Review

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Plasmon-enhanced organic and perovskite solar cells with metal nanoparticles

<https://doi.org/10.1515/nanoph-2020-0099>

Received February 9, 2020; revised March 16, 2020; accepted March 18, 2020

Abstract: Solution-processing thin-film solar techniques, such as organic solar cells (OSCs) and perovskite solar cells (PeSCs), hold great promise as cost-effective renewable energy sources with feasible large-scale manufacturing. However, these devices are suffering from the incomplete photon absorption and thereby cannot unlock the full potential of device efficiency despite their rapid development in recent decades. Incorporation of plasmonic metal nanoparticles (NPs) into the thin active layers has been considered as a breakthrough strategy to solve this inherent limit and represent an imperative milestone toward the highly efficient OSCs and PeSCs, arising from the significantly enhanced light absorption and electrical characteristics in fundamental. Herein, the recent advances in fabrication and incorporation strategies of plasmonic NPs are reviewed. The in-depth efficiency and stability enhancement mechanisms are investigated and highlighted. Meanwhile, potential strategies and perspectives for their further development of NP-based solution-processing OSCs and PeSCs are presented.

Keywords: organic solar cells; perovskite solar cells; plasmonics; metal nanoparticles.

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1 Introduction

The ongoing energy crisis combined with global warming and air pollution in recent decades induced with traditional fossil fuel has indicated the urgent requirement for the development of cost-effective, feasible, and large-scale manufacture; environmental stability; and green energy technologies. To circumvent the energy crisis, renewable natural energy sources, such as solar energy, tidal power, and wind energy, have been explored as potential energy candidates [1]. The development of solar energy through photovoltaic energy conversion is the most promising alternative as sunlight is long-term sustainable, environmentally friendly, and abundant for energy production [2–7]. Inorganic solar cells, such as traditional silicon (Si)-based or gallium arsenide-based, have been extensively reported to harvest sunlight and convert it into electrical power on a wafer-based scale, achieving high-power conversation efficiencies (PCEs) and superior environmental stability [2, 8]. Although inorganic solar cells possess the major share of current photovoltaic market nowadays, their expensive crystal growth techniques are not allowed to generate energy at a low price comparable to fossil fuels.

For the quest of cost-effective solar technologies, solution-processed techniques have been explored with shortened manufacturing time [9–11]. Thin-film solar cells, especially organic solar cells (OSCs) and perovskite solar cells (PeSCs), have appealed attention for years as the potential techniques to generate energy on a large scale with simple solution process [12–22]. In particular, they represent exceptional features such as compatibility with roll-to-roll process, flexibility, and lightweight, exceeding the inorganic solar cells [23–26]. Besides, the PCEs of OSCs and PeSCs have been rapidly developed in recent years [27–30]. To date, the PCEs of single-junction and tandem-junction OSCs have been significantly improved to 17.3% [31] and 16.35% [32], respectively, whereas the PCE of PeSCs has reached to a relatively high value of 25.2% certified by the National Renewable Energy Laboratory (NREL) [<https://www.nrel.gov/pv/cell-efficiency.html>], equally matched to the Si-based solar cells.

The dominant factor for realization of highly efficient solar cells is to balance the light absorption and the extraction of photogenerated excitons [33]. In general, the diffusion length of solution-processed organic semiconductors is much smaller than highly crystalline inorganic materials [34]. Therefore, the photoactive layers, namely, conjugated polymers or fullerene derivatives, in OSCs are commonly very thin with the order of 100 nm to trade off the low exciton collection rate induced by short diffusion length [35, 36]. In this case, effective approaches should be explored to maximize the light harvesting across the solar spectrum range and achieve high PCEs with the reduced absorber thickness [37, 38]. However, because of the small physical dimensions of OSCs, the prevailing strategies utilized in inorganic solar cells for light harvesting enhancement, such as textured pyramids, are not suitable in OSCs and need further modification. On the contrary, perovskite films possess long diffusion lengths up to 1 μm and superior ambipolar transport ability [39], which relieves the stringent thickness rule. Although PeSCs have realized efficient light harvesting with planar device architectures as well as relatively thicker absorber (~ 500 nm), yet in fact, the obtained PCEs of PeSCs are still below the theoretical limit, which requires further improvement [40].

Incorporation of plasmonic metal nanoparticles (NPs) is the most promising strategy to effectively improve the light harvesting in OSCs and PeSCs [41–47]. Metal NPs can substantially enhance the optical absorption of devices without influencing the device architecture due to the excitation of localized surface plasmon resonance (LSPR) and the far-field light scattering effect [48–50]. Besides, they have been also investigated to enhance the electrical characteristics, including exciton dissociation, charge transport, and collection in devices [51–54]. In this review, we address the characteristics of metal NPs and their applications in highly efficient OSCs and PeSCs. We discuss the plasmonic fundamentals of metal NPs along with the fabrication methods to control their sizes and shapes. We develop the evolution of device performance and the application of plasmonic NP-based OSCs and PeSCs and investigate the underlying enhancement mechanisms, as well as the future outlook in our perspective.

2 Metal NP fundamentals

Metal particles with nanometer dimensions have gained substantial attention in OSCs and PeSCs for decades due to their unusual optoelectronic and chemical properties

[55–57]. Given the diversified types of enhancements in plasmonic OSCs and PeSCs, it is necessary to comprehend the origins of these features. Fundamentally, when the size of metal NPs reduces to below the incident wavelength in the quasi-static limit, strong interactions can be perceived between the free electrons in the metal NPs and the electromagnetic radiation [58]. Plasmons are the collective oscillations of free electrons followed by the production of dipoles localized in the vicinity of the metal NP surfaces arising from the strong interactions with the incident lights [59]. Metal NPs have been employed in buffer layers, photoactive layers, or at the interface of OSCs and PeSCs to increase short-circuit current density (J_{sc}) and PCE arising from the absorption enhancement [60–65]. Specifically, the incorporation of metal NPs can boost the light harvesting in OSCs and PeSCs by two mechanisms: a near-field plasmonic enhancement and an increase of the forward scattering cross section as shown in Figure 1 [3]. The plasmon resonance wavelength depends on the size, shape, distribution, and surrounding dielectric environment of metal NPs, determined by the fabrication methods [42, 66]. Plasmonic light trapping in OSCs and PeSCs and feasible strategies to control the size and shape of metal NPs are elaborated and summarized in this section.

2.1 Physical properties

Metal NPs show a strong ultraviolet (UV)–visible absorption, distributing within the absorption band of the active layer of OSCs and PeSCs, such as conjugated polymers and perovskite materials. Therefore, the employment of metal NPs either inside the buffer/active layers or between interfaces of OSCs and PeSCs devices can effectively enhance the light trapping by increasing the optical path length for light harvesting. The physical derivation of the enhanced absorption can ascribe to plasmonics, which are the coherent oscillations of the free conduction electrons excited by the incident light. Particularly, for metal NPs with dimensions similar or smaller than the wavelength of incident light, strong interactions are perceived between the free conduction electrons in the NPs and the electromagnetic electric fields. Coupled oscillations of electromagnetic light and the electrons oscillating are defined as LSPRs [67]. As the resonantly localized field amplification occurs, a dipolar field is generated at the vicinity of the plasmonic metallic NPs. This field results in strong near-fields outside the particles, increasing scattering cross section and electromagnetic light absorption by light trapping via plasmonics in both OSCs and PeSCs [4, 33].

Figure 1: Plasmonic light trapping mechanism in metal NP-based OSCs.

(A) Plasmonic light scattering effect. (B) Localized surface plasmon resonance effect. (C) Surface plasmon polariton excitation of 2D periodic NP array at the NPs/photoactive layer interfaces. Reproduced with permission from Stratakis and Kymakis [3]. Copyright 2013, Elsevier.

If the size of the metal NP is below the incident wavelength, the scattering (σ_{sc}) and absorption (σ_{abs}) cross sections are given from the quasi-static approximation via the following equations [68]:

$$\sigma_{sc} = \frac{1}{6\pi} \left(\frac{2\pi}{\lambda} \right)^4 |\alpha|^2 \quad (1)$$

$$\sigma_{abs} = \frac{2\pi}{\lambda} \text{Im}(\alpha) \quad (2)$$

where $\alpha = 3V(\epsilon_p - \epsilon_m)/(\epsilon_p + 2\epsilon_m)$ is the polarizability of the metal NP, and λ is the wavelength of incident light. For spherical NPs, the polarizability can be calculated via $\alpha = 4\pi r^3(\epsilon_p - \epsilon_m)/(\epsilon_p + 2\epsilon_m)$. Here ϵ_p and ϵ_m are the permittivity of the plasmonic NP and the embedding semiconductor medium, and V is the volume of the metal NP, respectively. Figure 2 demonstrates the electromagnetic field distribution of plasmonic metal NPs influenced by the size and surrounding medium in detail [69]. It is well-defined that σ_{sc} relies on both the size of the metal NP and the surrounding local dielectric semiconductor. It can be concluded that when the light frequency is such that $\epsilon_p \approx -2\epsilon_m$, the metal NPs exhibit maximum polarizability and LSPR, which is nonpropagating excitations of free electrons within metal NPs. One exceptional characteristic of LSPRs is the enhanced electromagnetic field due to the strong local resonance, resulting in efficient light concentration with enhancement factors as high as 100. Plasmonic fields surrounding the metal NPs damp exponentially related to the distance from the NPs. The frequency of the resonance and decay lengths of the electrical field are determined by

the metal NP materials, the dimensions, geometric shapes and configurations of the metal NPs, and the optical parameters of the surrounding environment, which renders process tunability.

On the basis of (1) and (2), the particle dimension certainly takes charge of the extinction process, determining whether metal NPs function as scattering centers or local electromagnetic field enhancers or both. Figure 1 classifies the physical principles resulting in the enhancements in plasmonic OSCs. The enhancements of device performance can be ascribed to the modifications in optoelectrical properties. Specifically, smaller metal NPs with diameter of 5–20 nm can be utilized as sub-wavelength antennas. In this case, enhanced absorption dominates owing to LSPR excitation. The local plasmonic field couples to the photoactive layer in OSCs and PeSCs, which enhances absorption and accordingly exciton dissociation. In contrast, relatively larger diameter particles (>50 nm) perform as subwavelength scattering in photovoltaic applications that couple and trap freely propagating incident photons into active layer.

Under this circumstance, enhanced absorption is dominated by the increased optical path length, induced by the re-emitted light within the device. However, if the particle is too large, multipole oscillations will be strengthened, which reduces the scattering efficiency of Q_{sc} . Besides, when particle dimension exceeds the Rayleigh approximation, the resonance will broaden and redshift. Overall, smaller particles mainly absorb the photons, whereas larger ones scatter light more efficiently. The scattering efficiency (Q_{sc}) can be described by the relation: $Q_{sc} = \sigma_{sc}/(\sigma_{sc} + \sigma_{abs})$ [40]. While plasmonic

Figure 2: Electric field distribution and dielectric function for metal NPs.

Electric field distribution of plasmonic metal NPs influenced by the size (A–F) and surrounding medium (G–J), respectively. (K–L) Dielectric function for small Au and Ag NPs. Reproduced with permission from Fan et al. [69]. Copyright 2014, Nature Publishing Group.

NPs provide efficient near-field enhancement and scattering, it is necessary to guarantee that the absorption by the plasmonic NPs is minimal, especially for smaller particles.

Absorption by the plasmonic NP cannot produce photocurrent; thus, σ_{sc} should outweigh σ_{abs} for valid utilization of the plasmonic NPs.

At the distance of r from the center of spherical metal NPs, the maximum field enhancement from LSPR embedding in a nonabsorbing semiconductor can be expressed via the relation [70]:

$$\eta_{\max} = \left| 1 + \frac{\alpha(\omega)}{2\pi r^3} \right|^2 \quad (3)$$

where ω is the frequency of the incident light. The field enhancement ($\eta_{\max}$) is essentially an upper limit approximation on account of the nonabsorbing environment.

Furthermore, metal NPs can also consist of periodical array applied in organic photovoltaics (OPVs) as shown in Figure 1C. Here, incident electromagnetic wave excites resonant scattering modes, which is described as surface plasmon polaritons (SPPs) at the interface of NP-photoactive layer. Besides, two-dimensional (2D) metal NPs array can supply in-plane momentum for scattered light to be coupled to propagation or waveguide modes [71, 72]. The in-plane momentum can be calculated by the equation of $q\frac{2\pi}{\tau}$, where τ is the pitch and q ($= \pm 1, \pm 2, \pm 3, \dots$) is the diffraction order. In this case, incoming light can couple into waveguide modes through momentum matching under the following conditions [73]:

$$k_{\text{wg}} = k \sin \vartheta + q \frac{2\pi}{\tau} \quad (4)$$

where k_{wg} represents the momentum for coupling; $k \sin \vartheta$ is the in-plane momentum of the incident light. The geometrical morphology of the metal NPs arrays, such as their pitch and size, should be well-designed and controlled to fulfill the optimal momentum conversion and further absorption enhancement in devices.

Indeed, Nishijima et al. [74] have investigated the effect of random and periodic particle configurations on the light field enhancement of plasmonic resonance. An enhancement of extinction and a broader plasmon resonance were observed in NPs with increased disorder, which could be ascribed to grating-like losses arising from diffraction. Finite difference time domain (FDTD) modeling calculations demonstrated an augmentation of the enhancement by more than two orders of magnitude for the random nanodisk patterns; however, those hotspots were more sparsely distributed. The randomly distributed NPs are one of the cheapest approaches to enhance light harvesting of solution-processed solar cells, favored for industrial applications.

Notably, the electromagnetic resonance spectrum of noble metal NP is distributed ranging from visible to infrared (IR) region, which is attractive to OSCs and PeSCs.

Therefore, silver (Ag) and gold (Au) NPs have been hotly pursued in devices for decades. Indeed, other metal NPs can show plasmonic properties as well; specifically, aluminum (Al) NPs exhibit limited metal absorption due to their effectively reduced reflection losses from the high resonant frequency [33, 75]. Besides, copper (Cu) NPs with appropriate capping agents to improve stability in air have also been employed in OSCs [76, 77].

According to the location of plasmonic metal NPs employed in the front or rear side of the device architecture, their integration in OSCs and PeSCs can be divided into the following categories: charge transport layers, photoactive, and between interfaces [33, 71]. These categories are essentially dissimilar in principle concerned with the plasmonic NP-based absorption enhancement. Positioning the metal NPs in the front or rear side of the devices is a potential choice for plasmonic scattering as they can effectively isolate the electric activity of the active layer and the optical properties of the NPs and avoid destructive interference. Metal NPs can be integrated into the charge transport layers, photoactive layer, or between interfaces in OSCs. It is also noteworthy that the incorporation of NPs into the photoactive layer can result in the improvement of structural durability with slower degradation rate under the illumination radiation [78], which causes a further performance enhancement. The enhancements of device performance and changes to device physical mechanisms in plasmonic OSCs were investigated to derive from the modifications in morphological, electrical, and optical characteristics [79]. Specifically, modifications in electrical properties of OSCs, such as exciton generation, hot carrier transfer, and charge extraction, played an important role in performance enhancement induced by improved open-circuit voltage (V_{oc}), fill factor (FF), and photocurrent generation. For PeSCs, only few research efforts have been devoted into plasmonics applications so far, which are generally similar to those explored in OSCs. It is expected that PeSCs with plasmonic NPs will be addressed as the thorough comprehension of the electrical and optical effects. Besides, polymer solar cells (PSCs) should receive particular concern because of their environmental instability, especially for the incorporation of Al or Ag NPs [80]. The effects of plasmonic metal NPs in both OSCs and PeSCs and the resultant enhancements will be discussed in more detail and shown in the following sections.

2.2 Fabrication methods of metal NPs

Structural parameters of metal NPs make a great difference to manipulate the excitation, trap, and coupling process

of photons in OSCs and PeSCs. To date, considerable numbers of fabrication technologies have been exploited for the plasmonic NPs with controllable morphology [46, 81, 82]. The NPs with versatile shapes and morphologies show distinct optical responses arising from the collective oscillations giving rise to LSPR and plasmonic scattering. The availability of microfabrication and nanofabrication methods with large scale and low cost is a crucial point to the commercial application of photovoltaic module. In this section, we will discuss several fabrication methods to form versatile and scalable metal NPs with a wide range of sizes, shapes, and high yields applied in OSCs and PeSCs, such as chemical synthesis technologies, laser ablation methods, and thermal annealing routes.

Regarding the chemical synthesis technologies, the metal NPs are synthesized mainly by the reduction of precursors with controlled aspect ratio. Brust et al. [83] and Turkevitch [84] aqueous preparation methods are commonly utilized for the fabrication of NPs smaller than 10 nm and 10–40 nm in diameter up to a limit, respectively. Ligand exchange step is always followed in this method, on account of avoiding aggregation in the growth process [85]. For example, Au halides are generally used as precursors for the synthesis of Au NPs, which are obtained by dissolving bulk Au in aqua regia to form chloroauric acid or in metal cyanide to form Au chloride. In this case, the introduction of an appropriate reduction agent is significant to prepare uniformly shaped NPs with narrow size distribution [46, 86]. Specifically, citrate is often used to function as the reduction agent in fabrication of Au NPs with spherical morphology [87, 88]. By adjusting the concentration ratio of citrate and Au precursor, the size

of Au sphere can be regulated, which is indicated by the color variation of the solutions as shown in Figure 3A. The light scattering effects of incorporated NPs into the poly-(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) layers are presented in Figure 3B.

Besides, laser ablation methods are usually employed to prepare metal NP patterns in OSCs and PeSCs in order to excite LSPR or plasmon scattering [89]. In this method, the solid target dispersed in a liquid medium is treated with pulsed picosecond and femtosecond laser [90] ablation to obtain the plasmonic NPs, which are appealing candidates for incorporation in OSCs and PeSCs, especially for the photoactive layer [91, 92]. This method features the advantage of easily producing plenty of NPs free of unnecessary reagents such as stabilizers, surfactants, and passivation layers, when compared to the chemical synthesis methods [93, 94]. It is noteworthy that surfactants on the surface of NPs possibly accelerate unwanted exciton quenching through nonradiative energy transfer between the NPs and active layers; thereby decreased plasmonic effect is observed. Photoconversion efficiency has been reported to be decreased after the addition of chemically synthesized Au NPs without capping in the photoactive layer [94]. In contrast, laser-ablated Ag NPs doped in the active layer of OSCs can cause enhanced photodegradation stability [54]. However, it is hard to obtain monodispersed colloids of metal NPs with this technique [90, 91]. Stratakis and Kymakis reported Au NPs formed by femtosecond laser ablation with initial colloidal solution of Au metallic target dispersed into a Pyrex cell and covered absolute ethanol [92]. This technique supplies massive NPs with neither counter-ions nor surface-active substances.

Figure 3: Characteristics of Au NPs synthesized with the chemical technology.

(A) Gold NPs solutions with sizes of 20, 30, 40, and 60 nm. (B) The light scattering effects of incorporated Au sphere with diameter of 40 nm, Au hemisphere with diameter of 40 nm, and Au hemisphere with diameter of 100 nm into the PEDOT:PSS layers. Reproduced with permission from Notarianni et al. [46]. Copyright 2014, Elsevier.

Kubiliute et al. demonstrated ultrapure, water-dispersed Au NPs produced by fs-white light continuum generation in colloidal solutions to precisely control the size [95]. The narrow-size distributed NPs with preferentially spherical shape showed enhanced stability without sedimentation for months.

Another captivating method for the production of metal NPs is thermal annealing route combined with traditional deposition techniques to fabricate various NPs patterns on different positions in OSCs and PeSCs [96–98]. Mallik et al. [99] reported bimetallic Au and Ag NPs with a unique core-shell structure with UV-photoactivation technique. In this method, Au NPs were functioned as seed particles and catalyzed the reduction of Ag ion under UV irradiation to produce the bimetallic NPs with $\text{Au}_{\text{core}}-\text{Ag}_{\text{shell}}$ configuration [99]. Xu et al. [100] demonstrated a simple coevaporation of Au and Ag thin films onto the indium tin oxide (ITO) substrate, followed by the vacuum thermal annealing method to create Au–Ag alloy NPs with tunable molar ratio.

3 Plasmonics in OSCs

Metal NPs incorporated with the single or tandem OPV cells substantially improve the optical absorption of devices via the light trapping induced predominantly by the excitation of near-field LSPR with the small NPs or the far-field light scattering with the large NPs [48]. Besides, the application of metal NPs in OSCs has been demonstrated to improve the electrical characteristics, including exciton dissociation, charge transport, and collection [51–54]. These effects enhance the device performance in various configurations of the plasmonic NPs, when employed in the photoactive layer or the buffer layer (charge transport layer), between the interface as shown in Figure 4 [101]. Generally, the optimization of device performance is achieved through adjusting the materials, geometric shapes, size distributions, and topological distributions of plasmonic NPs in the device architecture, which can be guided by the theoretical simulations, such as FDTD modeling [5, 60, 102]. Here, we demonstrate the light absorption enhancements with plasmonic NPs in OSCs in detail.

3.1 Optical absorption

When incorporated plasmonic NPs with size much smaller than the wavelength of incident light, the enhanced absorption in the OSCs originates predominantly from the

excitation of near-field LSPR mode. Plasmonic metal NPs are investigated to be effective on improving the device performance of OSCs when doped into multiple functional layers within the device architecture.

Theoretically, incorporation of the plasmonic metal NPs into photoactive layers is the optimum strategy, as it can maximize the contribution of LSPR to the light harvesting under this circumstance. Deliberated design is needed in positioning the NPs in photoactive layer as exciton quenching, nonradiative decay, and charge carrier recombination can occur [51, 54, 103, 104] on the surface of unpassivated NPs. Packing NPs inside an inert cladding layer with core-shell structure to passivate the chemically synthesized NPs as well as laser-ablated NPs can effectively alleviate this issue [105, 106]. Spyropoulos et al. [92] presented a 40% PCE enhancement in OSCs after embedding laser-ablated Au NPs into the photoactive of poly(3-hexylthiophene):phenyl-C61-butyric acid methyl ester (P3HT:PCBM) in 2012. Notably, the spectral ranges of incident photon to charge carrier efficiency (IPCE) enhancement and quantum efficiency were investigated to match with the LSPR region of Au NPs doped in the photoactive medium. Therefore, the efficiency enhancement can be ascribed to improved light harvesting and subsequent exciton generation arising from LSPR and scattering effects. Xie et al. [107] demonstrated high-efficiency PSCs with an efficiency enhancement of 22% via incorporating poly(ethylene glycol) (PEG)-capped Au NPs of sizes 18 and 35 nm in both anodic buffer layer and photoactive layer simultaneously in 2011 shown in Figure 5A. The incorporation of PEG-capped Au NPs into anodic buffer layer of PEDOT:PSS led to enhanced hole collection, whereas their incorporation into photoactive layer of P3HT:PCBM resulted in the optical absorption enhancement and charge transport balance. Specifically, the absorption enhancement within the photoactive layer can be assigned to the strong near-field LSPR effect penetrated in the photoactive polymers. Meanwhile, coupling between plasmonic NPs in individual buffer and photoactive layers was not detected. These findings indicated that incorporation plasmonic NPs in different configurations simultaneously can be utilized to fulfill larger enhancement of device performance, which provided guidance for designing high-efficiency OSCs with NP incorporation.

Integration of NPs into the buffer layer (charge transport layer) is one of the easy, effective, and nondestructive approaches to harness the plasmonic effects. Incident light at wide angles can be scattered into the photoactive layer and fulfill the light trapping, thereby increasing the light path length within the OSCs and possibly resulting in total internal reflection. Besides, the scattered light can

Figure 4: Multiple synergistic effect of optical absorption enhancement and electrical characteristics occurred in OSCs with the incorporation of plasmonic metal NPs.

(A) Schematic illustration of the plasmonic solar cell architectures with different spatial locations of metal nanostructures. (B) Core-bishell design concept for metal nanostructures embedded within an active layer. (C) Nanoplasmonic device structure consisting of Ag/TiO₂/C₆₀ and Ag/SiO₂/C₆₀ stacked films to simulate the core-bishell designs of Ag@TiO₂@Pa and Ag@SiO₂@Pa, respectively. (D) Energy diagram of electron excitation based on between-band transfer for the SiO₂ interface. (E) Energy band diagram of metal-insulator-semiconductor for the device with a TiO₂ layer. Current-voltage characteristics in the dark and under simulated AM1.5G solar illumination of a typical device with 1 nm of SiO₂ (F) and 3 nm of TiO₂ (G) between nanostructured Ag film and C₆₀. The inset of (F) demonstrated the dependence of SiO₂ thickness on short-circuit current. Reproduced with permission from Yao et al. [101]. Copyright 2019, American Chemical Society.

potentially excite SPPs along the intervening planar surfaces. Incorporation of plasmonic metal NPs in multiple layers can be an effective strategy to further improve the device performance.

Wu et al. [108] incorporated Au NPs into the PEDOT:PSS buffer layer and systematically investigated the influence of plasmonic structure on the performance of OSCs shown in Figure 5B. The enhancement degree of light absorption in the plasmonic-enhanced OSCs mainly depended on the local enhancement of LSPR-induced local field at the vicinity of Au NPs. The rate of exciton generation was improved; meanwhile, the lifetime of photogenerated excitons in the active layer was reduced by LSPR effect.

Accordingly, interactions between the plasmons and the photogenerated excitons led to an increased probability of exciton dissociation, decreasing the recombination level of geminate excitons. Yao et al. added nanoprisms both in the front and rear side, specifically PEDOT:PSS layer and C₆₀-bis layer, and permitted an enhancement of 18%, from 7.7% to 9.0% as shown in Figure 6 [110].

Embedding NPs at interfaces within devices can excite LSPRs at their surrounding along with SPPs along the planar surfaces. Thus, the embedded NPs can simultaneously enhance absorption and collect charge carriers in OSCs. Stenzel et al. presented the ITO–Cu phthalocyanine–indium sandwich structures combined with metal

Figure 5: Incorporation of plasmonic metal NPs into different positions in OSCs.

(A) Photoactive layer. (B) Buffer layer. (C) Between interfaces. Reproduced with permission from Xie et al. [107], Copyright 2011, American Institute of Physics; Wu et al. [108], Copyright 2011, American Chemical Society; Stenzel et al. [109], Copyright 1995, Elsevier.

nanoclusters shown in Figure 5C [109]. The integral photocurrent enhancement by a factor of nearly three was first recorded by blending Cu clusters, which was assigned to the LSPR and interband transitions in the Cu clusters. A breakthrough occurred in a study by Rand et al. [111] in 2004 when an array of 5-nm-diameter NPs was employed into the intermediate layer in tandem thin-film OSCs. A significant efficiency enhancement by a factor of more than 2 was demonstrated, which was assigned to the enhanced optical field induced by both LSPR and light scattering. Furthermore, this enhanced field existed far from the particle surface, reaching a long range up to 10 nm from the center of the NPs. Later on, Xu et al. [100] employed thermally annealed Au–Ag alloy NPs in OSCs with adequate molar ratio and obtained a 19% enhancement with PCEs. The enhancement can be ascribed to the amplified electric field at the NP surface arising from the near-field LSPR coupling.

In OSCs, incident light penetrates the substrates, electrodes, and buffer layers, which are finally absorbed by the thin photoactive layer. Enhanced incident photon absorption can be realized by employment of arrayed or random metal NP scatters in devices along the incident direction. For larger-diameter NPs employed in OSCs, far-field scattering effects play the main role in coupling incident light into photoactive layer and enhancing absorption in devices. Because of the light scattering, the plasmonic NPs with large scattering cross section can supply more effective path lengths, trap light, and improve in-coupling

efficiency in devices as shown in Figure 7 [112–118]. The scattering effect can be adjusted by optimizing the geometric parameters, including the size, shape, distribution, and surrounding medium of NPs in OSCs.

In a related article, Wang et al. proposed enhanced performance of OSCs with employment of large truncated octahedral Au NPs with an approximate size of 70 nm into a photoactive layer of poly(3-hexylthiophene):[6, 6]-phenyl C70 butyric acid methyl-ester (P3HT:PC₇₀BM), and poly[N-9'-hepta-decanyl-2,7-carbazole-alt-5,5'-(4',7'-di-2thienyl-2',1',3'-benzothiadiazole)] (PCDTBT:PC₇₀BM), and 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:PC₇₀BM) in 2011 [61]. In this case, the PCE enhanced from 3.54% to 4.36% for P3HT:PC₇₀BM-based devices, from 5.77% to 6.45% for PCDTBT:PC₇₀BM-based devices, and from 3.92% to 4.54% for Si-PCPDTBT:PC₇₀BM-based devices with 5 wt% Au NPs doping ratio, which can be assigned to the enhanced light absorption on account of scattering effects from LSPR modes. Wang et al. performed a comparative study of different NP shape incorporated in poly[N-999-hepta-decanyl-2,7-carbazole-alt-5,5'-(49,79-di-2-thienyl-29,19,39-benzothiadiazole)]:[6,6]-phenyl C71 butyric acid methyl-ester (PCDTBT:PC₇₁BM) devices, specifically for the shape-controlled Ag nanoplates and Ag NPs with well-defined size [119]. Power conversation efficiency enhancement of 37.5% and 25% has been demonstrated for Ag NPs and Ag nanoplates-based devices, respectively.

Figure 6: Schematic of materials and nanoprisms used in the dual plasmonic BHJ device and corresponding device performance. (A) Schematic diagram of the device configuration with dual incorporation of metal NPs into PEDOT:PSS and C_{60} -bis layer, respectively. (B–E) Device performance comparison with combination metal NPs in different layers. Reproduced with permission from Yao et al. [110]. Copyright 2014, Wiley-VCH.

The advantages of the nanoplates can be ascribed to their shape, which benefited from the efficient scattering and light trapping in photoactive layers. Later on, Kalfagiannis et al. [120] investigated the effect of NP positions deposited between anode and buffer layer or between photoactive layer and cathode. Placing NPs on top of ITO anode led to an efficiency enhancement of 17%, connected to the light scattering and LSPR effects, while locating NPs between P3HT:PCBM and Al cathode exhibited 25% higher photocurrent generation through the reduction of buffer layer resistance. In particular, this study also presented that scattering effect is not significantly influenced by the angle

of incidence or the polarization of light. The improved electromagnetic fields induced by LSPR were considered to benefit to enhance the rate of exciton generation and probability of exciton dissociation [120]. Baek et al. proposed a novel metal-metal core-shell nanocube (NC) structure for efficient plasmon-assisted PTB7:PC₇₀BM-based OSCs with a PCE of 9.2% [121]. The Au–Ag core-shell structure demonstrated a high scattering efficiency at long wavelength and minimized blue shift, when compared to uncovered Au NPs (Figure 8).

In addition to the LSPR and scattering effects induced by metal NPs in OSCs, the excitation of SPP modes with

Figure 7: Diagram of cross-section light scattering effect of the metal NPs.

(A, B) Schematic diagram of randomly distributed NPs dispersed in the absorbing medium. (C) Cross section of the unit cell where the scattering cross section exceeds the absorption cross section (left), and absorption cross section surpasses the scattering cross section (Right) of the NPs. Reproduced with permission from ref. [112]. Copyright 2016, American Chemical Society.

incorporation of metallic gratings also plays crucial roles in effective light trapping. Surface plasmon polariton is the guided electromagnetic wave traveling along the metal/dielectric interface. Through surmounting the mismatch between the momentum of in-plane SPP and incident photons with incorporation of metallic grating electrodes, the SPP modes can be excited, and the incident photons will be trapped at the corrugated metal–organic interface. Actually, employment of dual metallic nanostructures consisted of metal NPs, and metallic grating is a promising approach to further enhance the performance of OSCs. Li et al. [122] incorporated Au NPs in the active layer and an Ag nanograting electrode as the back reflector to simultaneously excite the LSPR and SPP mode in the PBDTTT-CT:PC₇₁BM-based inverted OSCs. A broadband absorption enhancement and positive electrical effects are successfully achieved through the hybridized LPR (from the Au NPs) and SPR (from the Ag nanograting), which results in a significantly enhanced performance of the OSCs.

3.2 Electrical performance

Electromagnetic field enhancement induced by LSPR effect can result in the improved photon energy absorption and excess excitons production in the photoactive film [123–126]. Subsequently, the produced excitons

interrelate with the plasmonic near-field of metal NPs to facilitate charge dissociation. The probability of exciton dissociation mainly depends on the internal electric field in OSCs, while the strong near-field induced by plasmonic NPs has been confirmed to enhance the probability [127]. Chen et al. [60] first proposed the performance improvement in OSCs by the integration of Au NPs into the hole transport layer (PEDOT:PSS) in 2009. An improvement of 20% in device performance was ascribed to the enhanced local electromagnetic field deriving from the near-field LSPR excitation. Furthermore, excitation of the LSPR induced by integration of Au NPs enhanced the probability in exciton generation and dissociation, which resulted in the noticeable improvement of the J_{sc} and the FF in OSCs. Later on, Wu et al. [108] employed Au NPs into buffer layer of OSCs and investigated their plasmonic effects on device performance. The rate of exciton generation drastically increased due to the enhancement in absorbed photons, which was ascribed to the LSPR modes and confirmed by the improved fluorescence intensity in steady-state photoluminescence (PL) spectroscopy. Besides, the probability of exciton dissociation of these devices enhanced from 79.2% to 84.4% with the addition of plasmonic NPs. Dynamic PL measurements indicated the reduced lifetime of photogenerated excitons, demonstrating the facilitated exciton dissociation due to the charge transfer process and plasmon–exciton coupling. Moreover, it is noteworthy

Figure 8: Schematic illustration, design and synthesis of plasmonic NPs.

(A) Schematic of a plasmonic OSC with the incorporation of metal NPs. (B–E) The scattering effect of the plasmonic metal NPs with core-shell structure. Reproduced with permission from Baek et al. [121]. Copyright 2014, American Chemical Society.

that the average lifetime of the photogenerated excitons decayed exponentially as the increased distance from the Au NPs surface, revealing the near-field essence of the enhanced exciton dissociation probability.

In addition to the noble metal NPs, other categories of metal NPs also have been demonstrated to enhance the probability of exciton dissociation. High-performance OSCs with incorporation of Cu NPs with size of 20 nm in P3HT layer were reported by Szeremeta et al. [77], and their optical and electrical properties were studied. It was confirmed that the enhanced efficiency did not rely solely on the light absorption improvement induced by plasmonic resonance, whereas Cu NPs played a substantial role in the increase of the exciton dissociation rate and photogeneration efficiency of charge carrier in active layer [77]. Liu

et al. [76] embedded Cu NPs into the anodic buffer layer of PEDOT:PSS and improved device efficiency of OSCs based on P3HT and PTB7 (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]]). In this case, the enhanced external quantum efficiency (EQE) and absorption can be ascribed to the enhanced saturation photocurrent density, related to the improvement in exciton dissociation rate.

The charge carriers produced by the exciton dissociation process should be transported and collected at the opposite electrodes for effective photocurrent generation and provide photocurrent direction. The charge carriers transport paths before collection have a significant effect on the bulk recombination and further electrical

properties in OSCs, namely, V_{oc} and FF. Actually, charge carriers hop between localized states is the usual method for charge transport [127]. In this section, we will discuss the influence of metal NPs on the charge transport and collection processes in OSCs. Wang et al. [128] reported positive effects due to the incorporation of Ag clusters formed by aggregation of Ag NPs with average size of 40 nm in PCDTBT:PC₇₀BM-based devices. The large-sized Ag clusters enhanced the values of V_{oc} , J_{sc} , FF, and EQE in the OSCs, due to the enhanced light harvesting originating from the effective reflection and scattering of the aggregated Ag NPs. Besides, the enhanced charge transport and reduced resistance also contributed to the improvement of efficiency for the Ag NPs incorporated OSCs. Lee et al. [129] integrated Au NP-modified nitrogen (N)-doped or boron (B)-doped carbon nanotubes (CNTs) into OSCs

to realize the multiple synergistic effects of exciton dissociation, charge generation, and transport enhancement. In consequence, a predominant PCE enhancement of the PTB7:PC₇₀BM-based device was obtained with the randomly distributed additives as shown in Figure 9.

Besides, the photocarriers mobility imbalance is commonly reported in OSCs, which induced the space charge limit for photocurrent [130, 131]. Sha et al. [132] propounded a plasmonic-electrical concept by incorporation of Ag NPs in different positions, which was employed to manipulate the recombination, transport, and collection of photocarriers via the redistribution of optical field in OSCs. The shortened transport path of the lower mobility photocarrier resulted in boosting the charge extraction and improving FF and V_{oc} . Ren et al. [133] proposed novel Au nanostars (Au NSs) incorporated between hole

Figure 9: Illustration of Au NP-modified nitrogen or boron-doped carbon nanotubes (CNTs) into OSCs.

(A–E) Schematic diagram, surface morphology, and optical spectra of Au NP-modified N- or B-doped CNTs. (F–H) Corresponding device performance. Reproduced with permission from Lee et al. [129]. Copyright 2015, Wiley-VCH.

transport layer and active layer. The excited asymmetric plasmonic modes enabled broadband absorption improvement in OSCs, rather than narrow spectral widths for regional enhancement. Simultaneously, the Au NSs could reduce the resistance of HTL and balance carrier through shortening the transport path length of relatively low-mobility holes. As a result, the PCE of the OSCs with the incorporation of Au NSs demonstrated a significant enhancement with both plasmon-optical and plasmon-electrical effects.

Morphology changes at the interface of the electrodes, buffer layer, and photoactive layer can also improve the carrier collection efficiency. The influence of embedding plasmonic metal NPs into the buffer layer of OSCs was dissimilar in contrast to the incorporated NPs in active layers. Choy et al. reported a 13% enhancement of power conversion efficiency (PCE) in OSCs after the addition of PEG-capped Au NPs into the buffer layer of PEDOT:PSS, which primarily originated from the increased J_{sc} and FF [134]. The enhanced performance can be theoretically and experimentally ascribed to the increased interfacial roughness and enlarged interfacial area between PEDOT:PSS layer and P3HT:PCBM layer as well as increased PEDOT:PSS conductivity. The roughened interface has been demonstrated to benefit for the enhancement in hole collection efficiency. Fundamentally, it can be indicated that the device mechanisms of the minimal improvement from light absorption in the photoactive layer attributed to the lateral distribution feature of the near-field LSPR modes around Au NPs. These findings demonstrate that it is significantly imperative to delve into both optical and electrical characteristics for NPs employment to understand the device physics and optimize device performances.

The energy level differences among various functional materials in OSCs play an important role in carrier extraction. Therefore, adequate structure design to reduce the energy difference is crucial for high-performance OSCs. Particularly, the introduction of plasmonic metal NPs can effectively alter the local electrical field and change the function work of functional materials, leading to favorable band alignment. Cheng et al. [52] presented a high-performance 10-nm Au NP-embedded OSCs with enhanced J_{sc} , V_{oc} , and PCE by a factor of 8%, 9.5%, and 22%, respectively. Accordingly, they performed an in-depth investigation of the optimized performance after incorporation of Au NPs via impedance spectroscopy (IS) and valence band photoelectron spectra (VBPS), which can show the carrier dynamics and energy level changes. The IS results indicated that the improved photocurrent was induced by the suppression of electron-hole recombination and the enhancement in hole collection, as a consequence of the

reduced contact resistance at the P3HT:PCBM/PEDOT:PSS interface. The VBPS results revealed a downshift of the Fermi energy level for the buffer layer (PEDOT:PSS) following the incorporation of Au NPs; thereby the energy barriers between the highest occupied molecular orbit level of P3HT and Fermi energy of PEDOT:PSS were reduced, resulting in the enhanced collection efficiency. The barrier height and depletion width were also decreased at the interface, which improved the hole transport, arising from the lower contact resistance. Furthermore, the downshifted Fermi energy of PEDOT:PSS and the suppressed electron-hole recombination led to the enhancement of V_{oc} . The variation of the energy level can be assigned to the hole concentration enhancement in PEDOT:PSS layer after the integration of high electron-affiliative Au NPs.

Zhang et al. [135] integrated Au NPs into the electron transport layer of TiO_2 , resulting in the enhanced charge extraction by plasmonic-electrical effects in OSCs. As a consequence, the P3HT:PCBM-based OSCs achieved a peak PCE of 8.74%. Besides, the Au NPs/ TiO_2 -based OSCs worked within a plasmonic wavelength region of 560–600 nm, which was much longer than the absorbed wavelength of less than 400 nm for the TiO_2 -based control devices. It was confirmed that the charge transfer of excited carriers from plasmonic NPs to TiO_2 and trap filling in TiO_2 films was responsible for these improvements in OSCs, rather than the induced field effect at the TiO_2 surface as shown in Figure 10. The device performance with incorporation of plasmonic metal NPs in OSCs is demonstrated in Table 1.

3.3 Device stability

A novel perspective on the function of metal NPs incorporated into the photoactive layers has been reported in recent years to improve the structural stability, causing reduced device degradation rate of OSCs under prolonged solar illumination. In this case, plasmonic NPs can function as stabilizers to impede the singlet oxygen and quench the triplet excitons to avoid the photo-oxidation process. This property can elucidate the difference of the enhanced absorption and IPCE in OSCs. Paci et al. [78] embedded Ag NPs into the P3HT:PCBM layer to enhance the morphological and structural properties of OSCs. The devices showed a superior photovoltaic performance with mitigated degradation rate after continuous irradiation for a long period. Overall, the employment of metal NPs could result in a plasmon-mediated absorption enhancement to improve the device efficiency, as well as an increased structural stability to benefit the

Figure 10: Diagram of plasmonic metal NP-induced charge injection process.

Electrons are extracted from PCBM layer to TiO_2 layer in OSCs. Reproduced with permission from Zhang et al. [135]. Copyright 2013, Wiley-VCH.

device durability. Subsequently, the same group utilized surfactant-free Au NPs into the photoactive layer and obtained improved photo and thermal stability in OSCs. Figure 11 demonstrates the schematic of the photo-oxidation process and the role of Au NPs acting as triplet quenchers [136]. Kakavelakis et al. [137] employed laser-ablated Al NPs to achieve highly efficient and stable OSCs. An efficiency enhancement of 30% was obtained due to the multiple scattering effects, as well as the long operation time of ~ 150 hours induced by the plasmonic Al NPs.

4 Plasmonics in PeSCs

Perovskite materials have gained tractions for solar cells in recent decade due to their high absorption coefficient, low exciton binding energy, wide absorption wavelength, high bipolar charge mobility, and long photocarrier diffusion length. Basically, PeSCs permit relatively thicker photoactive film than OSCs for more reliable light harvesting; hence, less light can escape once it enters into the absorber. Moreover, PeSCs are solution processed, combining high performance with cost-effective techniques. Meanwhile, the tunable bandgap and high color purity, with reasonable ionization energy (IE) comparable to that of common hole-injection materials, enable perovskite attractive emitting materials applied in light-emitting diodes (LEDs) [138–140]. Perovskite can function as both a good emitter and a good absorber, which makes it unique among common semiconductors employed in solar cells and LEDs.

So far, the PCEs of PeSCs have undergone a rapid growth over the past few years, with the state-of-the-art value of 25.2% certified by NREL [<https://www.nrel.gov/pv/cell-efficiency.html>], which are comparable with the

commercial Si solar cells. Although perovskite films have been already efficient light harvesters for past years, yet in fact, the obtained PCEs of PeSCs are still below the Shockley–Queisser limit, requiring new methods to further improve their absorption [40, 141, 142]. In fundamental, wavelength-dependent light distribution in devices renders the not-enough broadband light absorption in PeSCs. Specifically, photon capture ability is not high within the IR frequencies because of the rapid decays of extinction coefficient, which influences considerably the conversion efficiency from incident photon to electron. Besides, because of the high refractive indices of perovskite, the inner interface reflection of PeSCs is stronger than OSCs, which leads to the unanticipated light losses in devices. Besides the technical reason, minimal thickness of the perovskite layer should be pursued to reduce the lead content under the consideration of the potential ecotoxicological issues, which causes a dilemma for the effective light absorption. Therefore, optimization of the optical design of the PeSCs should be explored to address this issue to reach a determined performance.

Incorporation of plasmonic metal NPs is a realistic way to enhance light absorption without changing the device configuration. Zhang et al. initially employed the core-shell metal-dielectric structure (Au@SiO_2 NPs) in photoactive layer to improve the PCE of organometal halide PeSC to 11.4% on average, whereas the control device is only 10.7% [63]. The enhanced performance could be attributed to the reduced exciton binding energy and the improved charge carrier generation after the inclusion of metal NPs, rather than the light absorption enhancement, confirmed by the time-resolved and steady-state temperature-dependent PL measurement. Although the physically fundamental origin of the improvement in PeSCs was unknown, this confirmed that plasmonic NPs could be utilized to improve the device performance. Subsequently, the same group adopted core-shell Ag@TiO_2

Table 1: Device performance with incorporation of plasmonic metal NPs in OSCs.

Absorber materials	Plasmonic NPs	Position of NPs	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)	Mechanism	Refs.
P3HT:PCBM	Au NPs	Active layer	9.77 (8.27)	0.6 (0.6)	63.38 (53.22)	3.71 (2.64)	LSPR	[92]
P3HT:PCBM	PEG-Au NPs	Active layer	9.74 (8.35)	0.61 (0.61)	65.00 (61.92)	3.85 (3.16)	Scattering	[107]
P3HT:PCBM	Au NPs	Buffer layer	10.22 (9.16)	0.59 (0.59)	70.32 (66.06)	4.24 (3.57)	LSPR	[108]
PTCBI	Ag NPs	Interface of tandem device	4.90 (4.25)	0.93 (0.47)	55 (55)	2.5 (1.1)	Enhanced exciton dissociation	[111]
P3HT:PCBM	Au–Ag alloy NPs	Electrode/buffer layer interface	8.74 (7.37)	0.62 (0.62)	55 (55)	3.03 (2.54)	LSPR	[100]
PCDTBT:PC ₇₁ BM	Ag NPs	Active layer	12.12 (11.63)	0.87 (0.90)	61 (57)	6.4 (5.9)	Scattering	[119]
P3HT:PCBM	Ag NPs	Electrode/buffer layer interface	9.33 (7.89)	0.58 (0.59)	53 (52)	2.82 (2.41)	Scattering	[120]
P3HT:PCBM	Ag NPs	Electrode/active layer interface	9.9 (7.89)	0.57 (0.59)	48 (52)	3.2 (2.41)	Resistance reduction	[120]
PCDTBT:PC ₇₀ BM	Au@Ag NCs	Buffer layer	11.10 (10.32)	0.87 (0.87)	63 (58)	6.08 (5.21)	Scattering	[121]
PTB7:PC ₇₀ BM	Au@Ag NCs	Buffer layer	17.38 (16.43)	0.74 (0.74)	68 (64)	8.74 (7.78)	Scattering	[121]
PBDTTT-CT:PC ₇₁ BM	Au NPs	Active layer	18.39 (17.09)	0.76 (0.76)	62.87 (58.43)	8.79 (7.59)	LSPR	[122]
PIDTT-DFBT:PC ₇₁ BM	Ag nanograting	Electrode	14.13 (12.66)	0.98 (0.96)	65 (62)	9.03 (7.54)	SPP	[101]
PTB7-Th:PC ₇₁ BM	Ag@TiO ₂ @Pa NPs	Active layer	18.05 (16.32)	0.81 (0.80)	73 (71)	10.72 (9.28)	Scattering	[101]
P3HT:IC ₆₀ BA	Ag@TiO ₂ @Pa NPs	Active layer	11.96 (10.56)	0.85 (0.83)	70 (67)	7.10 (5.89)	Enhanced exciton generation	[101]
PTB7-Th:BTR:PC ₇₁ BM	Ag@TiO ₂ @Pa NPs	Active layer	21.90 (20.70)	0.78 (0.77)	73 (71)	12.51 (13.01)	Scattering	[101]
P3HT:PCBM	Au NPs	Buffer layer	10.18 (8.95)	0.59 (0.59)	69.8 (65.9)	4.19 (3.48)	Enhanced exciton generation	[60]
PTB7:PC ₇₀ BM	Cu NPs	Buffer layer	17.10 (16.01)	0.73 (0.72)	59.8 (59.3)	7.43 (6.79)	Enhanced exciton dissociation	[76]
PCDTBT:PC ₇₀ BM	Ag NPs	Active layer	11.61 (10.79)	0.86 (0.86)	69 (68)	7.1 (6.3)	Scattering	[128]
PTB7:PC ₇₀ BM	Au NPs:NCNT	Active layer	18.21 (16.71)	0.72 (0.73)	71.78 (68.03)	9.24 (8.12)	Enhanced charge transport	[129]
PTB7:PC ₇₀ BM	Au NPs:NCNT	Active layer	18.50 (16.71)	0.74 (0.73)	72.61 (68.03)	9.75 (8.12)	Enhanced exciton dissociation	[129]
PBDT-TS1:PC ₇₁ BM	Au NSs	Buffer layer/active layer interface	18.72 (17.08)	0.81 (0.81)	67.66 (66.89)	10.25 (9.26)	Charge transport	[133]
P3HT:PCBM	PEG-Au NPs	Buffer layer	8.94 (8.5)	0.63 (0.62)	62 (58)	3.51 (3.1)	Broadband enhancement	[134]
							Balanced charge collection	
							LSPR	
							Charge collection	

Table 1 (continued)

Absorber materials	Plasmonic NPs	Position of NPs	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)	Mechanism	Refs.
PTB7:PC ₇₁ BM	Au NPs	Buffer layer	18.07 (17.23)	0.71 (0.71)	68.1 (65.5)	8.74 (8.02)	Enhanced charge extraction	[135]
P3HT:PCBM	Ag NPs	Active layer	7.03 (4.78)	0.61 (0.55)	48 (40)	2.06 (1.05)	Enhanced device stability	[136]
P3HT:PCBM	Al NPs	Active layer	11.31 (8.59)	0.6 (0.6)	59 (61)	4.00 (3.14)	Scattering Enhanced device stability	[137]

Figure 11: Schematic of the photo-oxidation process in the Au NP-embedded active layer. Reproduced with permission from Paci et al. [136]. Copyright 2012, The Royal Society of Chemistry.

NPs to boost the peak efficiency of the PeSCs to 16.3%. The device demonstrated a systematic enhancement in photocurrent; however, enhanced light harvest was not considered as the main reason for this enhancement [143]. Indeed, highly polarizable NPs effectively improved the radiative decay of excitons and the reabsorption of emitted light, corresponding to an innovative photon recycling mode. This study illuminated the subtle interactions between the radiative dipoles of the excitons in the perovskite material and the dipoles of the plasmonic NPs. Such plasmonic and photonic schemes can facilitate the performance of PeSCs to the Shockley–Queisser limit (theoretical limit). More recently, Yao et al. [101] proposed a designed core-bishell structure of Ag/TiO₂/Pa (benzoic acid–fullerene) NPs, enabling their compatibility with perovskite absorbers. Furthermore, the TiO₂/Pa bishell with appropriate energy alignment could trigger efficient plasmon–exciton coupling, thus promoting exciton dissociation and charge carrier collection. The enhanced light absorption and charge extraction of PeSCs with the Ag/TiO₂/Pa NPs contributed to the enhanced J_{sc} and FF, respectively (Figure 12). In consequence, the device

performance with the inclusion of Ag/TiO₂/Pa NPs presented an improvement by 10.2% from 18.4% to 20.2%.

Metal NPs can also be added into the buffer layers of PeSCs, demonstrating different mechanisms for the improvement of light harvesting without immediate contact with the perovskite semiconductors [144]. Lee et al. dispersed Au NPs with an average diameter of 15 nm into the hole transport layer of spiro-OMeTAD, eliminating the demand for an insulating shell [145]. The inclusion of Au NPs resulted in only a slight improvement in PCE, from 12.66% for the control device to 12.74%. The improved EQE profile was a combined response of a slight enhancement in J_{sc} , remained FF, and a slightly decreased V_{oc} after the incorporation of Au NPs. In this case, Au NPs were reported to aggregate near the spiro-OMeTAD/perovskite interface, rather than dispersed uniformly throughout the spiro-OMeTAD layer, which induced an unexpected energetic barrier at the interface and led to the slightly reduced V_{oc} . In fundamental, the boosted device performance was ascribed to the absorption improvement and decreased resistance of the spiro-OMeTAD buffer layer.

As mentioned before, the perovskite film presented poor absorption in the IR frequency, influencing the conversion efficiency from photon to electron. Incorporation of plasmonic NPs has been investigated to be an efficient way to circumvent this issue. Yue et al. [146] demonstrated that the employment of optimized closely spaced Ag NP array could cause an IR-band absorption enhancement of 58.2% through a full-wave simulation method (Figure 13). Here, plasmonic NPs were reported to benefit for the production of hotspots in the perovskite films, significantly enhancing their localized light absorption due to the nonlinear absorption mechanisms and light-flow circulation. Lu et al. reported plasmonic-enhanced PeSCs with inclusion of irregular alloy Au–Ag popcorn NPs into the mesoporous layer [64]. This device presented broadband

Figure 12: Performance characterizations of plasmonic devices.

(A) Absorptive power distribution of device with adding of Ag@TiO₂ or Ag@TiO₂@Pa compared to the reference OSC. (B, C) Current density and EQE performance with and without the incorporation of NPs. Reproduced with permission from Yao et al. [101]. Copyright 2019, American Chemical Society.

optical absorption enhancement from UV to near-IR wavelength range induced by the integrated NPs. Furthermore, the plasmonic NPs could also induce increased charge transfer at the TiO₂/perovskite interface, resulting in an ultimate PCE enhancement of 15.7%, from 8.9% to 10.3%.

As the potential toxicity issues related to lead [147], commercialization of PeSCs needs the lowest possible thickness of the perovskite films to decrease the lead content. However, insufficient light absorption could occur in this case due to the ultrathin active layers. Employment of plasmonic NPs has been confirmed to be an effective way to address this dilemma. Cai et al. [148] proposed a novel nanoplasmonic lumpy structure consisting of a large Ag NP at the core and smaller Ag NPs at the surrounding, which was integrated at the rear/front surfaces of the perovskite films. The lumpy Ag NP-induced LSPR effects and light scattering led to the enhanced photocurrent of a PeSC with 50-nm absorber, which is higher than the flat control device with 300-nm absorber. Interestingly, when the thickness of perovskite layer reduced to 10 nm, photocurrent was predicted to show a fourfold enhancement. This report represents an important step in the field of high-performance thin-absorber lead-based or lead-free PeSCs. The

device performance with incorporation of plasmonic metal NPs in PeSCs is summarized in Table 2.

So far, the reported works have mainly focused on the enhanced light harvesting by incorporation of plasmonic NPs in single-junction PeSCs. However, perovskite/crystalline Si tandem solar cells are hotly pursued nowadays due to the easy adjustment of bandgap in perovskite materials and their low nonradiative recombination rates, which can further enable substantial improvements in PCE [149, 150]. Thus, appreciated design of the tandem device to improve the device optics with plasmonic NPs coupling can be an effective approach to achieve more efficient PeSCs in future.

5 Conclusions and outlook

The cost-effective plasmonic metal NP-based solution-processed OSCs and PeSCs represent an important stride to the prominently enhanced device efficiency and stability. Fundamentally, plasmonic NPs can be facily incorporated into either the photoactive or the buffer layers or at interfaces for enhanced optical absorption due to LSPR

Figure 13: Model of multiple particle array-incorporated PeSCs. (A) Model of sandwiched PeSC. (B) Diagram of simulated design of multiple particle arrays embedded in perovskite layer. Reproduced with permission from Yue et al. [146]. Copyright 2016, Elsevier.

and light scattering effect and enhanced electrical properties in exciton dissociation, charge transport, and collection of the OSCs and PeSCs, without compromising the device architecture. Careful consideration should be given on the fabrication methods of NPs with controlled parameters, while theoretical simulation has been reported to provide supportive guidelines for their designs. A thorough investigation of the underlying enhancement mechanisms relating to interrelationships between the plasmonic NPs parameters including shape, size, distribution, and surrounding medium with the device performance characteristics is studied and highlighted. Moreover, enhanced photodegradation stability is also observed via the NP incorporation into the photoactive layer.

To date, the reported works have demonstrated the improvements in device performance for OSCs and PeSCs arising from the enhanced J_{sc} , V_{oc} , and FF and present a wide range of in-depth enhancement mechanisms. For PeSCs, it is still unknown whether the plasmonic light trapping is the foremost factor for the reduction of optical losses. Therefore, more researches are required to clarify the absorption increase of plasmonic NPs with respect to their potential in electrical properties enhancement for OSCs and PeSCs. Besides, efforts to address the stability issue with plasmonic

Table 2: Device performance with incorporation of plasmonic metal NPs in PeSCs

Absorber materials	Plasmonic NPs	Position of NPs	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	PCE (%)	Mechanism	Refs.
CH ₃ NH ₃ PbI _{3-x} Cl _x	Au@SiO ₂ NPs	Active layer	16.91 (14.76)	1.02 (1.04)	64 (67)	11.4 (10.7)	Enhanced charge generation	[63]
CH ₃ NH ₃ PbI ₃ CH ₃ NH ₃ PbI ₃	Ag@TiO ₂ NPs Ag/TiO ₂ /Pa NPs	Buffer layer	22 (20.2)	1.06 (1.03)	69 (67)	16.3 (14.5)	Photon recycling	[143]
		Active layer	21.27 (20.32)	1.11 (1.10)	81 (78)	19.2 (17.6)	Scattering	[101]
CH ₃ NH ₃ PbI ₃	Au@SiO ₂ NPs	Buffer layer	20.04 (19.63)	0.95 (0.96)	66.96 (67.23)	12.74 (12.66)	Enhanced exciton generation LSPR	[145]
CH ₃ NH ₃ PbI ₃	Au-Ag popcorn NPs	Active layer	16.46 (15.51)	0.95 (0.92)	66 (63)	10.3 (8.9)	Decreased resistance Enhanced charge transfer	[64]

NP incorporation in various layers of OSCs and PeSCs should be pursued. Furthermore, reduction of the manufacturing cost for such systems with large scale should be further investigated to commercialize applications. We hope this work will accelerate new insights and further investigations to boost the development of plasmonic metal NP-based OSCs and PeSCs, especially for future commercialized applications.

Acknowledgments: This work was supported by the National Key Research and Development Program of China and the National Natural Science Foundation of China (grants 2017YFB0404500, 61590930, 61825402, 61675085, and 61705075).

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