Organic Electronics 60 (2018) 1–8

Contents lists available at ScienceDirect

Organic Electronics

journal homepage: www.elsevier.com/locate/orgel

Plasmonic enhancement for high efficient and stable perovskite solar cells by employing "hot spots" Au nanobipyramids

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ARTICLE INFO

Keywords:
Perovskite solar cells
Plasmonic effect
Hot spots
Trap density of states
Stability

ABSTRACT

Metal plasmonic effect is one promising way for improving the performance and stability of the perovskite solar cells via optical-electrical behalves, and the ability is in proportion to the enhanced local electromagnetic fields induced by metal nanostructures. In our work, unique gold nanobipyramids (Au NBs) structures were explored and incorporated in the hole transport layer of planar heterojunction PSCs. This typical "bipyramid-like" metal nanostructure with sharp tips has the multiple and strong plasmonic absorption properties from visible to the NIR, exhibiting high plasmonic-induced probability. In addition, generated "hot spots" around Au NBs provided much stronger EM fields enhancements than conventional Au nanoparticles, hence enhanced light harvesting and improved interfacial charge dynamic process can be achieved simultaneously. As for the further investigation of the electrical property, hot holes injection induced by Au NBs effectively filled in the interfacial traps under operation condition, contributing to the improvement of the open circuit voltage, the elimination of the hysteresis effect and the long-term stability. Accordingly, the best PSC incorporated with Au NBs showed the PCE of 18.84% whereas the reference device just showed the PCE of 16.02%. Our work demonstrated that plasmonic metal nanostructures possessing the feature of "hot spots" offered a great potential to further expand the performance limitation and operation tolerance of the PSCs.

1. Introduction

Metal halide perovskite materials have attracted much attention due to the advantages of tunable band energy, high absorption coefficient and long carriers diffusion length [1–4]. The power conversion efficiencies of perovskite solar cells (PSCs) undergoes a rapid development from 3.8% to 22.7% within a few years and have potential to be further increased [5,6]. Although multidisciplinary efforts have led to the rapid increase of the PCE to the level of silicon/CIGS solar cells, further improvements of PSCs performance and stability are still necessary for accelerating the commercialization. To date, substantial strategies, including the design of the organic/inorganic perovskite materials with different components, synthesis of new transporting layers and the interfacial-modification engineering, have been devoted to breaking through the limitation of performance [7–12]. Nonetheless, considering that both the light-harvesting and charge dynamic processes are the key points influencing the performance of the PSCs, it is more meaningful to develop the technology with dual optical-electrical tunable effects.

Plasmonic metal nanoparticles are nanoobjects with fascinating properties, making them a subject of great interest regarding the field of optoelectronics [13–18], especially the successful applications as an effective optical-electronic engineering tool in PSCs [19–22]. The localized surface plasmon resonance (LSPR) effect can be excited from the light-induced collective oscillation of their conduction band electrons on the surface of metal nanostructures, which result in the local electromagnetic fields (EM fields) enhancement around metal surfaces [23]. By adjusting of the materials, size, shape, and surrounding medium of the nanostructures, it could achieve the effective control of the range of the LSPR and the intensity of the local EM fields [24]. The LSPR of spherical nanoparticles is essentially located in the visible wavelength with single plasmonic peak. While anisotropic architectures are extremely interesting since they present different frequencies of resonance

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https://doi.org/10.1016/j.orgel.2018.05.030
Received 1 May 2018; Received in revised form 14 May 2018; Accepted 20 May 2018
Available online 22 May 2018
1566-1199/

with a broadband absorption (from visible to NIR) depending on the polarization (longitudinal, transverse), which expand the scale of applications [25,26].

As for the optical aspect, plasmonic effect could enhance the light coupling and scattering into the active layer of PSCs. Au@TiO_2 nanorods, Au@SiO_2 nanorods and Au nanostars have been successfully applied to the PSCs, showing the efficient broadband absorption enhancement [19,22,27]. When it comes to the electronic aspect, it is generally attributed to the reduced exciton binding energy and the promotion of carrier transport and collection [21,28].

In spite of constantly processing the studies on the plasmonic enhanced effect for PSCs, the ultimate principle, specifically on interfacial charge dynamic process, should be identified and further addressed in plasmonic PSCs. Furthermore, whether in optical feature or in electrical feature, excellent ability of the EM field enhancement via metal nanostructures is crucially required in plasmonic PSCs research. Thus the exploration of typical metal geometry with much stronger EM field factor is extremely rewarding.

In regard to the plasmonic field, unique “hot spots” effect, which means the much drastically intensified EM field, could be generated at the corners of sharp features on metal nanoparticles by taking advantage of the “lightning rod” effect [29,30]. For the anisotropic geometries, sharp structures such as nanocubes, nanorices and nanobipyramids have proven to be very interesting since the EM field around their tips is much stronger compared to saponaceous nanorods with same specifications [31–33]. Considering this, development of the typical plasmonic nanostructures is the preferable choice of further improving the performance of the PSCs through the adjustment of the dual optical-electronic properties.

In this article, unique Au nanobipyramids (Au NBs) structures are explored and embedded in the hole transport layer (HTL) of planar heterojunction PSCs. This “pyramid-like" metal nanostructure has the wide and strong plasmonic absorption properties with the region from visible to the near-infrared, thus the Plasmon Resonance can be excited more effectively by avoiding the light trapping competition with the perovskite active layer. Besides the well-known contribution of enhanced light harvesting, the modulation of the electrical properties by Au NBs is more attractive in plasmonic PSCs, which is assumed as the main role of the improvement of the device performance. Under the excited state, unique “hot spots” characteristic could induce more intense EM field enhancements around the corners of Au NBs than conventional Au nanoparticles, which could significantly facilitate the exciton dissociation, charges transportation at the interface of PSCs. More importantly, owing to the hot holes injection effect by Au NBs under illumination, interfacial traps of the PSCs can be effectively filled, suppressing the charge recombination and shifting the quasi-Fermi energy level at the HTL/perovskite interface. Benefiting from these advantages, PSCs incorporated with optimal concentration of Au NBs show the typical PCE of 18.05% whereas the reference device just showed the typical PCE of 15.01%, accompanying with the improvement of the open circle voltage and the excellent tolerance of ambient air and operation. We think that plasmonic metal nanostructures with the advantage of “hot spots” feature could offer a great potential to further break the performance limitation of the PSCs as well as maintain the long-term operational stability.

2. Results and discussion

2.1. Characterization of Au NBs

The synthesis of nano-bipyramids was achieved via the seed-mediated growth approach [34]. Fig. 1a showed the SEM images of the Au NBs, and Fig. 1b and c showed the TEM image of the Au NBs. It can be seen that the bipyramids show regular diamond-like shapes with straight edges. The average length and diameter of bipyramids were 45–50 nm and 15–18 nm respectively, with aspect ratios between 3 and 3.3. EDX spectrum was also used to confirm the content of the Au NBs, and the Au peaks were clearly observed (shown in Fig. S1 and Table S1).

In fact, the plasmon wavelengths of the anisotropic metal architectures can be regulated from the visible to near-infrared regions by varying shape and aspect ratio of the nanostructures. Fig. 1d showed the absorption spectrum of the Au NBs, with two strong plasmonic peaks, attributed to the longitudinal and the transverse plasmonic absorption. The longitudinal and transverse plasmon resonance wavelengths of the initial Au NBs sample dispersed in aqueous solutions were 806 and 521 nm, respectively. Considering that the absorption edge of conventional $CH_3NH_3PbI_3$ was around 800 nm (shown in Fig. 1d), such an elaborate design avoided the competition with the perovskite layers as well as promise the extra light-trapping in low energy region (wavelength > 700 nm).

In addition to the wide absorption feature of the Au NBs, another unique characteristic of the Au NBs, was the “hot spots” property, which was emphasized in our study. Researches showed that “hot spots” can be generated at the tip of a sharp feature on a nanoparticle by taking advantage of the “lightning rod effect” [30,35]. The attractively induced dipoles were more easily formed on the corners and tip of the geometry, leading to the increased polarization vector density. Thus the drastically intensified EM field can be achieved around the sharp nanostructures, which was much larger than that of conventional metal nanostructures [36,37]. In fact, for the application of the plasmonic optoelectronic devices, the enhanced EM factor of the metal nanostructures was closely related to the improved performance of the devices, hence the typical metal nanostructures with strong intensified EM field has the huge potential to contribute to the plasmonic devices.

To gain a better understanding of the relationship between EM-field enhancement and the architecture of the metal nanostructures, We performed simulations for three structures with similar specifications: Au nanospheres (diameter ~20 nm), Au nanorods (same dimension as Au NBs) and Au NBs. A theoretical investigation (finite difference time-domain method: FDTD) on was utilized to calculate the distributions of E-field enhancement. Fig. 2 showed the simulation results of the field intensity enhancements of the Au NBs, Au NRs and Au NPs, respectively. The field intensity enhancements were calculated under the excitation at their plasmon wavelengths. The largest EM field enhancement appeared on the Au NBs and highly localized at the corner sites (Fig. 2a and b). Nevertheless, although the EM fields were enhanced on Au NRs and Au NPs, there was no hot spots formed.

The maximum fields intensity enhancement factors along the central length axis were plotted in Fig. 2f. The maximum enhancement factors of the Au NBs, Au NRs and Au NPs were 127(at 524 nm), 46(at 521 nm) and 15(at 535 nm), respectively. The simulation confirmed the superior EM fields enhancement effect of the Au NBs compared with the other nanoparticles without “hot sports” feature, which was crucial for plasmonic enhanced PSCs. For the experimental comparison, Au NPs and Au NRs were also synthesized, and the TEM images and absorption spectrum were shown in Fig. S2. Under the same concentration, Au NBs exhibited the stronger absorption intensity and sharper plasmonic peak than Au NRs and Au NPs, which was corresponding with the theoretical calculation.

2.2. PSCs with "hot spots" Au NBs

2.2.1. Optical and material properties of the films

For the applications of the Au NBs in PSCs, an inverted planar heterojunction structure (ITO/PSS:PEDOT/VO_x/$CH_3NH_3PbI_3$/$PC_{61}BM$/BCP/Ag) was designed, and the schematic of plasmonic PSCs was shown in Fig. 3a. Here such a multi-layer PSS:PEDOT/VO_x hole transporting layer (HTL) could effectively promote the charge transporting due to the excellent conductivity and appropriate energy level alignment [38,39]. Meanwhile, inorganic VO_x layer prevent the invasion of the moisture and oxygen. For the study of the plasmonic enhancement,