



Review

Optical enhancement effects of plasmonic nanostructures on organic photovoltaic cells

Hui Joon Park^{a,*}, L. Jay Guo^{b,*}^a Division of Energy Systems Research, Ajou University, Suwon 443-749, South Korea^b Department of Electrical Engineering and Computer Science, University of Michigan, Ann Arbor, MI 48109, USA

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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.

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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

* Corresponding authors.

E-mail addresses: huijjoon@ajou.ac.kr (H.J. Park), guo@umich.edu (L.J. Guo).

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-C₆₁-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 C₇₁-butyric acid methyl ester (PC₇₁BM) [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):PC₇₁BM [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:PC₇₁BM 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:PC₇₁BM 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

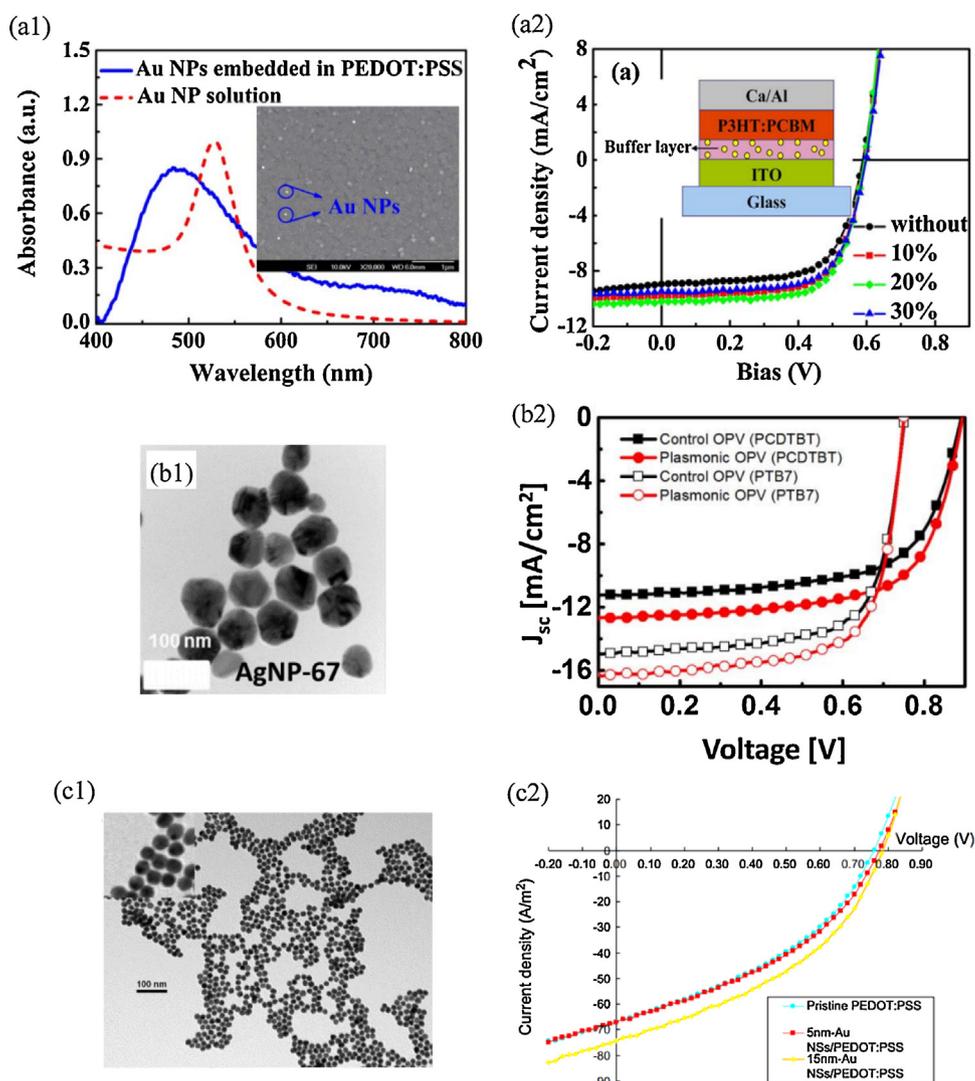


Fig. 1. Effects of plasmonic nanoparticles embedded in buffer layer of (a1)–(a2) P3HT:PCBM system, (b1)–(b2) PCDTBT:PCBM and PTB7:PCBM systems, (c1)–(c2) MEH-PPV:PCBM system: (a1) Absorption spectra of Au NPs embedded in the PEDOT:PSS matrix and in solution. Inset: SEM image of the PEDOT:PSS film prepared 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:PC₇₁BM and PTB7:PC₇₁BM 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.

layer, and PCE improvements are originated from the enlarged interfacial area between active layer and PEDOT:PSS and reduced sheet resistance and Stavtyska-Barba *et al.* [38] showed that metal nanoparticles can induce morphological or chemical changes in PEDOT:PSS layer that may contribute to the performance of OPV cells.

3. Metal nanoparticles in photoactive layer

Optical enhancement effects from plasmonic metal nanoparticles in photoactive layer also have been widely studied. For example, Au nanoparticles in P3HT:PC₇₁BM, PCDTBT:PC₇₁BM, and poly{[4,4'-bis(2-ethylhexyl)dithieno(3,2-b:2',3'-d)silole]-2,6-diylalt-[4,7-bis(2-thienyl)-2,1,3-benzothiadiazole]-5,5'-diyl} (Si-PCPDTBT):PC₇₁BM blend systems [39] and Ag nanoparticles in PCDTBT:PC₇₁BM blend system [40] showed improved absorption of light by scattering from relatively large metal nanoparticles (>40 nm) of the incident light, which effectively increases the optical path length (Fig. 2). In these works, metal nanoparticles were also advantageous to improve charge-transport in photoactive layer, decreasing series resistance of PV cells. Furthermore, absorption enhancement from metal nanoparticles with different shapes such as nanowires (in P3HT:PCBM blend) [41] and nanoplates (in P3HT:PC₇₁BM and PCDTBT:PC₇₁BM blend) [42] were also demonstrated, and mixture of small nanoparticles (<20 nm) and larger nanoparticle (>40 nm) in P3HT:PCBM blend showed that they could induce LSPR and scattering effect, respectively, giving about 40% improved PCE. However, metal nanoparticles can be exciton recombination sites at the interface between nanoparticle and photoactive layer that can reduce the performances of PV cells, therefore, the surface characteristics of

nanoparticles as well as structural parameters such as size, dispersion and concentration should be precisely controlled [43,44]. Meanwhile, there are reports that metal nanoparticles can affect nano-morphologies of blends. Cu₂S nanoparticles could be utilized to tune the blend morphologies of P3HT:PCBM for improved cell performances [45], and Ag [46] and Au [47] nanoparticles in P3HT:PCBM blend improved morphological properties of blend, giving better PV stability on continuous illumination in air in addition to the optical advantages from plasmonic effect.

4. Nanoimprint lithography-based plasmonic nanoparticles

Plasmonic nanoparticle arrays can be prepared using NIL-based process. Different with other approaches utilizing non-regular nanoparticles, NIL-based nanoparticle fabrication process has advantages such as easy controllability of dimension and high uniformity in large-area format [48]. To prepare large-area and uniform metallic nanostructures, elastomeric stamps having dense 20 nm nanodot patterns, based on high modulus PDMS [49], were fabricated using SiO₂ hole type mold (Fig. 3). Fabrication procedures of SiO₂ hole type mold, based on self-assembled block copolymer template, are described elsewhere [50]. Using an angled deposition of metal onto the PDMS nanodot structures, high-density sub-20 nm size Ag plasmonic nanostructures, expected to work as local field enhancer, were successfully fabricated (Fig. 4a). The position and the magnitude of extinction of peak, related to the localized surface plasmon resonance (LSPR), can be tunable by changing the thickness of the metal [50], similar to that reported by Lucas *et al.* [48].

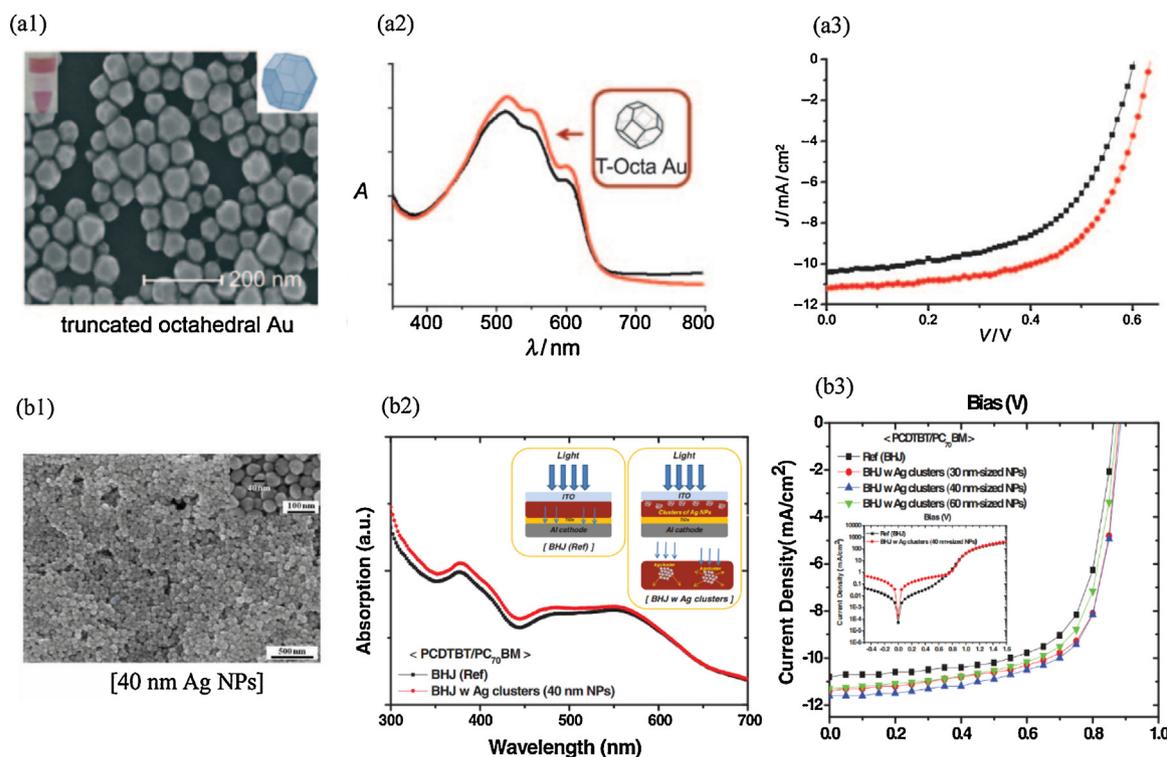


Fig. 2. Effects of plasmonic nanoparticles embedded in photoactive layer. (a1)–(a3) Au nanoparticles in P3HT:PC₇₁BM blend, (b1)–(b2) Ag nanoparticles in PCDTBT:PC₇₁BM blend: (a1) SEM image of truncated octahedral Au. (a2) UV/vis spectra of plain BHJ film and BHJ film with truncated octahedral Au (5 wt%) for P3HT:PC₇₁BM. (a3) *J*–*V* curves of devices with plain BHJ (black) or BHJ with 5 wt% Au nanoparticles (red). Reproduced with permission [39]. Copyright 2011, Wiley. (b1) SEM image of synthesized Ag nanoparticles. (b2) UV/vis spectra of the plain PCDTBT:PC₇₁BM BHJ film and the BHJ film with 40 nm-sized NPs based Ag clusters (1 wt%). The inset schematic figures show the light trapping and optical reflection by the scattering and excitation of localized surface plasmons. (b3) *J*–*V* curves of devices with the plain PCDTBT:PC₇₁BM BHJ and the BHJ with Ag clusters from a ratio of 1 wt% and several NPs diameters (30 nm, 40 nm, and 60 nm). The inset figure shows *J*–*V* curves of the devices with the plain PCDTBT:PC₇₁BM BHJ and the BHJ with the 40 nm-sized NPs based Ag clusters (1 wt%) in the dark current. Reproduced with permission [40]. Copyright 2011, Wiley.

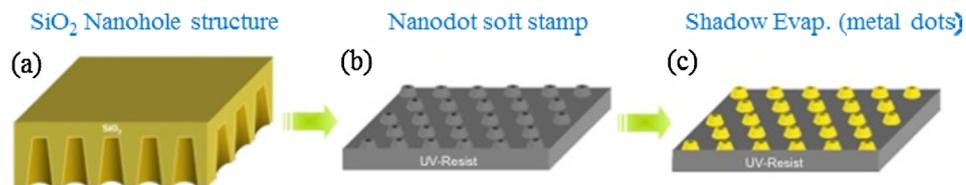


Fig. 3. Schematic of the process for fabricating plasmonic nanodot arrays: (a) SiO₂ nanohole type structure; (b) nanodot soft stamp; (c) plasmonic metal nanodots.

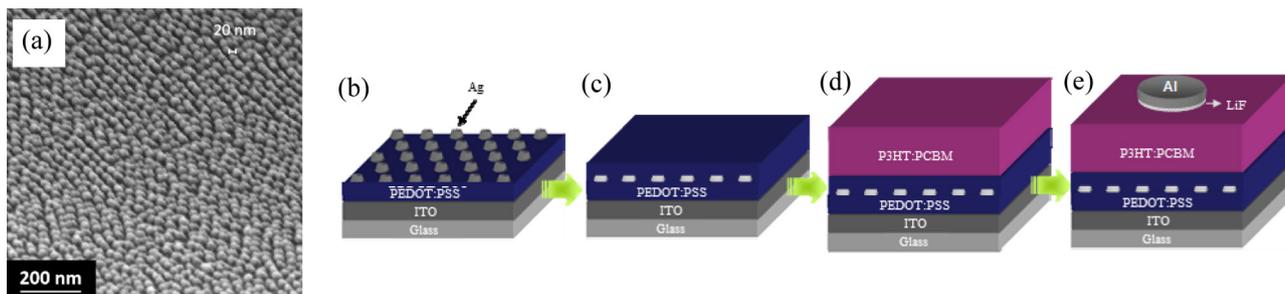


Fig. 4. (a) SEM of Ag plasmonic nanodot arrays deposited on nanodot type PDMS stamp using angled deposition, (b)–(e) fabrication procedures of normal configuration OPV cell with Ag plasmonic nanodot arrays.

Ag nanostructures formed on soft PDMS stamp or hard SiO₂ mold, treated by fluoro-surfactant, could be efficiently transferred to PEDOT:PSS layer that could be used as HTL of normal configuration OPV (Fig. 4b). Thin PEDOT:PSS was further casted to restrict direct contact between metal nanoparticles and photoactive layer, leading to quenching of generated excitations (Fig. 4c). After spin-casting P3HT:PCBM blend for BHJ photoactive layer (Fig. 4d), LiF and Al were thermally deposited as a cathode electrode (Fig. 4e). As shown in Fig. 5, photoactive layer shows the improved absorption with Ag plasmonic nanodot array, and increased power conversion efficiency (PCE) (from 3.31% to 3.66%), originated by improved short circuit current (from 8.53 mA cm⁻² to 9.58 mA cm⁻²), was obtained.

5. Periodic nanostructures

Periodic nanostructures such as nanogratings that can easily control the geometrical parameters are also applicable to OPV cells to manage the light in the device structures [1,29,30,51,52]. For example, it has been demonstrated that Ag nanograting, embedded in PEDOT:PSS buffer layer, can enhance the absorption of incident

light by SPR and waveguide effect, giving 40% improved short circuit current and 2.5 fold enhanced external quantum efficiency at a certain wavelength (Fig. 6) [11]. Consequently about 35% improved PCE was achieved using phthalocyanine (CuPc) and C₆₀ as donor and acceptor, respectively. In this work, metal nanograting structure was also utilized as transparent electrode that can substitute ITO electrode.

Metal nanogratings on OPV cells as light-trapping structure were also studied. By adding periodic nanostructure at the interface between photoactive layer and metal electrode, also working as reflector in OPV, the optical path length across a broad wavelength range of incident light could be enhanced. Periodic nanostructures could be easily introduced by printing photoactive layer, before the film is fully dried after spin-casting, with nanopatterned PDMS stamp. After releasing the stamp, further metal deposition for electrode completed the light-trapping nanograting structure at the interface between metal and dielectric materials.

Fig. 7a shows SiO₂ nanograting, utilized to fabricate PDMS stamp. The calculated enhancement effects of absorption after introducing the metal nanograting structure are shown in Fig. 7b, and the experimental results are demonstrated in Fig. 7c and d. The

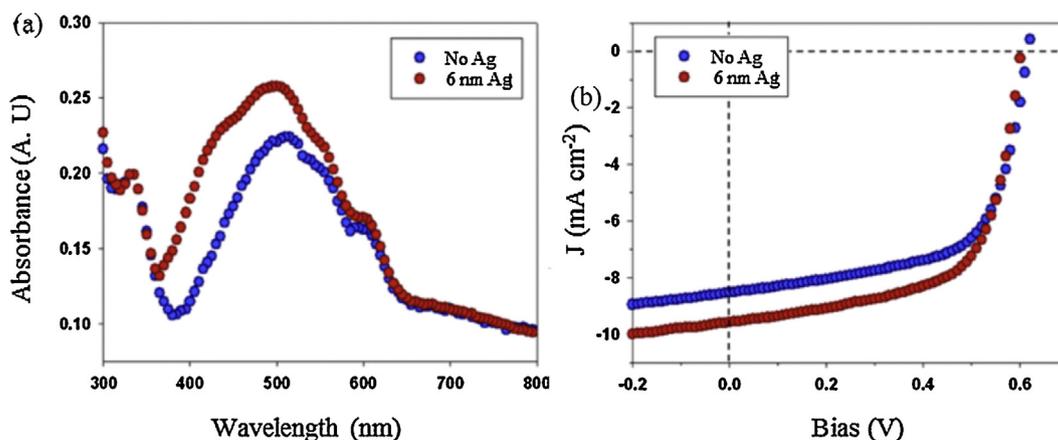


Fig. 5. (a) Absorption spectra of photoactive layer with and without plasmonic Ag nanodot arrays. (b) *J*-*V* plot of OPV cells with and without plasmonic Ag nanodot arrays (with Ag: $J_{sc} = 9.58 \text{ mA cm}^{-2}$, $V_{oc} = 0.60 \text{ V}$, FF = 63.5%, PCE = 3.66%, without Ag: $J_{sc} = 8.53 \text{ mA cm}^{-2}$, $V_{oc} = 0.62 \text{ V}$, FF = 62.6%, PCE = 3.31%).

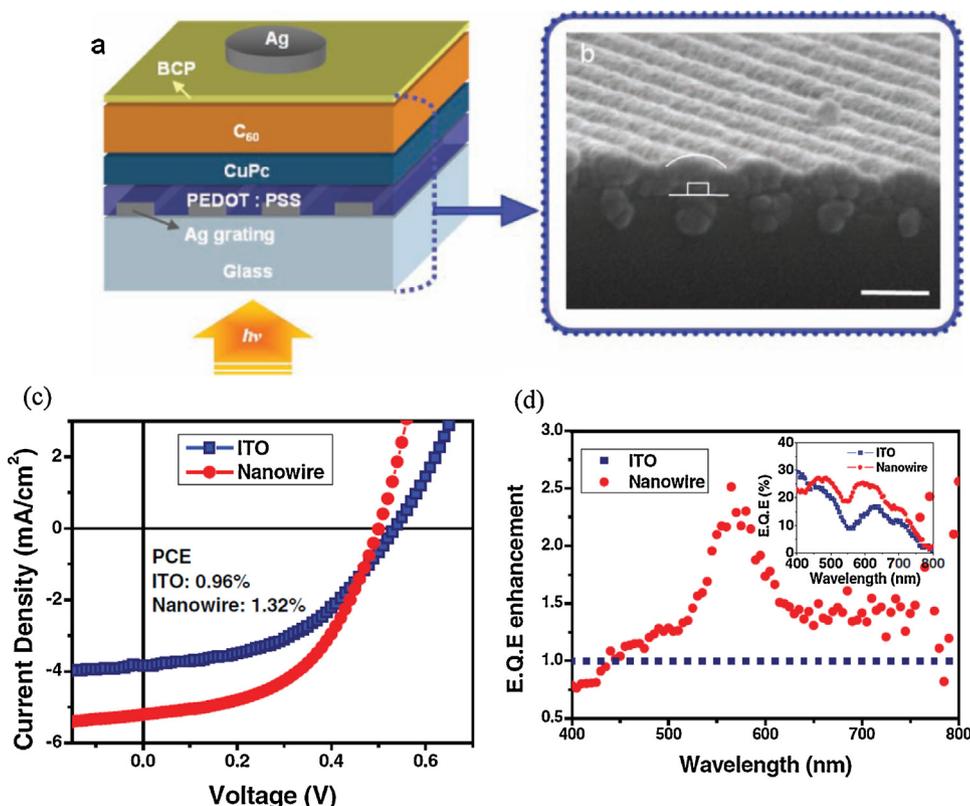


Fig. 6. (a) Schematic of the fabricated small molecular weight OPV cell. The fabricated devices have the layered structure of Ag nanowire anode, PEDOT:PSS, CuPc, C₆₀, BCP, and cathode (thick Ag film) from bottom to top. (b) Cross-sectional view of one of the fabricated devices, but without 70 nm thick Ag cathode. Organic materials have the sinusoidal shape due to the height profile of the Ag nanowire array and the nature of thermal evaporation process. Organic layers are depicted with solid lines and the square shows the position of the Ag nanowire on glass substrate. The scale bar is 200 nm. (c) J - V curve of the nanowire and control ITO devices. (d) External quantum efficiencies (EQE) enhancement of nanowire device with reference to ITO device. The inset gives the measured EQE of the nanowire and ITO devices. Reproduced with permission [11]. Copyright 2010, Wiley.

designed structure was 700 nm period metal nanograting having 350 nm line width. According to the calculation, the absorption enhancement in P3HT:PCBM system with those nanostructures was 2.71-fold (TM: 3.08, TE: 2.34) and this enhancement was expected to increase the short-circuit current (J_{sc}) without changing other factors. As expected, the real device fabricated using this structure showed the increased J_{sc} (from 8.84 to 10.85 mA cm⁻²) and external quantum efficiency (EQE). Consequently, the PCE was improved from 3.36% to 4.16%.

6. Discussion

While most researchers in the field are exploiting plasmonic enhanced PV structures by matching the SPP resonance to the peak absorption of the semiconductor material, we think this strategy is only valid for very thin layer of active materials where light at peak absorption wavelength still cannot be absorbed completely in the round trip in the thin layer. Under the normal device construction where the thickness is optimized so that light can be absorbed efficiently at peak absorption, adding plasmonic particles would actually degrade the device performance as the particles themselves could also have strong absorption. In this case, we believe it is more desirable to have the SPP resonance wavelength to locate at the weak absorption range of the organic semiconductor, so that it can boost the absorption of the material, and lead to overall higher photocarrier generation. In fact, the periodic structures described in Section 5 have the plasmonic peak at the wavelength range where the organic semiconductors absorb weakly, which may explain the overall 35% improvement in the PCE [11].

The absorption effect also depends on the particle size. For example, scattering dominates for particles sizes greater than 50 nm while absorption dominates for smaller particles. Therefore larger particles are desirable for light scattering and light trapping, and they can efficiently enhance the absorption of light in buffer layer as well as photoactive layer. However, as for smaller nanoparticles (<20 nm) case, because the field enhancement is localized around those nanoparticles and decay quickly with distance from the surface, embedding them to photoactive layer is more efficient than adding them to buffer layer. On the other hand, those nanoparticles in photoactive layer can act as recombination site of photogenerated excitons. To prevent this, the interface between nanoparticle and organic semiconductor needs to be controlled by treating the surface of nanoparticles (e.g. with thin insulating layer), however, the thickness of the additional layer also should be considered not to degrade the optical enhancement effect.

Furthermore, one also needs to consider that the metal nanostructures do not cause issues in excessive film roughness that could also degrade the device performance. Because the thicknesses of organic semiconductor thin films in OPV are usually tens of nanometer scale, the existence of additional nanostructure in those layers affects the morphologies of the films. For example, as shown in Fig. 6, metal nanogratings in HTL induce the sinusoidal shape device architecture and, in worst case, this structure can induce shunt pathway reducing the fill factor of PV cells. Therefore, the effect of morphological change, originated from the nanostructure, on the performances of OPV cells should be clarified to maximize the optical enhancement effect.

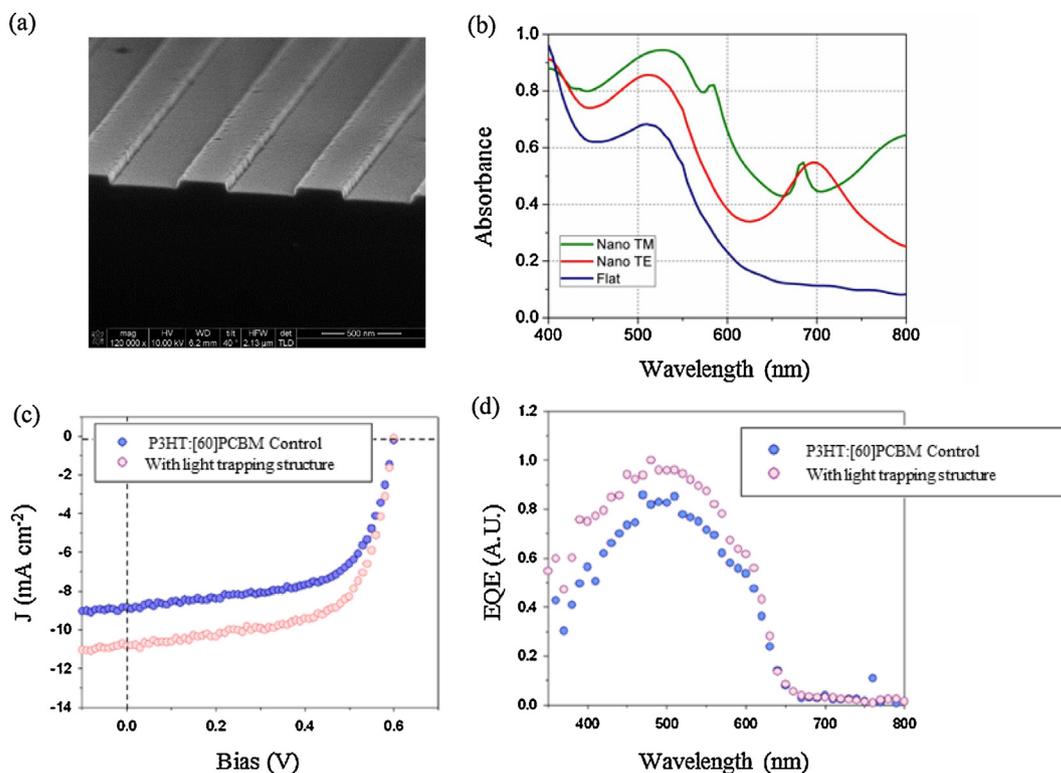


Fig. 7. (a) SiO_2 nanogratings, utilized to fabricate PDMS stamp. (b) Calculated absorption of light with and without light trapping structure. TE and TM waves mean transverse electric and transverse magnetic waves, respectively. The polarized light having the E-field parallel to the nanograting direction is defined as TE and the polarized light having E-field perpendicular to the nanograting direction is defined as TM. (c) J - V plots of OPV cells with and without nanogratings (with: $J_{sc} = 10.85 \text{ mA cm}^{-2}$, $V_{oc} = 0.60 \text{ V}$, FF = 63.8%, PCE = 4.16%, without: $J_{sc} = 8.84 \text{ mA cm}^{-2}$, $V_{oc} = 0.60 \text{ V}$, FF = 63.2%, PCE = 3.36%). (d) External quantum efficiency spectra of OPVs with and without nanogratings.

7. Conclusion

Metal nanostructures incorporated in buffer layer or photoactive layer of OPV cells can affect optical properties as well as electrical properties of the OPV devices. By choosing proper organic semiconductors and adjusting the dimension of metal nanostructures such that SP enhanced spectral range matches the peak absorption of organic semiconductor, further enhanced PCEs are expected. Another approach is to have peak enhancement of the metallic structure to match the low absorption range of the organic semiconductor and to significantly enhance the light absorption in this range. Therefore, the size and shape of plasmonic nanostructures and device architectures with structures, affecting extinction wavelength and absorption/scattering behavior of plasmonic nanostructures, should be precisely designed to utilize plasmonic optical enhancement to OPV devices.

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