



## Review

## A review of recent plasmonic nanoparticles incorporated P3HT: PCBM organic thin film solar cells



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## ABSTRACT

An optimum thickness of organic active layer of 100 nm or possibly less results in poor optical absorption in organic photovoltaic cells (OPV). The optical absorption can be improved by using a thick organic active layer, but the charge carrier collection efficiency will decrease due to low charge carrier mobility for most of the polymeric organic semiconductor. This phenomenon imposes a trade-off between optical absorption and charge carriers transport inside OPV. Recently, metallic nanostructures such as gold (Au) and silver (Ag) with various sizes and morphologies have been identified as an alternative route to boost the performance of OPV at this specific limited thickness (ie.  $\leq 100$  nm). Multiple plasmonic effects such as optical and electrical effects are induced upon introducing metallic nanoparticle(s), NP(s) into OPV. This review highlights recent progress in plasmonic-enhanced poly(3-hexylthiophene-2,5-diyl): phenyl-C61-butyric acid methyl ester (P3HT: PCBM)-based OPV with NP(s) located either inside organic active layer or carrier transport layer (CTL) or at various interfaces within the OPV cell architecture. With understanding of the physical plasmonic effects for Au and Ag in OPV, such plasmonic NP(s) act as a new class of strategy for performance optimization.

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## 1. Introduction

One of the great challenges faced by society today is fast-rising energy demand due to expanding population from year to year. Among all renewable energies, solar energy has potential to fulfill these needs because it is free and abundant. Photovoltaic is a promising technology that could generate and store electrical power on a very large scale. Therefore, photovoltaic power has potential to solve energy problem for our society in next generation. At present, 50% of the market share in worldwide photovoltaic production is based on crystalline silicon (Si) solar cell [1] and the efficiency could achieve up to 15–17% for polycrystalline Si and 16–18% for monocrystalline Si with the thickness around 160–240  $\mu\text{m}$  [2]. However, Si solar cell is expensive due to the cost of Si materials and processing [3,4]. To overcome this issue, researchers explore new materials for the next generation photovoltaics such as thin film photovoltaic [5–7], dye sensitized photovoltaic [8–10], quantum-dot photovoltaic [11–13], organic photovoltaic [14–16] and perovskite photovoltaic [17–19]. Even though perovskite photovoltaic achieves the highest efficiency compared to that other photovoltaics as listed above [20,21], the stability of this device is low and it tends to degrade [22–24]. To date, the best candidate to replace high cost Si photovoltaic is OPV [25,26], which can be produced at a lower cost [27,28] and possesses long term stability [29,30]. In addition, OPV is light-weight [31,32] and can be fabricated at room temperature without vacuum condition [33,34] via solution methods [35,36]. However, the performance of OPV is relatively low compared to that of crystalline Si photovoltaic [20]. Low charge carrier mobility for most of the polymeric organic semiconductor (typically  $10^{-4}$   $\text{cm}^2/\text{Vs}$  or less) [37] has limited the thickness of the organic active layer (<100 nm) [38], which results in poor optical absorption [39]. Therefore, the enhancement of the absorbance of polymeric organic semiconductor with the specific limited thickness still remains a challenge. In 1998, Stuart and Hall discovered that by introducing silver nanoparticles, AgNP(s) on the surface of the silicon-on-insulator (SOI) photodetector, nearly factor of 20-fold enhancement in photocurrent was achieved. The results indicated that metallic NP(s) were able to scatter light and induce local surface plasmon resonance among itself [40]. This finding is very important in light-harvesting technology applications especially in water splitting, thermoelectric, photovoltaic, photocatalytic and photodynamic therapy platforms [41–44]. In photovoltaic application such as OPV, NP(s) may act as ‘light-trapping’ material and promote the optical absorption properties of OPV, while maintaining the thickness of the active layer below 100 nm. This review article gives an overview of surface plasmonic-enhanced OPV based on P3HT: PCBM from 2011 to 2015. Firstly, we introduce the physical property of surface plasmon. Then, we highlight experimentally OPV based on two types of plasmonic nanomaterials, namely AuNP(s) and AgNP(s) at different layers of OPV. Finally, conclusion and outlooks based on plasmonic OPV are listed out.

## 2. Physical property of surface plasmon

Metallic NP(s) with different morphologies and sizes have been widely used in OPV application in order to trigger surface plasmonic effect. Depending on their location inside OPV, it commonly leads to three different mechanisms, namely (i) light scattering, (ii) localized surface plasmon resonance (LSPR) and (iii) surface plasmon polariton(s), SPP(s).

### 2.1. Light scattering

Metallic NP(s) absorb and re-scatter light simultaneously after

light photon strikes on its surface. The first mechanism involves metallic NP(s) located at outside of the organic active layer as shown in Fig. 1. In this case, NP(s) could locate at (a) interface of transparent conductive oxide substrate (TCO)/carrier transport layer (CTL) (b) inside CTL or (c) interface of CTL/organic active layer. In the region near to heterogeneous interface, NP(s) preferentially scatter light into medium with higher permittivity [45]. Light scattered with certain angular spreads increases optical path length through multiple scattering events, thereby increasing photon absorption efficiency. In case if the OPV consists of reflecting metal top electrode, light reflects and couples back with NP(s) by the same mechanism. This enables more lights to pass through the organic active layer compared to that without reflecting metal top electrode.

### 2.2. Localized surface plasmon in quasistatic approximation

Localized surface plasmon (LSP) is induced when frequency of the oscillation excited electron of metallic particle is matched with the frequency of the incident photon (see Fig. 2a). The local enhancement of the electromagnetic field as a result of the resonance effect leads to the effective light concentration near the surrounding of the metallic particle, mostly in the visible to infrared region [46]. For spherical NP(s) with radius  $a$ , the given polarizability,  $\alpha$  can be expressed as

$$\alpha = 4\pi a^3 \left[ \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m} \right] \dots \quad (1)$$

Here,  $\epsilon_p$  is the permittivity of the metallic NP(s) and  $\epsilon_m$  is the permittivity of the surrounding medium. It is clear that the polarizability of metallic NP(s) is maximal as  $\epsilon_p$  is approaching  $-2\epsilon_m$ . Since the excited plasmons are localized and cannot propagate within the metallic NP(s), it is also known as localized surface plasmon resonance (LSPR). If the size of metallic NP(s) is much smaller compared to wavelength of the incident photon, the absorption,  $C_{\text{abs}}$  and scattering,  $C_{\text{sca}}$  cross-section are given by Ref. [47]:

$$C_{\text{abs}} = \frac{2\pi}{\lambda} \text{Im}[\alpha] = 4\pi k a^3 \left[ \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m} \right] \dots \quad (2)$$

$$C_{\text{sca}} = \left( \frac{1}{6\pi} \right) \left( \frac{2\pi}{\lambda} \right)^4 |\alpha|^2 = \frac{8\pi}{3} k^4 a^6 \left| \frac{\epsilon_p - \epsilon_m}{\epsilon_p + 2\epsilon_m} \right|^2 \dots \quad (3)$$

where  $k$  is the wavenumber of the incident photon,  $2\pi/\lambda$ . Based on the equations stated above, LSP frequency strongly depends on the effective size and shape of the NP(s), arrangement and distribution of NP(s), and the local environment [48]. As the particle size is decreased, the efficiency of absorption will dominate over the scattering frequency and vice versa [49]. The scattering frequency,  $Q_{\text{sca}}$ , is defined as

$$Q_{\text{sca}} = \frac{C_{\text{sca}}}{C_{\text{sca}} + C_{\text{abs}}} \dots \quad (4)$$

In this mechanism, small NP(s) (5–20 nm) introduced into organic active layer could induce near field effect or LSPR upon photoexcitation (see Fig. 2b), which results in an enhancement of optical absorption efficiency. These antennas are useful especially in polymeric organic semiconductor with diffusion length less than 20 nm [3]. Careful design to control distribution of the metallic NP(s) inside active layer is important because it tends to phase segregate from the organic materials, thereby increasing recombination from carrier trapped on metallic NP(s) [50].

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