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Panchromatic thin perovskite solar cells with broadband plasmonic absorption enhancement and efficient light scattering management by Au@Ag core-shell nanocuboids

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ABSTRACT

Enhancing the low-energy sunlight harvesting is of great importance for improving the efficiency of organic-inorganic halide perovskite solar cells (PSCs) but still remains a big challenge. Herein, we propose an improved light harvesting and management strategy by using rationally-designed Au@Ag core-shell nanocuboids as plasmonic inclusions, aiming at achieving panchromatic thin PSCs. Compared to conventional metal nanostructures with a single narrow plasmon resonance band, the Au@Ag nanocuboids exhibit multiple broader and stronger plasmon resonances that can be tuned by adjusting structural dimensions to spectrally match the absorption band of the perovskite, particularly in its weak absorption region. By carefully tailoring the location of the Au@Ag nanocuboids in the electrodes, both plasmonic near-field enhancement and increased light-scattering effects can be fully exploited to boost up the performance of the PSCs. As a result, the hybrid devices demonstrate high photon-to-electron conversion efficiency (IPCE) over the entire visible range, with a remarkable IPCE enhancement (ΔIPCE/IPCE) of 20–60% in the range of 550–750 nm, compared with pristine devices. This also leads to an average power conversion efficiency (PCE) of 17.83% for the optimized Au@Ag incorporated cells, with a champion PCE of 18.31% recorded for the best plasmonic PSC, corresponding to a PCE enhancement of 20.8%.

1. Introduction

In the past decades, developing highly efficient yet inexpensive solar cells has been of supreme importance for fossil fuel preservation and environment protection. Among the emerging solar cell technologies, perovskite solar cells (PSCs) have attracted increasing attention in recent years due to their simple fabrication process, low-cost and high power conversion efficiency (PCE) [1–12]. Recently, PCE exceeding 22% has been achieved in perovskite solar cells [10]. However, it is still far from their theoretical limit, leaving rooms for improvement. One of the most effective approaches to further boost the efficiency of PSC is to increase the light harvesting efficiency [3,6], apart from improving the charge collection efficiency. In general, $CH_3NH_3PbI_{3-x}Cl_x$ based PSCs can harvest over 80% of the input high-energy illumination of 400–600 nm, but it fails to absorb the low-energy sunlight (λ_{Lo}) of

600–800 nm as effectively as it does in the high-energy zone (λ_{Hi}) due to the relatively poor extinction in the λ_{Lo} zone [6,13–15]. Actually, it is a hard task to achieve high incident photon-to-electron conversion efficiencies (IPCEs) at both λ_{Hi} and λ_{Lo} zones (Table S1, Supporting Information) [16–21], since a balanced high IPCE among the whole investigated wavelength range requires a precise control and optimization of the thickness, morphology, composition, traps, interface and grains of a relatively thick perovskite film (~ 400 nm) to yield a balanced high light harvesting and low charge recombination [16,18,20–25]. Moreover, this problem becomes more serious for semitransparent cells for building, because a thin perovskite layer (~250 nm) is usually required to keep semitransparency of the device [25–27]. This indicates that the effective utilization of the λ_{Lo} sunlight is a necessary approach to further promote the cell efficiency, which still remains a big challenge [6,16,25]. In this regard, developing a

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general, simple yet effective approach for a general researcher to realize broadband light harvesting and balanced high IPCE is highly desired for making panchromatic solar cells.

Extending the absorption edge of photoactive materials is a viable strategy to improve the light harvesting efficiency and maximizing the performance of various types of solar cells and other solar devices [28–33]. The well-known localized surface plasmon resonance (LSPR) of noble metallic nanoparticles (NPs) has been employed to enhance cell efficiency, by taking advantages of the LSPR induced synergistic effect of plasmonic enhancement in light absorption [29–34], increased light trapping/scattering [35,36], and direct resonant energy transfer [37–39]. To date, plasmonic NPs made of Au and/or Ag have been intensively studied for a plethora of applications in various kinds of solar cells, such as dye-sensitized solar cells (DSSCs) [29,30,39], organic photovoltaics (OPVs) and PSCs [35–38,40]. In the DSSC and OPV cases, the improvement in device efficiency is mainly due to the contribution of increased light harvesting by plasmonic NPs [29,30,35,36]. Unfortunately, such enhancement mechanism has not been observed in the plasmonic NP incorporated PSCs to date [38,41,42]. Most of the previous studies exploited spherical Ag, Au or Ag/Au@metal oxide NPs to boost the efficiency of solar cells [36–38,40,41]. Those Ag or Au nanospheres usually exhibit narrow plasmonic excitation bands (less than 100 nm in bandwidth) centered at 380 and 530 nm [36,37,41,42], which overlap with the strong extinction zone of the organic-inorganic metal halide perovskites ($CH_3NH_3PbI_3$, *etc.*). For example, Yuan et al. has recently revealed that the dominate contribution to the enhanced performance of plasmonic PSCs is the hot electron injection from Au NPs to TiO_x rather than plasmon-induced absorption enhancement [38]. This is simply because the plasmonic enhancement effect becomes less effective or nonexistent in the zone where the original absorption of the photoactive layer is already very significant [43]. This also explains why the conventional Ag or Au nanospheres can dramatically increase the light harvesting efficiency of DSSCs and OPVs but perform poorly in PSCs, that is, the extinction ability of common photoactive materials in DSSCs and OPVs is relatively lower than that in metal halide perovskites [43]. In this regard, using the conventional spherical plasmonic NPs to improve the light absorption of PSCs is usually ineffective. The key to boosting the light collection capability and improving the efficiency of plasmonic NP incorporated PSCs lies in the broadening of the solar absorbing spectrum, especially in the λ_{Lo} region. To achieve this goal, novel plasmonic nanostructures that sustain broadband and tunable LSPR excitations are of paramount importance, yet seldom used in PSCs thus far.

The LSPR band of a metal NP depends on its shape, size and composition [44–48]. For example, a rod-like Au nanostructure generally exhibits two geometry-dependent LSPR bands due to the geometry anisotropy in the transverse and longitudinal directions, thus providing an additional degree of freedom, in comparison with a nanosphere, to alter its plasmonic extinction band by manipulating the aspect ratio [44,47]. Moreover, plasmon hybridization in a metal core-shell nanoparticle produces new plasmonic resonance bands such as subradiant and superradiant modes, higher-order resonances, and Fano resonances etc. [49,50]. In this study, we successfully designed and synthesized a series of Au@Ag core-shell nanocuboids by a wet chemistry method [46]. The prepared nanocuboids have four broadened, tunable and intense plasmon resonance bands spanning the whole spectral range of 300–800 nm. By incorporating the Au@Ag nanocuboids with optimized dimensions in the sophisticated PSCs with well-prepared thin electrodes, the LSPR effects including plasmonic absorption enhancement and light scattering management can be fully exploited, leading to a synergistic enhancement in the performance of the plasmonic PSCs. The excellent plasmonic properties of the Au@Ag nanocuboids yielded a champion PCE of 18.31% and an average PCE of 17.83% (measured over 30 devices) for the hybrid PSCs, corresponding to 20.8% and 17.6% enhancement compared with pristine devices, respectively.

2. Experimental section

2.1. Materials

Titanium (IV) isopropoxide (97%, TTIP), acetic acid, methylamine (40% in methanol), hydriodic acid (57 wt% in water), diethyl ether, hydrogen tetrachloroaurate (III) hydrate ($HAuCl_4 \cdot 4H_2O$), cetyltrimethylammonium bromide (CTAB), cetyltrimethyl-ammonium chloride (CTAC), silver nitrate ($AgNO_3$), ascorbic acid (AA), sodium borohydride, lead (II) Chloride ($PbCl_2$, 99.99%), and N,N-Dimethylformamide (DMF, 99.9%) were obtained from Sigma-Aldrich. The methylammonium iodide (CH_3NH_3I) was obtained from Dyesol. All chemicals were used as received without further purification. Ultrapure water was used for all experiments.

2.2. Syntheses of Au nanorods and Au@Ag nanocuboids

Au nanorods were synthesized by using a seed-mediated method [46]. Seed solution was synthesized by adding 0.6 mL of an ice-cold $NaBH_4$ (10 mM) solution into 10 mL of $HAuCl_4$ (0.25 mM) and CTAB (0.1 M) solution under vigorous stirring at room temperature. The color of the seed solution changed from yellow to brown. Growth solution was prepared by mixing 5 mL of $HAuCl_4$ (10 mM), 95 mL of CTAB (0.1 M), 1 mL of $AgNO_3$ (10 mM) and 0.55 mL of AA (0.1 M), consecutively. The solution was homogenized by gentle stirring. Then 0.12 mL of freshly prepared seed solution was added to the colorless solution and kept undisturbed in dark for 24 h. Prior to use, the Au nanorods solution was centrifuged twice at 8000 rpm for 10 min to remove excess CTAB and finally re-dispersed in DI water.

The Au@Ag core-shell nanocuboids were prepared according to a reported procedure with appropriate modifications [44,45]. Specifically, to coat the Au nanorods with Ag shells of varied thickness, 6 mL of the Au NRs solution were centrifuged and re-dispersed into an aqueous CTAC solution (0.08 M) at the same volume. Then, 1.2, 1.8, 2.0 and 2.4 mL of $AgNO_3$ (0.01 M) were subsequently added into four Au nanorods solutions of 6 mL, followed by respective addition of 0.6, 0.9, 1.0 and 1.2 mL ascorbic acid solutions (0.1 M). The resultant solutions were kept in an isothermal oven at 65 °C for 4.5 h.

2.3. TiO₂ paste preparation

Organic-free anatase TiO_2 nanoparticle colloid with solid content of 3.5% was synthesized according to our previous work [51]. The AuNRs and Au@Ag nanocuboids were washed by DI water and collected by 8000 rpm centrifugation for five times to remove residual CTAB before adding into the TiO_2 paste. Appropriate amount of AuNRs or Au@Ag was dispersed in the TiO_2 paste by magnetic stirring and ultrasonication.

2.4. Electrodes and device fabrication

TiO_2 electrodes for mesoscopic perovskite solar cells were fabricated according to our previous work with modification [51]. Prior to deposition of the Au@Ag nanocuboids on the mesoscopic TiO_2 film, a ~30 nm compact TiO_2 layer was deposited on the patterned and well-cleaned FTO glass substrates [4]. For the mesoscopic TiO_2 film, TiO_2 pastes with/without AuNRs or Au@Ag were spin-coated at 2000 rpm for 50 s. For the coating of the plasmonic NP layer, the Au nanorods or Au@Ag aqueous solutions with various concentration (*e.g.* 1×10^{-10}, 2×10^{-10}, 4×10^{-10} M, Au based) were spread by spin-coating at 1000 rpm for 50 s. Four kinds of electrode configurations, namely Au@Ag below (#1), on the top of (#2), embedded in (#3), and embedded in and also on the top of (#4) the mesoscopic TiO_2 layer, were constructed by a layer-by-layer deposition process. After the coating of each layer, the electrodes were dried at 100 °C for 10 min. The thickness of the mesoporous TiO_2 film was controlled to be around 200 nm.