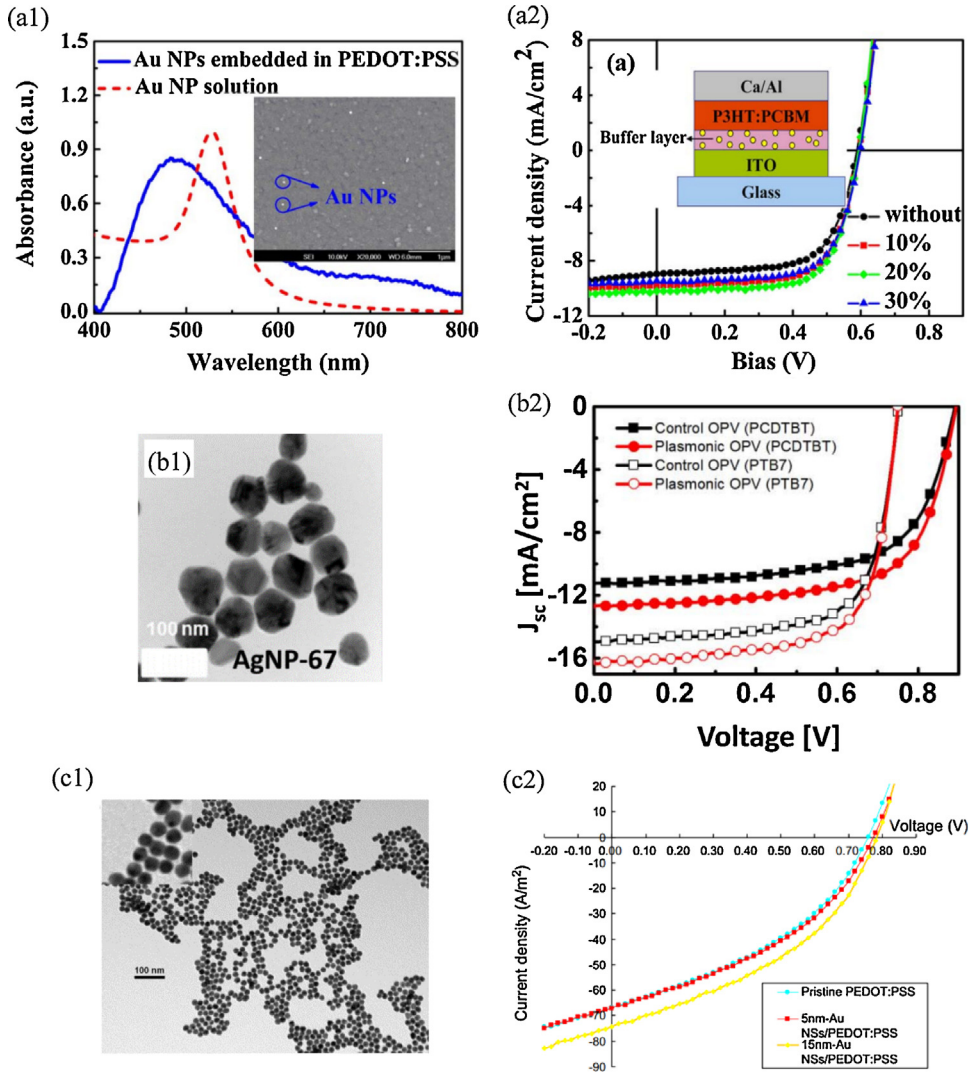

Fig. 1. Effects of plasmonic nanoparticles embedded in buffer layer of (a1)–(a2) P3HT:PCBM system, (b1)–(b2) PCDTBT:PCBM and PTB7:PCBM systems, (c1)–(c2) MEH-PPV:PCBM system: (a1) Absorption spectra of Au NPs embedded in the PEDOT:PSS matrix and in solution. Inset: SEM image of the PEDOT:PSS film prepared with 20% Au NP solution blended into the matrix. (a2) *J*–*V* characteristics of devices incorporating PEDOT:PSS doped with various concentrations of Au NP solutions. Reproduced with permission [22]. Copyright 2009, American Institute of Physics. (b1) TEM image of Ag nanoparticles. (b2) *J*–*V* curves of the best plasmonic OPV (red circles) and the control OPV (black squares). The filled and open symbols denote the PCDTBT:$PC_{71}BM$ and PTB7:$PC_{71}BM$ devices, respectively. Reproduced with permission [9]. Copyright 2013, Macmillan Publishers Ltd. (c1) TEM image of Au nanoparticles. (c2) *J*–*V* characteristics of devices under illumination. Reproduced with permission [33]. Copyright 2011, Elsevier Ltd. *J*–*V* curves of all OPV cells were recorded under AM 1.5 G illumination at 100 mW cm^{-2}.