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Efficiency Improvement of MAPbI₃ Perovskite Solar Cells Based on a CsPbBr₃ Quantum Dot/Au Nanoparticle Composite Plasmonic Light-Harvesting Layer

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Abstract: We demonstrate a method to enhance the power conversion efficiency (PCE) of MAPbI₃ perovskite solar cells through localized surface plasmon (LSP) coupling with gold nanoparticles:CsPbBr₃ hybrid perovskite quantum dots (AuNPs:QD-CsPbBr₃). The plasmonic AuNPs:QD-CsPbBr₃ possess the features of high light-harvesting capacity and fast charge transfer through the LSP resonance effect, thus improving the short-circuit current density and the fill factor. Compared to the original device without Au NPs, a 27.8% enhancement in PCE of plasmonic AuNPs:QD-CsPbBr₃/MAPbI₃ perovskite solar cells was achieved upon 120 μ L Au NP solution doping. This improvement can be attributed to the formation of surface plasmon resonance and light scattering effects in Au NPs embedded in QD-CsPbBr₃, resulting in improved light absorption due to plasmonic nanoparticles.

Keywords: Au nanoparticle; perovskite solar cell; quantum dot; CsPbBr₃; localized surface plasmon

1. Introduction

As one of the most competitive materials in the photovoltaic field, organic–inorganic hybrid halide lead perovskites (ABX₃, where A is a monovalent cation, B is a divalent cation and X is a halide ion) have attracted great attention in recent years [1–4]. Through structural engineering [5,6], surface interface engineering [7,8], solvent engineering [9,10] and incident light management engineering [11,12], current organic–inorganic hybrid perovskite-based photovoltaic devices have demonstrated power conversion efficiencies (PCEs) of over 25.2% [13]. They show broad application prospects in the new generation of the green energy industry. Organic–inorganic perovskite solar cells (CH₃NH₃PbX₃ = MAPbX₃, X = Cl, Br and I) have excellent charge transport properties, long carrier diffusion length, full spectrum and strong light absorption. The properties of the perovskite light absorbing layer, electron transport layer and hole transport layer have an important influence on the efficiency of the perovskite solar cell, and most importantly, the perovskite film directly affects the photovoltaic performance of the device. Therefore, a high-quality, defect-free perovskite film is a necessary condition for the perovskite solar device to have high photovoltaic performance.

The literature indicates that the grain size of the roughened perovskite film can affect charge transport, and the addition of Br[−] or Cl[−] ions to MAPbX₃ can improve the crystallinity and stability of the material [14–19]. Although perovskite materials have a high absorption coefficient (10⁴ cm^{−1}), the thickness of the film is still an important factor limiting the light-harvesting efficiency. In past literature, the thickness of the perovskite layer was controlled below 500 nm. However, theoretical calculations show that sufficient light absorption can be achieved only when the thickness of the film exceeds 1 μ m to promote further efficiency [20,21]. This increase in thickness adversely affects

thin-film batteries as the transmission distance of the carrier becomes long, so the charge collection efficiency is lowered. In addition, the increase in thickness increases the grain boundary and internal defects of the perovskite film, which intensifies the charge recombination [21]. Therefore, enhancing the light absorption of the film without increasing the thickness of the film has become one of the most important topics in the field of thin-film solar cells [22–25]. One light-harvesting method is to reduce the reflectance of the surface by fabricating a surface structure which distributes the incident light to various angles by reflection, refraction and scattering, thereby increasing the optical path length of the light in the photovoltaic device and improving the light absorption efficiency. Among the many light-harvesting methods, the surface plasmon effect is one of the most suitable methods for thin-film photovoltaic devices [26,27]. Noble metal (gold and silver) nanoparticles have proven to be an effective route to increase the light-harvesting capability in solar cells due to their localized surface plasmon resonance effects (LSPR). By adjusting the shape and size of the metal nanoparticles, the characteristic wavelength of the plasmon effect can be changed [28–30], thereby improving light absorption, carrier generation, and power conversion efficiency; this has been successfully used to improve the PCEs of solar cells [31–36].

It is well known that the all-inorganic cesium lead halide perovskites (CsPbX_3 , $\text{X} = \text{Cl}$, Br and I) have all the advantages of organic–inorganic hybrid halide lead perovskites and, more importantly, are more stable in comparison to organic–inorganic hybrid halide lead perovskites [37,38]. The light absorbance of an all-inorganic CsPbX_3 perovskite is situated in the visible range of 380–700 nm. Such light absorbance can produce metal LSPR by the near-field effect. The typical plasmon peak of gold nanoparticles (Au NPs) at 525 nm is completely consistent with the perovskite CsPbBr_3 , indicating that Au NPs can effectively enhance the performance of perovskite solar cells. When CsPbBr_3 quantum dots (QDs- CsPbBr_3) and Au NPs are combined, synergistic effects can be expected because the fluorescence from QD- CsPbBr_3 enhances the localized plasmon effect of Au NPs, and concurrently, the enhanced Au NP electric field enhances the fluorescence of QD- CsPbBr_3 via localized plasmon excitation [39,40]. In this study, the Au NPs were first dispersed in perovskite QD- CsPbBr_3 solution (AuNPs:QD- CsPbBr_3), and the effects of different amounts of Au NP solution (μL) ranging from 40 μL to 120 μL on the perovskite MAPbI_3 thin-film solar cells are discussed. Plasmonic AuNPs:QD- CsPbBr_3 / MAPbI_3 perovskite solar cells with an $\text{Ag}/\text{C}_{60}/\text{MAPbI}_3/\text{poly}(3,4\text{-ethylenedioxythiophene})$ polystyrene sulfonate (PEDOT:PSS)/AuNPs:QD- CsPbBr_3 /indium tin oxide (ITO) patterned glass substrate structure exhibited improved performance. Our results indicate that AuNPs:QD- CsPbBr_3 in perovskite solar cells play an important role in improving solar cell performance, resulting in a 27.8% increase in PCE.

2. Materials and Methods

2.1. Synthesis of Plasmonic AuNPs:QD- CsPbBr_3 Perovskite Solution

The perovskite QD- CsPbBr_3 was synthesized by using hot-injection and ice-water bath methods. First, a Cs-oleate precursor solution was prepared via the mixing of 81.4 mg cesium carbonate (Cs_2CO_3 , 99.995%) in 3 mL of 1-octadecene (ODE, 90%) and 0.25 mL of oleic acid (OA, 90%); this mixture was then heat-treated at 200 °C for 30 min until it dissolved to a clear solution, indicating that the Cs_2CO_3 reacted with OA. Subsequently, a mixture of 0.2 g lead (II) bromide (PbBr_2 , 99.999%), 10 mL ODE, 1 mL OA and 1 mL oleylamine (OAM, 70%) was stirred and heated at 140 °C for 20 min. Afterwards, the temperature was increased to 200 °C and the mixture was stirred until the PbBr_2 dissolved completely. A volume of 0.8 mL of Cs-oleate precursor solution was subsequently injected rapidly into the PbBr_2 reaction solution, and the reactant was immediately bathed using an ice-water bath for 30 s after 5 s of injection. The synthesized QD- CsPbBr_3 solution was added to 40, 80, or 120 μL of the citrate-containing Au NP solution and shaken for 10 s. Afterwards, 8 mL of ethyl acetate (EA, 99.8%) was added, and the mixture was centrifuged at 5000 rpm for 15 min to collect the mixed precipitate, which was then dispersed in 1 mL of toluene (99.99%) and oscillated by sonication for 3 min to complete the plasmonic AuNPs:QD- CsPbBr_3 perovskite solution.

2.2. Fabrication of Plasmonic AuNPs:QD-CsPbBr₃/MAPbI₃ Perovskite Solar Cells

The procedure for fabricating plasmonic AuNPs:QD-CsPbBr₃/MAPbI₃ perovskite solar cells can be found in Figure 1. Patterned indium tin oxide (ITO) glass was sequentially washed by sonication in acetone, alcohol and isopropanol solution for 30 min, and then treated with UV-ozone for 10 min. A 25-nm-thick plasmonic AuNPs:QDs-CsPbBr₃ light-harvesting layer was deposited by spin-coating a 40 mL green solution of AuNPs:QDs-CsPbBr₃ at 4500 rpm for 45 s, and then annealed at 120 °C for 5 min. A 70-nm-thick PEDOT:PSS hole transport layer was deposited by spin-coating at 5000 rpm for 30 s from a solution containing PEDOT:PSS (UR-AI4083, Uni-Onward Corp., New Taipei City, Taiwan) at a ratio of 1:6, and then annealed at 120 °C for 10 min. A 300-nm-thick perovskite MAPbI₃ absorber layer was deposited by two-step continuous spin-coating at 1000 rpm and 5000 rpm for 10 s and 20 s, respectively. When the second stage was spin-coated with a countdown of 3 s, the absorber layer was completed by dropping 100 µL of toluene and was then heated to 100 °C for 10 min. The perovskite MAPbI₃ solution was synthesized by a solvent-engineering method from a precursor prepared by mixing 159 mg methylammonium iodide (MAI) and 461 mg lead (II) iodide (PbI₂, 99.9985%) dissolved in cosolvents of 0.5 mL dimethyl sulfoxide (DMSO) and 0.5 mL dimethylformamide (DMF), which was heated at 70 °C for 60 min and then left to stand for 24 h. A 20-nm-thick C₆₀ electron transport layer was evaporated at a rate of 0.05 nm/s at a vacuum pressure of 1×10^{-6} torr. Ag electrodes were deposited at a rate of 2.5 nm/s to 3.0 nm/s with a vacuum pressure of 4.8×10^{-5} torr for a total thickness of 100 nm. The device working area was about 2 mm × 5 mm in this research. After fabrication, the devices were encapsulated in a N₂-filled glove box by sealing the active area using another piece of glass. The complete QD-CsPbBr₃/MAPbI₃ and plasmonic AuNPs:QD-CsPbBr₃/MAPbI₃ perovskite solar cell configurations are shown in Figure 2. The inset of Figure 2b shows a transmission electron microscopy (TEM) image of the AuNPs:QD-CsPbBr₃. It can be seen that Au NPs were embedded in the QD-CsPbBr₃. The diameters of the Au NPs and QD-CsPbBr₃ were about 5 nm (red circle) and 10 nm, respectively.

Figure 1. Plasmonic perovskite solar cell process steps. Preparation of (a) a plasmonic gold nanoparticle:CsPbBr₃ hybrid perovskite quantum dot (AuNPs:QDs-CsPbBr₃) light-harvesting layer on patterned indium tin oxide (ITO)-coated glass, (b) PEDOT:PSS hole injection layer, (c) perovskite MAPbI₃ active layer and (d) C₆₀ electron transport layer; (e) Scrapping the film and defining the study area; (f) Ag electrode deposition and the plasmonic perovskite solar cell device.

Figure 2. Schematic of the (a) original QD-CsPbBr₃/MAPbI₃ and (b) plasmonic AuNPs:QD-CsPbBr₃/MAPbI₃ perovskite solar cell configurations. The inset shows a TEM image of the AuNP:QD-CsPbBr₃ characterization.

The QD-CsPbBr₃, 40AuNPs:QD-CsPbBr₃, 80AuNPs:QD-CsPbBr₃, and 120AuNPs:QD-CsPbBr₃ films were all annealed at 120 °C for 5 min before measurement. The surface morphologies were observed using a field emission scanning electron microscope (FESEM, ZEISS Sigma, ZEISS, Munich, Germany). The morphology and structure were analyzed using transmission electron microscopy (TEM) (JEM-2100F, JEOL, Tokyo, Japan). X-ray diffraction patterns (XRD) were recorded using an X-ray diffractometer with Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation operated at 40 kV and 25 mA (X'Pert PRO MRD, PANalytical, Almelo, the Netherlands). The photoluminescence (PL) spectra were recorded using a fluorescence spectrophotometer (F-7000, Hitachi, Tokyo, Japan) under UV light illumination ($\lambda_{\text{ext}} = 365 \text{ nm}$). The transmittance and absorbance spectra were measured using a UV/VIS/NIR spectrophotometer (UH-4150, Hitachi, Tokyo, Japan). The current density–voltage (J–V) curves of the devices were tested using a Keithley 2420 source meter under AM 1.5G irradiation. External quantum efficiencies (EQE) were measured utilizing a spectral response measurement system (QE-R3015, Enli Technology Co. Ltd., Taiwan).

3. Results and Discussion

The surface morphologies of QD-CsPbBr₃, 40AuNPs:QD-CsPbBr₃, 80AuNPs:QD-CsPbBr₃ and 120AuNPs:QD-CsPbBr₃ annealed at 120 °C for 5 min are shown in Figure 3, and the difference in grain size and agglomeration distribution can be clearly observed. The annealed QD-CsPbBr₃ films can be seen to be agglomerated and incompletely dispersed, which is detrimental to QD dispersion due to the lower concentration of dispersant than of QDs. The annealed 40AuNPs:QD-CsPbBr₃ films showed that the addition of Au NPs improved the QD dispersion and crystallinity, but there was still some agglomeration after heat treatment to form pore defects. When the Au NP solution volume was increased to 80 μL , the annealed 80AuNPs:QD-CsPbBr₃ films were found to have reduced large pore defects and greater grain size uniformity, but the QDs still showed some agglomeration. In addition, when increased to 120 μL , the annealed 120AuNPs:QD-CsPbBr₃ films, compared with the QD-CsPbBr₃, 40AuNPs:QD-CsPbBr₃ and 80AuNPs:QD-CsPbBr₃ films, showed better QD grain size and crystallinity and significantly improved QD agglomeration. This indicates that large Au NP contents cause the enhancement of QD agglomeration, and thus the crystallinity of films becomes better. This may be due to the addition of large amounts of Au NPs, causing the Au—Br complex would play a key role in the assembly of AuNPs:QD-CsPbBr₃ films.

Figure 3. Top-view SEM images of annealed (a) QD-CsPbBr₃, (b) 40AuNPs:QD-CsPbBr₃, (c) 80AuNPs:QD-CsPbBr₃ and (d) 120AuNPs:QD-CsPbBr₃.

Perovskite QD-CsPbBr₃ with and without the Au NPs were characterized by XRD to confirm the crystallinity influence of QD-CsPbBr₃ films before and after the addition of the Au NPs. The XRD patterns of annealed QD-CsPbBr₃, 40AuNPs:QD-CsPbBr₃, 80AuNPs:QD-CsPbBr₃ and 120AuNPs:QD-CsPbBr₃ films are displayed in Figure 4. The 80AuNPs:QD-CsPbBr₃ and 120AuNPs:QD-CsPbBr₃ XRD patterns and the Rietveld profile refinement, using the Match program analysis software, as shown in Figures S1 and S2. According to an earlier report [41], CsPbBr₃ has two phase transitions at different temperatures—one is an orthorhombic phase (lower than 88 °C) and the other is a cubic phase (higher than 130 °C for the bulk and 117 °C for the nanocrystals)—which were distinguished by the PbBr₆ octahedral tilting in the orthorhombic phase. It can be seen that the annealed QD-CsPbBr₃ films without Au NPs showed only two diffraction peaks, corresponding to the (100) and (200) planes. In addition, with increasing Au NP content, the crystal quality of annealed AuNPs:QD-CsPbBr₃ films was better than that of the annealed QD-CsPbBr₃ films without Au NPs; the (110) plane of AuNPs:QD-CsPbBr₃ films gradually becomes apparent. On the other hand, it was also found that a small amount of Au NPs combined with Br to form Au—Br complex (Au₂Br₆) and other diffraction peaks appeared, which not only reduced the QD agglomeration and improved the crystallinity quality of the films, but also did not affect the main crystal structure of the QDs. This indicates that the Au-Br complex has a self-assembling effect on QD-CsPbBr₃ to improve the film quality [42]. This is in good agreement with the SEM analysis. All the annealed AuNPs:QD-CsPbBr₃ films showed three main peaks at $2\theta = 15.55^\circ$, 21.55° and 30.65° , which were assigned to the (100), (110) and (200) planes, respectively. In particular, the annealed 80AuNPs:QD-CsPbBr₃ and 120AuNPs:QD-CsPbBr₃ films that appeared in crystal planes of (100), (110), (200), (210), (211), (220) and (300) implied the formation of the cubic CsPbBr₃ (JCPDS No. 54-0752). Importantly, the weaker peaks at 12.98° , 22.75° , 25.78° , 27.86° and 28.97° can be identified as the (110), (300), (220), (131) and (312) diffraction planes, respectively, indicating the presence of a Cs₄PbBr₆ phases (PDF# 73-2478). The CsPbBr₃ and Cs₄PbBr₆ bi-phases were observed when AuNP contents increased. This

means that Au NPs help the formation of Cs_4PbBr_6 crystals. The Cs_4PbBr_6 crystals exhibit a superior quantum yield and device performance than that of CsPbBr_3 crystals. [43,44]

Figure 4. X-ray diffraction (XRD) patterns of annealed QD- CsPbBr_3 , 40AuNPs:QD- CsPbBr_3 , 80AuNPs:QD- CsPbBr_3 and 120AuNPs:QD- CsPbBr_3 films.

Figure 5a shows the photoluminescence (PL) spectra of annealed QD- CsPbBr_3 , 40AuNPs:QD- CsPbBr_3 , 80AuNPs:QD- CsPbBr_3 and 120AuNPs:QD- CsPbBr_3 films. It was observed that the PL intensity of all the AuPs:QD- CsPbBr_3 films was higher than that of the QD- CsPbBr_3 film without Au NPs, and the PL intensity did not increase as the Au NP amount increased. NPs can increase or decrease the overall fluorescence of QDs by plasmon resonance energy transfer, fluorescence resonance energy transfer and charge transfer. These mechanisms will determine whether fluorescence enhancement or quenching is observed in the QDs. In the case of 40AuNPs:QD- CsPbBr_3 , light can be coupled to the LSP modes and increase the optical energy density near the QDs, thereby enhancing absorption. Therefore, the plasmon resonance energy transfer from excited NPs to nearby QDs is dominant, which increases the luminescence of the QDs. On the other hand, in the case of adding larger amounts of Au NPs, the main reason for the fluorescence reduction and quenching of QDs is speculated to be fluorescence resonance energy transfer. This result clearly shows that the fluorescence emission of QD- CsPbBr_3 was quenched by Au NPs. Since the PL spectrum of QD- CsPbBr_3 and the localized plasmon absorbance spectrum (525 nm) of Au NPs overlap significantly, the PL quenching can be considered mainly as energy/charge transfer, which should enhance localized plasmon excitation more effectively [45]. This is anticipated to enhance the generation of a photocarrier in the active layer when the plasmonic AuNPs:QD- CsPbBr_3 hybrid is used in perovskite solar cells. When the PL spectra were normalized (see Figure 5b), the annealed QD- CsPbBr_3 , 40AuNPs:QD- CsPbBr_3 , 80AuNPs:QD- CsPbBr_3 and 120AuNPs:QD- CsPbBr_3 films exhibited a green emission with a PL peak at 515–517 nm and full widths at half-maximum (FWHMs) of 21.4, 21.6, 22.4 and 24.2 nm, where the FWHMs became larger and were expected to increase light absorption. It can be observed that AuNPs:QD- CsPbBr_3 generated an induced electric field under light irradiation, and QD- CsPbBr_3 and Au NPs experienced plasmon coupling with each other, causing a red shift. The degree of red shift became significant with increasing amount of embedded Au NPs.

Figure 5. (a) Photoluminescence (PL) spectra and (b) normalized PL spectra of annealed QD-CsPbBr₃, 40AuNPs:QD-CsPbBr₃, 80AuNPs:QD-CsPbBr₃ and 120AuNPs:QD-CsPbBr₃ films.

Figure 6a presents the absorbance spectra of annealed QD-CsPbBr₃, 40AuNPs:QD-CsPbBr₃, 80AuNPs:QD-CsPbBr₃ and 120AuNPs:QD-CsPbBr₃ films. The transmittance spectra of all the films were greater than 85% in the wavelength range between 520 nm and 800 nm (Figure S3). However, the light absorbance of the QD-CsPbBr₃ perovskite decreased abruptly at wavelengths shorter than 520 nm due to the addition of Au NPs. In our study, the absorbance peak at about 525 nm was the unique LSPR band in the absorbance spectrum of pure Au NPs. In the short wavelength range from 400 nm to 520 nm, it was observed that the light absorbance of AuNPs:QD-CsPbBr₃ films was significantly enhanced compared to that of QD-CsPbBr₃ films without Au NPs. In addition, the absorbance of the samples improved with increasing amount of embedded Au NPs. Due to the addition of large amounts of Au NPs to generate fluorescence resonance energy transfer and quench the emission of QDs, which effectively enhances local plasmon excitation, the absorbance of 120AuNPs:QD-CsPbBr₃ significantly increased in the whole wavelength range of 400–800 nm. The absorbance spectra of the AuNPs:QD-CsPbBr₃/PEDOT:PSS/MAPbI₃ perovskite films with and without Au NPs are shown in Figure 6b. The transmittance spectra of the AuNPs:QD-CsPbBr₃/PEDOT:PSS/MAPbI₃ perovskite films with and without Au NPs showed film transmittances (see Figure S4) that were below 15% between 400 nm and 700 nm, but above 20% at greater than 750 nm. In particular, 120AuNPs:QD-CsPbBr₃/PEDOT:PSS/MAPbI₃ perovskite films showed the lowest transmittance (less than 20%) in the whole wavelength range of 400–800 nm. It can be seen that the light absorbance spectra of the QD-CsPbBr₃/PEDOT:PSS/MAPbI₃ perovskite films were lower than those of AuNPs:QD-CsPbBr₃/PEDOT:PSS/MAPbI₃ perovskite films when Au NPs were not embedded. On the other hand, the 120AuNPs:QD-CsPbBr₃/PEDOT:PSS/MAPbI₃ perovskite films had the highest observed light absorbance. This means that the LSPR effect of AuNPs:QD-CsPbBr₃ significantly enhanced the light-harvesting and photocarrier transmission of the perovskite solar cells in a wavelength range of 400–800 nm, which will help improve the PCE.

In order to estimate the influence of Au NP addition on the performance of perovskite solar cells, three QD-CsPbBr₃ precursors with different amounts of Au NP solution (μ L) ranging from 40 μ L to 120 μ L were prepared to form AuNPs:QD-CsPbBr₃ films. The original QD-CsPbBr₃ film without the Au NPs was prepared under the same conditions. Figure 7a shows the J–V curves of the original QD-CsPbBr₃/MAPbI₃ and three types of plasmonic AuNPs:QD-CsPbBr₃/MAPbI₃ perovskite solar cells. The related parameters of perovskite solar cells with different amounts of Au NPs are listed in Table 1. Obviously, the addition of the Au NPs improved the performance of the perovskite solar cells. The short-circuit current density (J_{sc}) of the perovskite solar cells was apparently improved when Au NPs were embedded in the QD-CsPbBr₃. The PCE of the devices increased from 8.53% to 10.9% with increasing Au NP solution addition from 0 μ L to 120 μ L. Further, the J_{sc} increased from 20.6 mA cm^{−2} to 22.5 mA cm^{−2}. The enhanced PCE was attributed to the J_{sc} increase of the device due to the incorporation of Au NPs with intense LSPR band into the

device. This suggests that Au NPs in QD-CsPbBr₃ can effectively improve the carrier gathering ability. In addition, the photocurrent of the 120AuNPs:QD-CsPbBr₃/MAPbI₃ perovskite solar cells was larger than that of the 40AuNPs:QD-CsPbBr₃/MAPbI₃ perovskite solar cell, which may be attributed to the 120AuNPs:QD-CsPbBr₃ with fluorescence resonance energy transfer and charge transfer, which helps to improve the photocurrent and light-harvesting; 40AuNPs:QD-CsPbBr₃ experienced a plasmon resonance energy transfer, which only helps to increase the light-harvesting of the device. On the other hand, as the amount of added Au NPs increased, the fill factor (FF) of the devices also increased. It was also observed that the addition of Au NPs had an almost insignificant influence on the open-circuit voltage (V_{oc}). We found that the series resistance value of plasmonic 120AuNPs:QD-CsPbBr₃ device (157.2 Ω) was smaller than that of the QD-CsPbBr₃ device (212.8 Ω), which indicates that the interfacial contact resistance of the fabricated devices was decreased by adding larger amounts of Au NPs, which directly benefited the improvement of J_{sc} and FF. This improvement factor can be attributed to 120AuNPs:QD-CsPbBr₃ has better film quality from SEM and XRD analysis. The optimal plasmonic 120AuNPs:QD-CsPbBr₃/MAPbI₃ perovskite solar cells in our study showed excellent performance, with a J_{sc} of 22.5 mA cm⁻², a V_{oc} of 0.9 V, a FF of 54%, and a PCE of 10.9%, which indicates that the addition of Au NPs in QD-CsPbBr₃ can efficiently improve the performance of perovskite solar cells. Because of the wavelength overlap between the fluorescence of QD-CsPbBr₃ and the localized plasmon peak of Au NPs, energy transfer that enhances LSP excitation can be obtained in the AuNPs:QD-CsPbBr₃.

Figure 6. Absorbance spectra of (a) annealed QD-CsPbBr₃, 40AuNPs:QD-CsPbBr₃, 80AuNPs:QD-CsPbBr₃ and 120AuNPs:QD-CsPbBr₃ films, and of (b) AuNPs:QD-CsPbBr₃/PEDOT:PSS/MAPbI₃ perovskite films with and without Au NPs.

To investigate the photocurrent response enhancement effect of AuNPs:QD-CsPbBr₃ on the perovskite solar cell properties, we conducted external quantum efficiency (EQE) measurements in the wavelength range from 350 nm to 800 nm. In Figure 7b, the EQE spectra of the original QD-CsPbBr₃/MAPbI₃ and three types of plasmonic AuNPs:QD-CsPbBr₃/MAPbI₃ perovskite solar cells are presented. Compared with the original perovskite solar cells, it was found that the EQEs of the three plasmonic perovskite solar cells with Au NPs were enhanced over the whole wavelength range of 350–800 nm. When the volume of added Au NP solution was 120 μL, the highest EQE values of the plasmonic perovskite solar cells were achieved, which indicated that the EQE measurement results were consistent with the PCE results. In addition, the EQE enhancement factors were obtained by dividing the EQE values of the plasmonic perovskite solar cell by the EQE values of the original perovskite solar cell, as presented in Figure 7c. This clearly shows an enhancement of the EQE values for all plasmonic perovskite solar cells based on a AuNPs:QD-CsPbBr₃ layer. When the amount of Au NP solution was more than 40 μL, the EQE enhancement factor was more apparent, which was mainly caused by the light absorption of AuNPs:QD-CsPbBr₃ in the devices. In particular, the plasmonic AuNPs:QD-CsPbBr₃/MAPbI₃ perovskite solar cells exhibited strong light absorption and fluorescence emission, which could be due to light absorption by the active layer and LSPR excitation. This helped

to significantly increase light absorption and photocarrier generation in the devices. It was worth noting that EQE enhancement factors of 120AuNPs:QD-CsPbBr₃/MAPbI₃ perovskite solar cell shows the value larger than 1.2 over a wide wavelength range of 400–750 nm. However, the J_{sc} enhancement ratio of 120AuNPs: QD-CsPbBr₃/MAPbI₃ perovskite solar cell (J_{sc} = 22.5 mA cm⁻²) was only 1.092 from the J–V curves compared to QD-CsPbBr₃/MAPbI₃ perovskite solar cell (J_{sc} = 20.6 mA cm⁻²). The measurement variation may be attributed to different instruments. Figure 7d depicts an energy level diagram, according to which PEDOT:PSS and C₆₀ performed roles as hole transport and electron transport layers, respectively, while QD-CsPbBr₃ or AuNPs:QD-CsPbBr₃ was used as a light collection layer. It can be seen from the energy level diagram that AuNPs:QD-CsPbBr₃ is supposed to block holes. However, a sufficiently thin layer can allow for tunneling of a hole as indicated by the blue horizontal arrow in the diagram. Figure 7e depicts a schematic diagram of the enhanced PCE mechanism for the plasmonic perovskite solar cells. The Au NPs in the QD-CsPbBr₃ improved their performance due to the LSPR effect, which raised the optical path length by light scattering and increasing the light absorption of the whole perovskite solar cell, thereby efficiently improving the PCE.

Figure 7. (a) Current density–voltage curve; (b) external quantum efficiency (EQE); (c) enhancement factor; (d) corresponding energy level diagram of each layer; (e) schematic diagram of the enhanced power conversion efficiency (PCE) mechanism for the plasmonic perovskite solar cells compared with that of the original cell.

Table 1. Performance parameters of plasmonic perovskite solar cells with and without Au NPs. (Average value with standard deviation from 20 devices).

Sample	Voc (V)	Jsc (mA cm ⁻²)	FF (%)	PCE (%)	PCE Enhancement (%)
QD-CsPbBr ₃ /PEDOT:PSS/MAPbI ₃	0.9	20.6	46.0	8.53	–
Standard deviation	0.009	0.309	0.380	0.104	
40AuNPs:QD-CsPbBr ₃ /PEDOT:PSS/MAPbI ₃	0.93	20.8	44.9	8.68	1.2
Standard Deviation	0.015	0.248	0.269	0.052	
80AuNPs:QD-CsPbBr ₃ /PEDOT:PSS/MAPbI ₃	0.91	21.9	47.1	9.4	10.2
Standard Deviation	0.014	0.245	0.286	0.048	
120AuNPs:QD-CsPbBr ₃ /PEDOT:PSS/MAPbI ₃	0.9	22.5	54.0	10.9	27.8
Standard Deviation	0.011	0.280	0.230	0.065	

4. Conclusions

Efficient plasmonic AuNPs:QD-CsPbBr₃/PEDOT:PSS/MAPbI₃ perovskite solar cells were fabricated through embedding Au NPs in perovskite QD-CsPbBr₃, which manage light-harvesting to enhance perovskite solar cells. Plasmonic AuNPs:QD-CsPbBr₃ films with increasing amounts of embedded Au NPs exhibited good crystal quality and strong light absorption properties. In addition, enhanced PL quenching could improve exciton ionization and charge separation due to LSPR excitation by resonance interaction, which could help to enhance the PCE. In comparison to the performance of the original perovskite solar cells, superior Jsc, FF, PCE and EQE properties of the plasmonic perovskite solar cells were confirmed. The PCE of the plasmonic perovskite solar cells was enhanced by 27.8% compared with that of the original perovskite solar cells. This is attributed to an improvement in the PCE and EQE of plasmonic perovskite solar cells caused by the LSPR effect in AuNPs:QD-CsPbBr₃ enhancing the light-harvesting and light scattering effect.

Supplementary Materials: Supplementary data to this article can be found online at <http://www.mdpi.com/1996-1073/13/6/1471/s1> (Figures S1–S4).

Author Contributions: L.-C.C. carried out the experiments, designed the study and gave significant suggestions on the whole manuscript. C.-H.T. conceived the original idea, performed data analysis and interpretation and wrote the manuscript. K.-L.L. and Y.-T.K. prepared the samples and performed all measurements. . All authors have read and agreed to the published version of the manuscript.

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