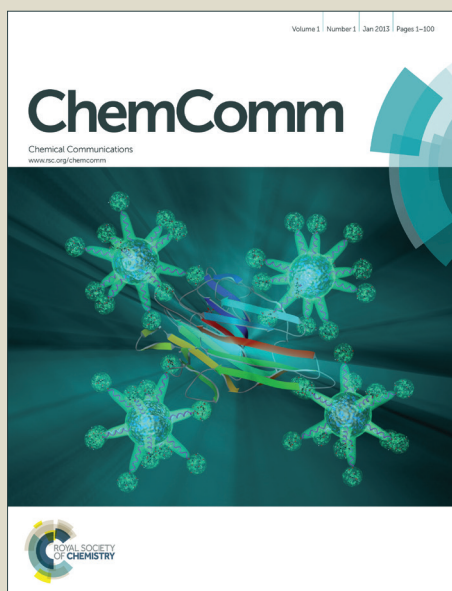


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ARTICLE

The Emerging Multiple Metal Nanostructures for Enhancing the Light Trapping of Thin Film Organic Photovoltaics

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Recently, various metal nanostructures have been introduced into organic solar cells (OSCs) for performance enhancement. Here, we review the recent progress on OSCs incorporated with multiple metal nanostructures including various metal nanopatterns and metal nanomaterials. Multiple physical effects arise from these incorporated nanostructures, which require careful distinction. Changes induced by the metal nanostructures are examined in detail from the optical and electrical aspects. With the comprehensive understanding of physical mechanisms for various metal nanostructures, further improvement in device performance and emerging applications can be expected for the new class of nanostructure-incorporated OSCs.

1. Introduction

With the interesting features of low cost, low-temperature fabrication, semi-transparency, and mechanical flexibility, organic thin-film solar cell (OSC) is currently one of emerging optoelectronic devices and shows a bright outlook for green energy industry. Over the last several years, the power conversion efficiency (PCE) of OSCs has increased from 0.1% in 2001 to nearly 9% nowadays.^{1–4} Currently, a critical challenge for OSCs lies in surpassing the performance even beyond the 10% PCE barrier.

The persisting issues of the short exciton diffusion length and the low carrier mobility in organic semiconductors are intrinsic.^{5–7} In consideration of these limitations, the active layers of OSCs are commonly kept thin, hence limiting the absorption efficiency of incident light. To address this issue, many light-trapping strategies have been developed including non-plasmonic design (the light-trapping design functions not mainly due to plasmonic effect) and plasmonic design (the light-trapping design functions mainly due to plasmonic effect). Patterned substrates^{8,9} and random wrinkles¹⁰ are two typically light-trapping examples which can be attributed to non-plasmonic design in OSCs. In this review, we focus on OSCs with performance enhanced plasmonically through the incorporation of various types of metal nanostructures including metal nanopatterns and metal nanomaterials for achieving highly efficient device. Here, we will examine the optical and electrical effects of metal nanopatterns and nanomaterials incorporated in the different layers of OSCs. The interfacial effects of metal nanostructures incorporated in the carrier transport layers (CTLs) on the performance of OSCs will also be described.

2. Multiple metal nanostructures for OSCs

2.1 Metal nanopatterns

Recently, plasmonic metal nanostructures have been extensively introduced into solar cells for highly efficient light harvesting.^{11–35} Through the various optical modes such as localized surface plasmon resonances (LSPRs), surface plasmonic resonances (SPRs), quasi-guided modes, Fabry-Perot modes, their hybrids, *etc.*, nanoscale metal structures with unique optical properties on multilayered device structures have attracted extensive research interests.

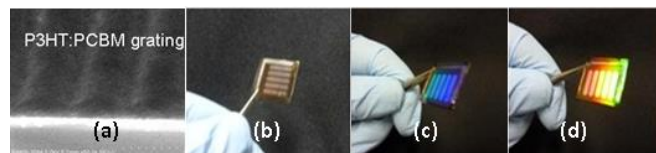


Figure 1. (a) The 2D grating patterned poly (3-hexyl thiophene) (P3HT):phenyl-C61-butyric acid methyl ester (PC₆₁BM) active layer, (b) to (d) the images of OSCs with Ag grating anode at different tilted angles. The diffraction color changes with the angles. Reproduced with permission.¹²

Patterned metal nanostructures such as 2-D metal nanogratings have been investigated experimentally and theoretically for improving light trapping in solar cells.^{11–19} A number of approaches can be employed to fabricate these patterned structures experimentally. For instance, metal can be directly deposited on diffraction grating substrates to form periodic grating patterns, onto which the active layer is spin-coated and a top semi-transparent electrode is required.³⁶ Alternatively, patterns can be directly formed on the active layer via an imprint method.^{12, 18, 19} Furthermore, due to the very thin thickness of the interface layer (~10 nm), the subsequently deposited silver anode can develop a metal grating pattern accordingly.^{12, 19} As shown in Figure 1 (a), pattern can be observed on the active layer of P3HT:PC₆₁BM.¹² While for device with the finished silver grating, different diffraction colors can be seen at different tilted angles as shown in Figure 1 (b)-(d).¹² Besides 2-D gratings, 3-D gratings^{37–41} and randomly

patterned metal nanostructures^{42–44} have also been reported to address the optical polarization dependency, as will be discussed later. Examples of 3-D gratings^{37, 41} and 3-D random nanostructures⁴² can be seen from Figure 2–Figure 3 and Figure 4, respectively.

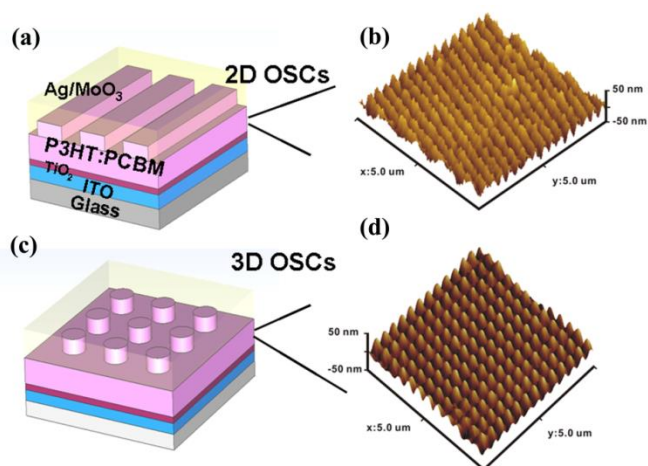


Figure 2. The schematics of (a) 2-D nanograting P3HT:PC₆₁BM and (c) 3-D nanopattern P3HT:PC₆₁BM OSCs; atomic force microscope images of active layer with (b) 2-D nanograting and (c) 3-D nanopattern. Reproduced with permission.³⁷

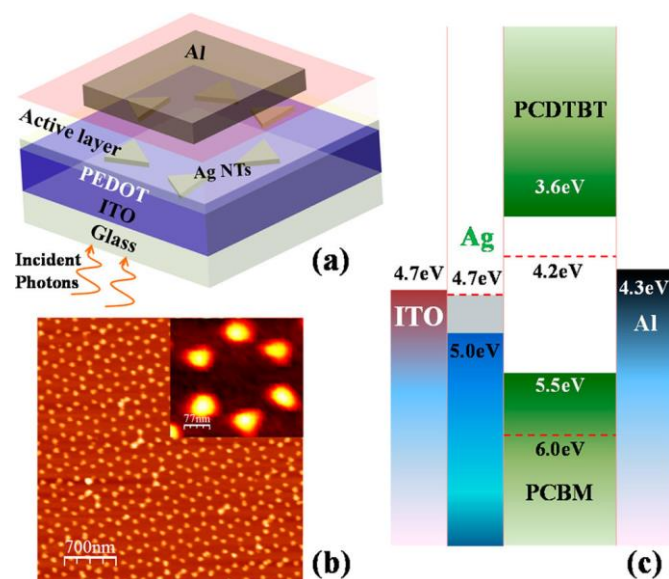


Figure 3. (a) Schematic of the plasmonic organic photovoltaic device configuration investigated. (b) atomic force microscope images of Ag-nanotriangle (NT) arrays. The height and side of the Ag triangles are ~20 and ~40 nm, respectively. Inset is a zoom-in of a representative unit of Ag-NT hexagonal array. (c) Schematic of the energy band alignment of the device. Reproduced with permission.⁴¹

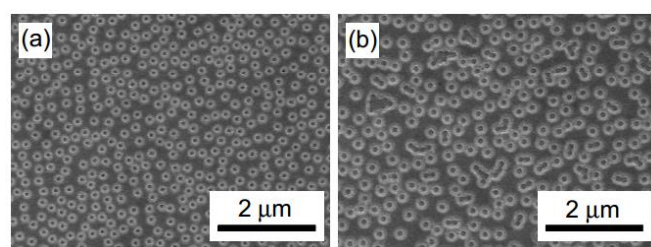


Figure 4. Top-view scanning electron micrographs of nanostructured MoO_x/Ag layers on poly(methyl methacrylate) with a total MoO_x thickness of 135 nm. These layers were fabricated utilizing polystyrene beads with a diameter of either (a) 140 nm or (b) 200 nm. Reproduced with permission.⁴²

2.2 Metal nanomaterials

Besides patterned metal nanostructures, various metal nanomaterials such as nanoparticles (NPs),^{20–31} nanorods,^{20, 31} nanowires,³² nanocubes,³³ nanoplates³⁰ and nanoprisms^{34, 35} have been introduced into the different layers of the multilayered structure of OSCs. The influence of metal nanomaterials on the optical and electrical properties of OSCs is strongly related to the geometry, material composition, size and concentration of the nanomaterials, which can be adjusted accordingly to different effects. For instance, the plasmon resonance band position is easily tunable by changing the size of Au NPs, as shown in Figure 5.³¹ Plasmonic nanomaterials can be prepared by thermal evaporation of thin metal film followed by annealing to form island-like structures,⁴⁵ or deposition of metal through a template.⁴⁶ As a more feasible and controllable and thus more prevalent approach, chemical synthesis of metal nanomaterials of NPs and other geometries through solution process has been extensively reported.^{21–24, 28, 31, 35}

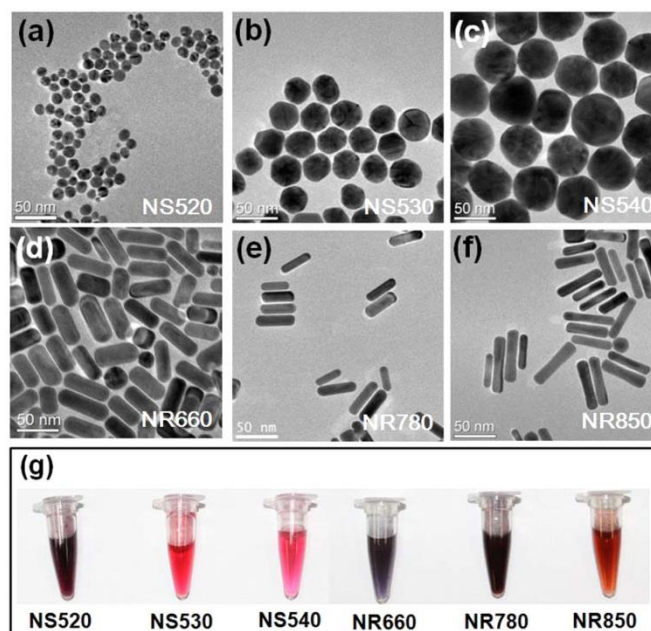


Figure 5. (a–f) Transmission electron microscopy images of Au NPs (NS520, NS530, NS540, NR660, NR780, NR850, with tunable localized surface plasmon resonance band positions at 520, 530, 540, 660, 780, and 850 nm respectively) of different sizes and shapes: (a) NS520, (b) NS530, (c) NS540, (d) NR660, (e) NR780, (f) NR850. Scale bars, 50 nm. (g) Photographs of representative Au NPs of different sizes and shapes in aqueous solutions. Reproduced with permission.³¹

2.3 Simultaneous incorporation of multiple metal nanostructures

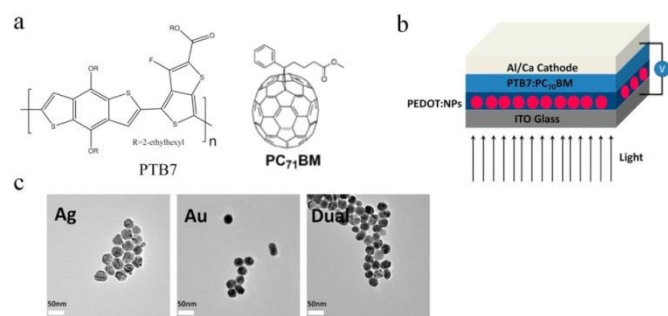


Figure 6. (a) Molecular structures of thieno[3,4-b]thiophene/benzodithiophene (PTB7) and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM). (b) Device structure of the solar cell device. (c) Transmission electron microscopy images of Ag, Au, and dual NPs. Reproduced with permission.⁴⁷

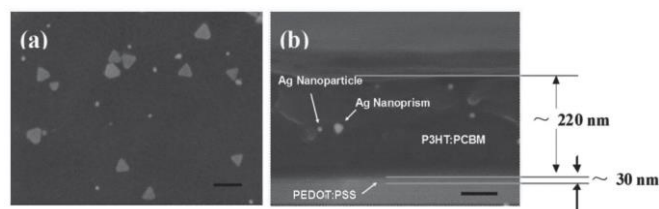


Figure 7. a) Top-view, and, b) cross-sectional SEM images of P3HT:PC₆₁BM film incorporated with mixed Ag nanoparticles and nanoprisms. The scale bar is 100 nm. Reproduced with permission.⁴⁸

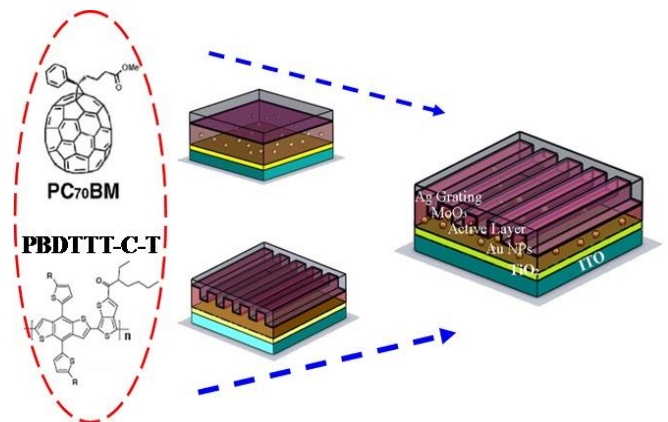


Figure 8. Chemical structures of poly[[4,8-bis-(2-ethyl-hexyl-thiophene-5-yl)-benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]-alt-[2-(2-ethyl-hexanoyl)-thieno[3,4-b]thiophen-4,6-diyl]] (PBDTTT-C-T) and PC₇₁BM (left). Schematic of the device structure: NP device (top), grating device (bottom), and dual metallic structural device (right). Reproduced with permission.⁴⁹

Up to now, many reports focus on the effects of a sole type of metal nanostructures within a single layer of the same device, for which the combinational or coupling effects between various structures have not been fully considered. Very recently, in order to further increase OSC efficiency, multiple metal nanostructures have been simultaneously incorporated into a single device to achieve optimal performance. The reported simultaneous incorporation of multiple metal nanostructures includes blending of metal NPs with different materials⁴⁷ (one instance is shown in Figure 6), geometries (as shown in Figure

7),⁴⁸ doping NPs of different size into both the front and rear interfacial layers,⁵⁰ or combining metal grating electrode and metal NPs within a single device (as shown in Figure 8).⁴⁹

Metal nanostructures incorporated into OSCs can affect the device in a wide range of aspects, including changes in the optical and electrical properties. As a result, the origin of the performance enhancement may be many-fold. Furthermore, the incorporation of multiple metal nanostructures into a single device brings an even greater challenge in studying the introduced effects: besides the combining influence from each of the individual nanostructures, coupling or interaction between these nanostructures (e.g. coupling or hybridization between multiple SPRs or SPR and LSPR, as will be discussed later) can occur which can be utilized to further improve the device performance (e.g. realizing broadband absorption enhancement). Consequently, it is crucial to carefully distinguish the different physical mechanisms at play when investigating OSCs incorporated with various metal nanostructures. In the following section, we will examine the effects of multiple metal nanostructures on OSCs from the optical and electrical aspects.

3. Effects of metal nanostructures on OSCs

3.1 Optical effects

Optically speaking, metal nanostructures can improve light harvesting in OSCs by light scattering and strong surface plasmon polariton (SPP) effects.^{28, 51, 52} Surface plasmons refer to waves interacting with the free electrons of certain metals, resulting in strongly enhanced electromagnetic fields on the surface.^{53, 54} Commonly used metals are gold, copper, silver, and their alloys, of which the plasmon resonant frequency lies in the visible region. SPR and LSPR are induced by light excitation of plasmons for planar metal surface and metal nanomaterials, respectively.^{53, 55-59} For the former case, SPRs are excited as guided surface waves bounded at the metal/dielectric interface when the wave-vector matching requirement between incident light and SPR is met, which can trap light effectively and propagate along the interface.^{57, 60} Unlike SPRs which propagate along the metal/dielectric interface and confined perpendicularly, LSPRs are non-propagating oscillation of electrons in sub-wavelength metal coupled to electromagnetic fields. When an oscillating electromagnetic field penetrates the sub-wavelength metal nanomaterials, electrons will be driven by a restoring force exerted by the electric field on the metal surface, giving rise to strong resonance with concentrated local electromagnetic field.^{57, 61-63} In addition to the LSPR which is only with dipole mode and usually prominent in small metal nanomaterials, high order multipole resonances can be supported by large size metal which can be used for enhancing light absorption.^{48, 64}

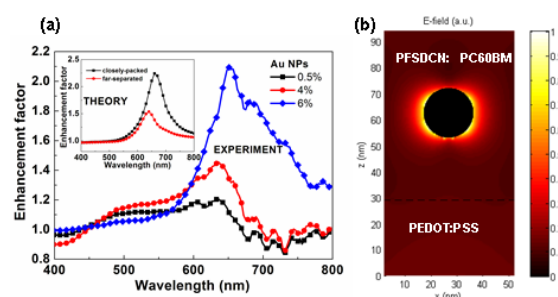


Figure 9. (a) Experimental and theoretical (inset) absorbance enhancement factor of the active layer with different amount of Au NPs. (b) Theoretical near field distribution around an Au NP in the polymer blend active layer of PFSDCN:PC₆₁BM. Reproduced with permission.²³

For metal nanomaterials with LSPRs, the strong near field of resonance will distribute around the nanomaterials within tens to a few hundred nanometers, which is very similar to the thickness of active layer of OSCs. In addition, the light path in the active layer can be elongated by metal nanomaterials through scattering, particularly for large size metal nanomaterials.^{65, 66} Therefore, a direct approach to enhance light absorption and thus device performance of OSCs is to incorporate metal nanomaterials into the active layer region,^{22, 23, 28, 29, 67-69} where light absorption and photoexcited carrier generation occur. Improved optical absorption has been reported theoretically and experimentally with strongly distributed LSPR near field inside the active layer of poly[2,7-(9,9-dioctylfluorene)-alt-2-((4-(diphenylamino)phenyl)thiophen-2-yl)malononitrile] (PFSDCN):[6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) embedded with small Au NPs (average diameter of 18 nm), as shown in Figure 9.²³ Importantly, the theoretical results demonstrate that the strong near field from LSPR of NPs mainly distributes laterally along the active layer, as shown in Figure 9 (b). The small Au NPs in the active layer contribute to the increase of short-circuit current (J_{sc}) from 4.16 mA/cm² to 4.67 mW/cm². Together with the improvement of open-circuit voltage (V_{oc}) and fill factor (FF) due to the electrical effects of Au NPs as will be discussed in Section 3.2, a 32% increase in OSC power conversion efficiency (PCE) from 1.64% to 2.17% has been reported.²³ In another report, the reflectance spectra of the OSCs fabricated with and without Au NPs in poly (3-hexyl thiophene) (P3HT):[6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) were characterized, as shown in Figure 10.²⁸ By introducing large Au NPs (70 nm), the diffused reflectivity of the device is lowered, indicating stronger optical absorption. Consequently, the incorporation of large Au NPs gives rise to improved J_{sc} and PCE from 10.3 mA/cm² to 11.18 mA/cm² and 3.54% to 4.36% respectively for P3HT:PC₇₁BM and from 12.9 mA/cm² to 13.8 mA/cm² and 3.92% to 4.54% respectively for poly{[4,4'-bis(2-ethylhexyl) dithieno(3,2-b:2',3'-d)silole]-2,6-diyl-alt-[4,7-bis(2-thienyl)-2,1,3-benzothiadiazole]-5,5'-diyl} (Si-PCPDTBT):PC₇₁BM OSCs, respectively.²⁸ The authors attribute the enhanced optical absorption of the device to the strong light scattering of the large Au NPs. In addition to Au

NPs, Ag NP clusters were shown to promote increased absorption in the active layer of poly[N-9''-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole) (PCDTBT):PC₇₁BM OSCs, as shown in Figure 11.²⁹ Using Ag NPs of different size and concentration, the optimal NP-incorporated OSCs (40 nm Ag NPs, 1 wt%) were shown to exhibit enhanced PCE of 7.1%, from 6.3% of OSCs without NPs.²⁹ Investigation of different metal materials such as metal alloys,^{70, 71} Cu⁷² and Al⁷³ as well as different geometries including nanorods,^{20, 31} nanowires,³² nanocubes,³³ nanoplates³⁰ and nanoprisms^{34, 35} has also been reported.

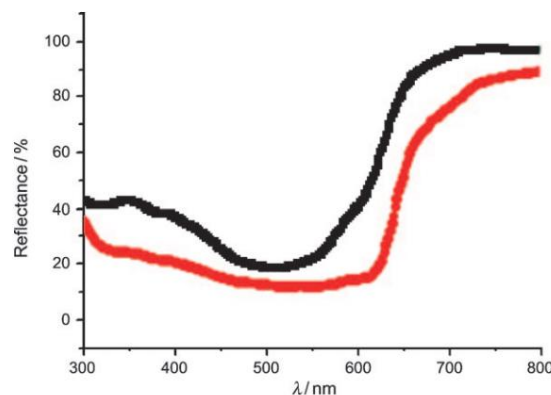


Figure 10. Diffuse reflectance spectra of the devices fabricated with P3HT:PC₇₁BM BHJ (black curve) and P3HT:PC₇₁BM with the addition of 5 wt% truncated octahedral Au NPs (red curve). Reproduced with permission.²⁸

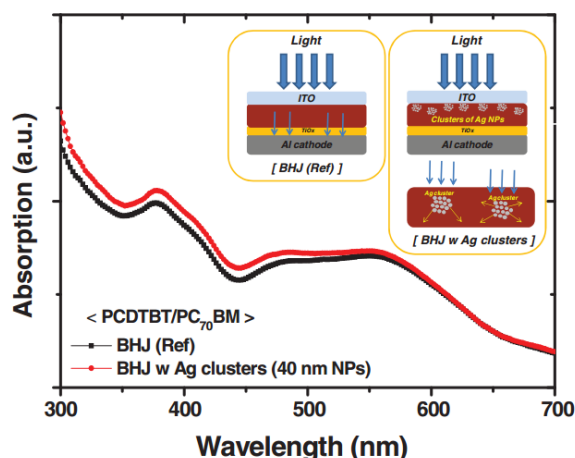


Figure 11. UV visible spectra of (b) the plain PCDTBT:PC₇₁BM bulk heterojunction (BHJ) film and the BHJ film with 40 nm-sized NPs based Ag clusters (1 wt%). The inset schematic figures show the light trapping and optical reflection by the scattering and excitation of localized surface plasmons. Reproduced with permission.²⁹

Meanwhile, numerous reports have been published on incorporating metal nanomaterials into the charge transport layers (CTLs) of OSCs including commonly used hole transport layers of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)^{64, 74-82} and MoO_x⁸³ and electron transport layers such as TiO₂^{84, 85} in order to improve OSC performance. Regarding the physical

origins, it is still under debate whether direct optical effects (if any) are the dominant contributor to the enhanced device performance, instead of any other possible effects including electrical or interfacial influence.

Yang *et al* blended Au NPs of 70-80 nm with the interconnecting layer of PEDOT:PSS in an inverted polymer tandem solar cell.⁸⁶ Simultaneously increased efficiencies in both the top and bottom subcells were demonstrated. As shown in Figure 12, the authors attribute the enhanced performance to the improved optical absorption from the blended Au NPs, while the electrical characteristics of the tandem cell are not compromised. In another study, Ag NPs of various size were embedded in the hole transport layer of PEDOT:PSS.⁸⁷ The optimal device PCE was increased from 6.4% to 7.6% in PCDTBT:PC₇₁BM OSCs, and from 7.9% to 8.6% in thieno[3,4-b]thiophene/benzodithiophene (PTB7):PC₇₁BM OSCs. As shown in Figure 13 (a)-(c), enhancement in the external quantum efficiency (EQE) which depends on both the optical and electrical properties follows a similar trend to the enhancement of optical absorption, while the internal quantum efficiency (IQE) which is determined solely from electrical properties remains mostly unaffected. The authors conclude that the enhanced photocurrent results from the absorption enhancement due to the strong optical scattering by the Ag NPs.

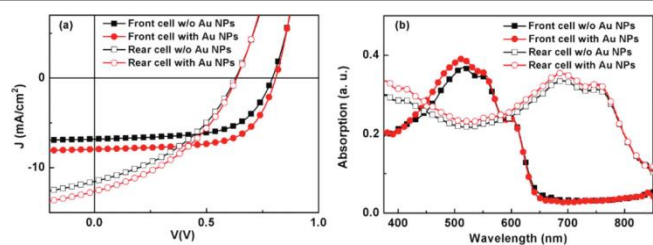


Figure 12. Comparison of single-cell results with and without Au NPs in the PEDOT:PSS layer: (a) current density versus voltage (J - V) characteristics of the front (ITO/TiO₂:Cs/P3HT:indene-C₆₀ bisadduct (IC₆₀BA)/PEDOT:PSS/Al) and rear (ITO/PEDOT:PSS/TiO₂:Cs/poly{[4,40-bis(2-ethylhexyl)dithieno(3,2-b;20,30-d)silole]-2,6-diyl-alt-(2,1,3-benzothiadiazole)-4,7-diyl} (PSBTBT):PC₇₁BM/MoO₃/Al) single cells under AM1.5G 100 mW · cm⁻² illumination; (b) absorption of front and rear single cells. Reproduced with permission.⁸⁶

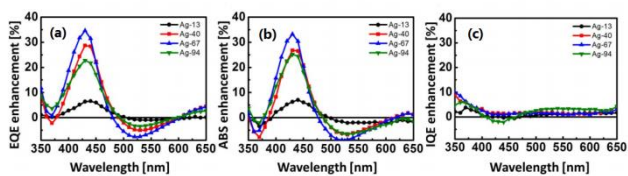


Figure 13. (a) The EQE enhancement of PCDTBT:PC₇₁BM OSCs with various sizes of Ag NPs incorporated. (b) The absorption enhancement of PCDTBT:PC₇₁BM OSCs incorporating various size-controlled Ag NPs. (c) The IQE enhancement of PCDTBT:PC₇₁BM OSCs with various sizes of Ag NPs embedded: AgNP-13 (black circles), AgNP-40 (red squares), AgNP-67 (blue triangles (up)), and AgNP-94 (green triangles (down)), Ag NPs with an average diameter of d nm are denoted as AgNP- d . Reproduced with permission.⁸⁷

Differently, in a recent study, direct optical effects are proven theoretically and experimentally to be a minor contributor to device performance improvement when Au NPs are doped in the PEDOT:PSS layer, in particular for NP size smaller than the

thickness of the CTL.²¹ The conclusion is based on (1) theoretical modeling shows that the strong near field around NPs from LSPRs mainly distributes laterally along the PEDOT:PSS layer rather than vertically into the adjacent active layer, as shown in Figure 14 (a); (2) no clear optical absorption enhancement can be observed in the active layer when NPs are embedded in the CTL, as shown in Figure 14 (b).²¹ Further characterization conducted by the authors reveals that rather than optical effects, changes in electrical and morphology are mainly responsible for the improved performance, including reduced resistivity of PEDOT:PSS, increased CTL roughness which improve charge collection and reduce exciton quenching.

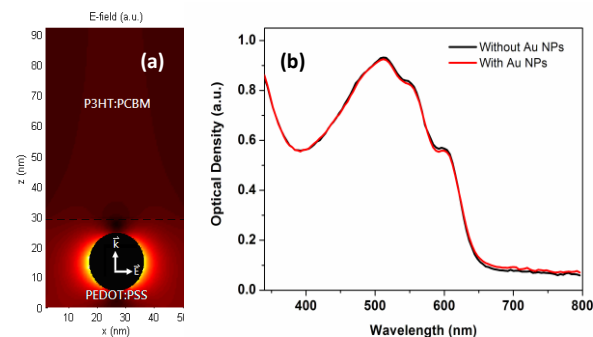


Figure 14. (a) Theoretical electric field profile in the PEDOT:PSS:Au NPs/P3HT:PC₆₁BM OSC and (b) optical density of PEDOT:PSS/P3HT:PC₆₁BM film with or without Au NPs incorporation (0.32 wt%). Reproduced with permission.²¹

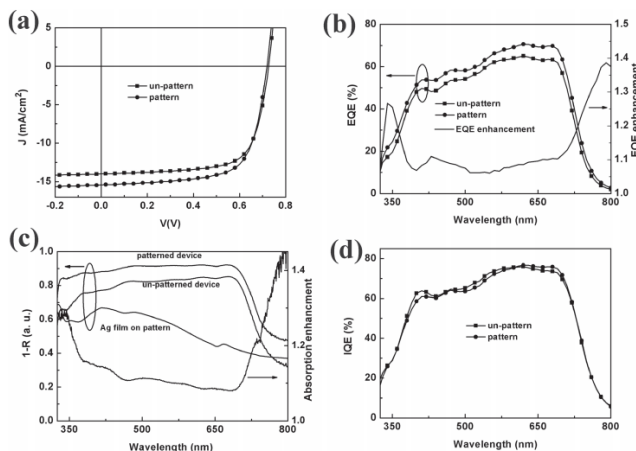


Figure 15. The current density versus voltage (J - V) characteristics of the solar cells under AM1.5G 100 mW cm⁻² illumination, (b) External quantum efficiency (EQE) of the devices with and without pattern, and EQE enhancement, (c) Reflected absorption spectra of the devices with and without pattern, Ag film on PDMS pattern, and absorption enhancement, and (d) Internal quantum efficiency of the devices with and without pattern. Reproduced with permission.¹¹

Besides metal nanomaterials, electrodes with metal nanopatterns have been demonstrated to be effective in further improving OSC performance. By using an imprint method to pattern active layer and deposit metal oxide/Ag, 2-D metal grating electrode is introduced to increase the device PCE from 3.09% to 3.68% for P3HT:PC₆₁BM OSCs,⁸⁸ and from 7.20% to

7.73% for PTB7:PC₇₁BM OSCs (Figure 15 (a)).¹¹ As shown in Figure 15 (b)-(d), it can be found that the EQE of device is considerably improved after Ag electrode patterning, while the extracted IQE of OSCs does not change noticeably before and after patterning. This indicates that the EQE and thus performance enhancement after grating patterning is mainly due to improved optical absorption enhancement from the surface plasmonic and scattering effects of the Ag grating.¹¹

2-D grating structures typically are optically sensitive to light polarization, with their diffractive properties largely dependent on the polarization. In order to overcome this issue, 3-D gratings³⁷⁻⁴¹ have been proposed and reported. In one of the studies, side-by-side comparison was made between OSCs using 3-D grating electrode and 2-D grating electrode with similar periodicity (Figure 2).³⁷ While the PCE of P3HT:PC₆₁BM OSCs using 2-D grating electrode increases from 3.09% (planar electrode) to 3.63%, a further enhancement is observed for OSCs using 3-D grating electrode, with the PCE improved to 3.85%, achieving a 24.6% PCE enhancement from planar electrode.³⁷ The authors conclude that the further enhancement from 2-D to 3-D grating can be explained by the polarization independent optical response, increased effective interfacial area and decreased series resistance.³⁷ Similarly, randomly patterned metal nanostructures⁴²⁻⁴⁴ have been reported which can address the polarization dependence of 2-D gratings.

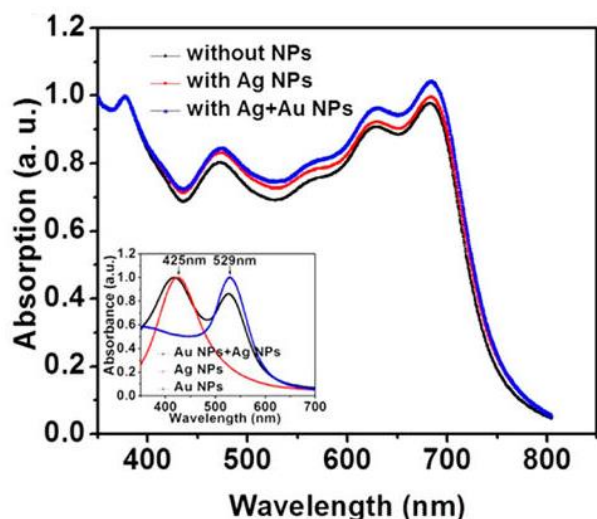


Figure 16. UV-vis absorption spectra of PTB7:PC₇₁BM without NPs, with Ag NPs and with dual NPs. Inset: UV-vis absorption spectrum of NPs in water. Reproduced with permission.⁴⁷

As discussed previously, the simultaneous incorporation of multiple plasmonic metal nanostructures into a single OSC device has been reported recently by blending of metal NPs with different materials^{47, 71} or geometries,⁴⁸ doping NPs of different size into both the front and rear interfacial layers,⁵⁰ or combining metal grating electrode and metal NPs within a single device.⁴⁹ While the resonance peak for metal nanomaterials can be tuned by adjusting the size, shape, and

optical environment of the nanomaterials, the wavelength region for plasmonic resonance of a single type of metal nanomaterials remains narrow, which consequently limits the spectral region for enhanced optical absorption provided by metal nanostructures. Therefore, it is desirable to extend the resonance region to achieve broadband absorption enhancement of metal nanomaterials. By using a dual NP scheme of Au and Ag NPs blended into the PEDOT:PSS layer, the PCE of PTB7:PC₇₁BM OSCs is increased from 7.25% to 8.67%, accounting for a 20% enhancement.⁴⁷ From the absorption spectrum of PTB7:PC₇₁BM device (Figure 16) and of different NPs in water (Figure 16 inset), it is observed that dual NPs greatly broaden the wavelength range for absorption enhancement compared with either Ag or Au NPs.⁴⁷ Similarly, broadband absorption enhancement is also reported for dual metal nanomaterials of different geometries. In a recent study, a combination of Ag NPs and nanoprisms was incorporated into the active layer of P3HT:PC₆₁BM OSCs.⁴⁸ Enhanced broadband plasmonic absorption as well as improved device performance is observed, as shown in Figure 17. Through theoretical and experimental studies, the authors conclude that the observed enhancement is due to the simultaneous excitation of many plasmonic low- and high-order resonance modes, which depend on material, shape, size and polarization.⁴⁸ Besides incorporating multiple metal nanomaterials, dual plasmonic nanostructures (a combination of metal NPs and nanopatterns) incorporated into a single OSC for improving device performance have been reported, leading to a high average efficiency of 8.79% (best PCE of 9.21%) in single-junction OSCs.^{49, 89} Broadband absorption enhancement is enabled by the simultaneously introduced hybridized SPRs (from the Ag nanograting) and LSPRs (from the Au NPs) in addition to waveguide modes and light diffraction, as shown in Figure 18.⁴⁹

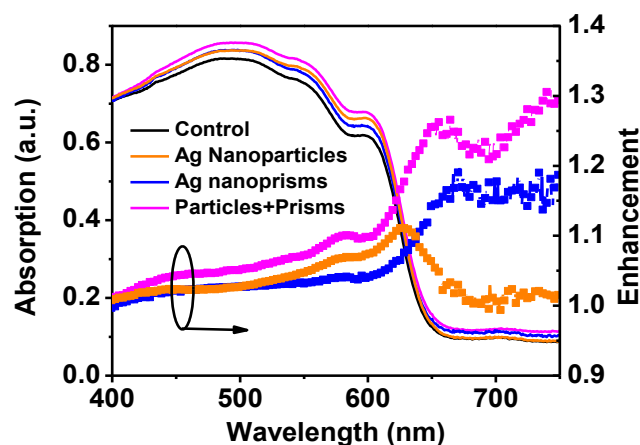


Figure 17. UV-vis absorption spectra of P3HT:PCBM film with or without incorporated Ag nanomaterials, and corresponding absorption enhancement. The Ag nanomaterial-doped active layers are 2 wt% Ag nanoparticles only, 2 wt% Ag nanoprisms only, and mixed 2 wt% Ag nanoparticles and 2 wt% Ag nanoprisms. Reproduced with permission.⁴⁸

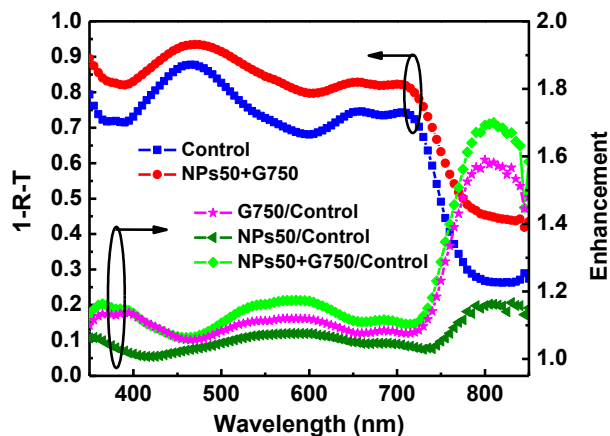


Figure 18. The extracted absorption (i.e., $1 - R - T$) of the control flat OSC and NPs50 + G750 OSC, and the absorption enhancement of NPs50 + G750, G750, and NPs50 compared to the control flat OSC. Reproduced with permission.⁴⁹

3.2 Electrical effects

Besides optical effects, another important factor contributing to the enhanced device performance in OSCs incorporated with metal nanostructures is the electrical effects induced by the nanostructures. Changes in electrical properties of active layers and CTLs have been reported by various groups, which play an equally important role in affecting OSC performance.

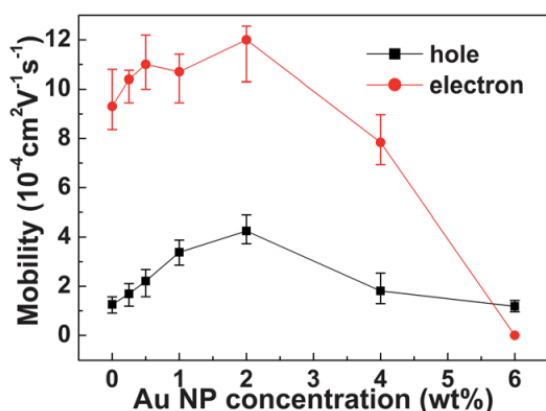


Figure 19. Effects of Au NP concentration on the hole and electron mobility in the active layer of PFSDCN:PC₆₁BM. Reproduced with permission.²³

An approximately two-fold increase in hole mobility (as shown in Figure 19) and increased conductivity were observed for PFSDCN:PC₆₁BM active layer embedded with 2 wt% Au NPs (from $1.26 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $4.25 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).²³ Since charge transport in many OSCs is dominantly limited by the slow carrier (hole), the improved OSC performance can be ascribed to the increased hole mobility as well as better balance between the electron and hole mobility. Nevertheless, trade-off with other non-optical effects is also observed when adjusting Au NP concentrations, since the optimal performance does not correspond to the hole mobility maximum (0.5 wt% Au NPs). While optical enhancement usually changes monotonically with

NP characteristics such as concentration or size, the final device performance will be the combined results of all the optical and electrical effects as described previously. The non-optical effects of Au NPs in the active layer may be manifold: on one hand, dopant states can be introduced by the NPs which provide hopping sites for improving hole mobility;⁹⁰ on the other hand, modifications on the nanoscale morphology of the polymer/fullerene blend is observed, especially at high NP concentration.²³ It has also been reported that the hole injection barrier is increased by introducing Ag NPs in the PCDTBT:PC₇₁BM active layer, leading to a smaller electron transport barrier and thus increased short-circuit current (J_{SC}) and fill factor (FF).²⁹ In a study of OSCs using 3-D grating electrode as discussed previously, besides polarization independent plasmonic effects, the authors also find the increased interfacial layer and thus the decreased series resistance of OSCs introduced by 3-D grating electrode to be a contributing factor in performance enhancement.³⁷ Since not all of the introduced changes in electrical properties are beneficial to device performance depending on the metal nanostructures, it is therefore a critical issue in the design of plasmonically enhanced OSCs to carefully investigate both the optical and electrical effects of the nanostructure incorporated OSCs, in order to fully understand the influence and further improve device efficiency.

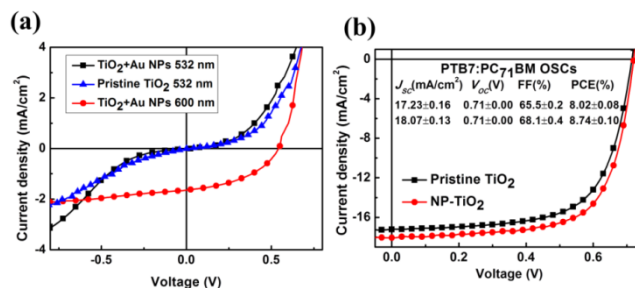


Figure 20. (a) J - V characteristics of P3HT:PC₆₁BM OSCs measured under monochromatic light of 532 nm and 600 nm with pristine TiO₂ and NP-TiO₂ composite (TiO₂+Au NPs) as the electron transport layers (for pristine TiO₂ only J - V characteristics under 532 nm monochromatic light are shown); (b) representative AM1.5G J - V characteristics of inverted single-junction PTB7:PC₇₁BM OSCs with TiO₂ and NP-TiO₂ composite (with the optimized NP concentration) as the electron transport layers; the device performances are summarized in the inset. Reproduced with permission.²⁴

While direct optical and direct electrical effects have been separately studied on the influence of incorporating metal nanomaterials on OSCs, a recent study reported an interesting optically induced electrical effect, i.e., plasmonic-electrical effect, in which the charge extraction of TiO₂ electron transport layer and thus the performance of OSCs is significantly enhanced by the embedded Au NPs in the presence of plasmonic excitation.²⁴ UV light soaking in wide-bandgap semiconducting metal oxides such as TiO₂ and ZnO is a well known issue, where UV light is required to transform the oxides into good electron transport materials. For TiO₂ CTL without Au NPs, the OSC device shows poor S-shape current density-voltage (J - V) characteristics under monochromatic light

unless exposed to short wavelength UV light (<400 nm). Meanwhile, plasmonic light with far longer wavelength of 560–600 nm can activate efficient device operation of OSCs using NP-TiO₂ CTL, as shown in Figure 20 (a).²⁴ Furthermore, the incorporation of Au NPs into the TiO₂ CTL leads to enhanced OSC efficiency of 8.74%, as shown in Figure 20 (b). The plasmonic electrical effect is studied theoretically and experimentally, and is attributed to the charge injection of plasmonically generated hot carriers from NPs into TiO₂, which can fill the trap states in TiO₂ and lower the effective extraction barrier, thereby facilitate electron extraction in OSCs.²⁴

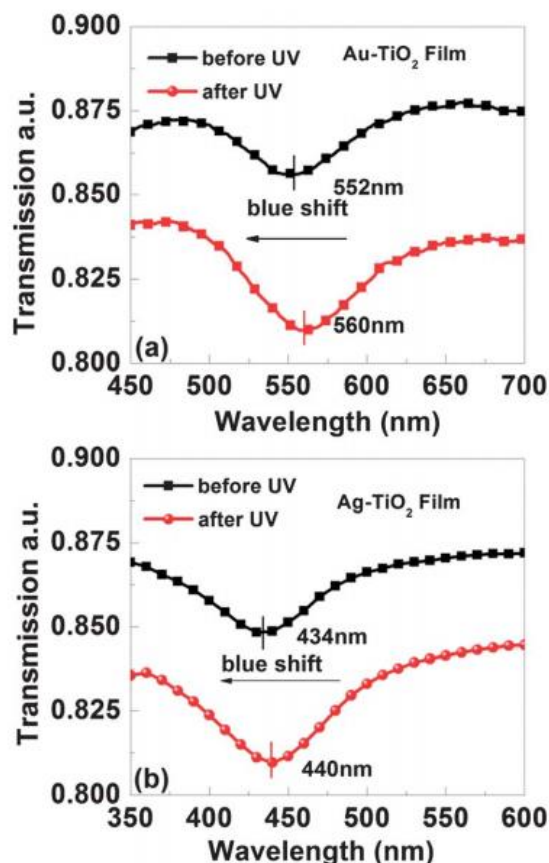


Figure 21. (a) Transmission spectrum of the glass/ITO/Au-TiO₂ sample before and after UV illumination. (b) Transmission spectrum of the glass/ITO/Ag-TiO₂ sample before and after UV illumination. Reproduced with permission.⁸⁴

A subsequent report of incorporating Au or Ag NPs into TiO₂ studied another optically induced charge accumulation effect in the metal-semiconductor composite, in which the transfer of UV-excited electrons in TiO₂ CTL to metal NPs and the enhanced accumulation of the electrons in the metal NP-TiO₂ composite is observed.⁸⁴ Under UV illumination, the accumulation of electrons in the NP-TiO₂ composite is evidenced by the blue shift of plasmonic absorption peaks after UV exposure, for both the Ag and Au NPs (Figure 21).⁸⁴ As a result, the work function of the composite CTL is effectively reduced by introducing metal NPs under UV illumination, as shown in Figure 22. As characterized by electron-only device (Figure 23), electron extraction in OSCs is improved by the

accumulated charges in the UV-irradiated NP-TiO₂ composite, leading to enhanced device performance.⁸⁴

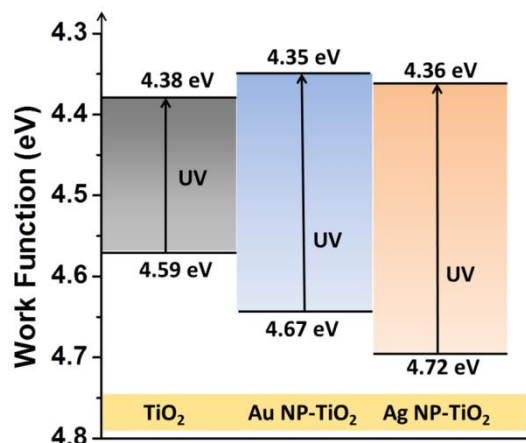


Figure 22. Diagram of work function changes of TiO₂ film, Au NP-TiO₂ film and Ag NP-TiO₂ film from the dark condition to under UV illumination (for 15 mins), measured by using Kelvin probe. Reproduced with permission.⁸⁴

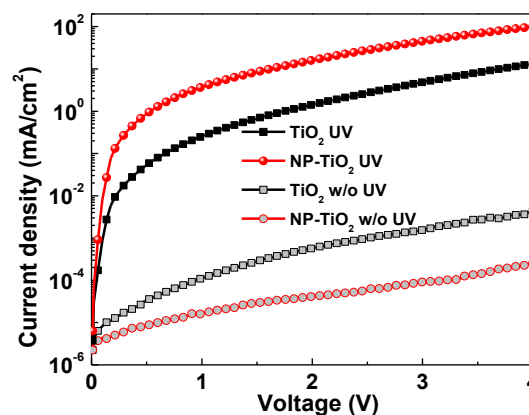


Figure 23. *J-V* characteristics of electron-only devices using TiO₂ and optimized Au NP-TiO₂ CTLs measured with and without (w/o) UV excitation. Reproduced with permission.⁸⁴

In addition to the various effects discussed above, metal nanomaterials can give rise to surface or interfacial modifications on the substrate material (such as electrodes). For instance, the work function of the indium tin oxide (ITO) anode can be increased to 5.01 eV by depositing UV ozone (UVO) treated Au NPs.⁹¹ Modified by the UVO-treated Au NPs, the ITO anode shows improved hole extraction properties, which can enhance the PCE of P3HT:PC₆₁BM OSCs. A more recent report on OSCs using graphene anode demonstrates that the approach is applicable to other electrode materials.⁹² UVO-treated Au nanoclusters were shown to increase the work

function of graphene from 4.1 eV to 4.8 eV, favoring hole extraction in OSCs while avoiding the use of PEDOT:PSS hole transport layer which is usually problematic for the hydrophobic graphene electrode.⁹² For cathode applications, it has been reported that thin Al nanoclusters on single-layer graphene can considerably decrease its work function from 4.56 eV to 4.14 eV, which can align well with the LUMO of P3HT in the P3HT:PC₆₁BM active layer, and facilitate electron extraction. Furthermore, the wettability of the hydrophobic graphene electrode is significantly improved, as shown in the changes of water contact angle of the graphene surface (Figure 24).⁹³ While the contact angle of pristine graphene is large (95.7°) indicating a hydrophobic surface, it is considerably reduced to only 48.0° after Al nanoclusters of 0.5 nm are deposited which promotes uniform coating of subsequent solutions, without compromising optical transparency of the graphene electrode.⁹³

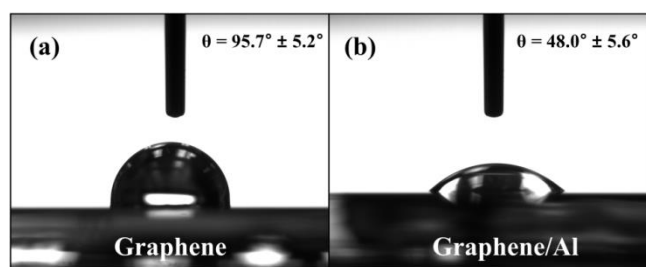


Figure 24. Surface contact angles of (a) plain graphene and (b) graphene/0.5 nm Al nanoclusters. Reproduced with permission.⁹³

Conclusions

In conclusions, we have reviewed the recent progress of OSCs incorporated with various types of metal nanostructures including metal nanopatterns and metal nanomaterials for further improving device performance. The incorporation of multiple metal nanostructures into OSCs can induce significant changes with different physical origins including optical and electrical effects. In the case of simultaneous incorporation of multiple nanostructures into a single device, coupling between the nanostructures can occur which offer an extra degree of freedom to further enhance the performance of OSCs. As a result, we discuss in detail the influence of various metal nanostructures from different aspects. Primary optical effects such as SPR (for metal nanopatterns) and LSPR (for metal nanomaterials) on the performance of OSCs are summarized and discussed, which are largely dependent on the characteristics of the nanoscale metals (shape, size, concentration, optical environment, etc.). Meanwhile, changes in the electrical properties are usually introduced in nanostructure-incorporated OSCs as well, which are equally important for enhancing performance and should be taken into account in device design. Interesting optically induced electrical effects such as plasmonic electrical effect and charge accumulation effect in the metal nanomaterial-metal oxide semiconductor composite are also reviewed in detail. Finally, additional interfacial modifications such as work function tuning and wettability enhancement by using metal nanomaterials are also described. Consequently, the comprehensive understanding of the detailed physical mechanisms for various metal nanostructures can promote the

further development of a new class of nanostructure-incorporated OSCs and its emerging applications.

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