



# Silver nanoparticle plasmonic effects on hole-transport material-free mesoporous heterojunction perovskite solar cells



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## ABSTRACT

Localized surface plasmon resonance excitation of noble metal nanoparticles (NPs) under light illumination can be incorporated to effectively improve light-harvesting devices. The present study aims at silver nanoparticles (Ag NPs) plasmonic effects on the photovoltaic characteristics of mesoporous heterojunction perovskite solar cells. Ag NPs were embedded into a compact TiO<sub>2</sub> layer, which commonly acts as hole-blocking layer in mesoporous perovskite solar cells. An optimum concentration of Ag NPs loaded on compact TiO<sub>2</sub>:Ag-NPs films of hole-transport material-free (HTM-free) perovskite solar cells leads to more than 30% enhancement in power conversion efficiency of the fabricated cells compared with what Ag nanoparticle-free samples can do. The improved performance can be attributed to the scattering effect from the incorporated Ag-NPs, which effectively extends the optical pathway of incident light that increases the photon absorption of the photoactive perovskite layer. In addition to the modulated optical properties of HTM-free perovskite solar cells, electrochemical impedance spectroscopy measurements show that electron transport time at the interfacial layer of TiO<sub>2</sub> and the photovoltaic perovskite layer decreases as a result of frequency response improvement in the photoanode interface.

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## 1. Introduction

Organic-inorganic, perovskite solar cells (PSCs), fabricated from methylammonium lead halides (CH<sub>3</sub>NH<sub>3</sub>PbX<sub>3</sub>, where X = I, Br, or Cl) by means of a solution process and vacuum evaporation procedures, have shown high power conversion efficiency (PCE) of around 20% with both mesoporous and planar heterojunction structures (Green et al., 2014; Saliba et al., 2016). The first highly efficient PSCs architecture has been developed by employing hole-transport materials (HTM) such as spiro-MeOTAD, nanoporous TiO<sub>2</sub> film as an electron transport material (ETM), compact TiO<sub>2</sub> layer as a hole-block layer, and mesoporous perovskite material that functions as a light harvester (Green et al., 2014; Saliba et al., 2016; Wang et al., 2015; Lu et al., 2015; Gao et al., 2015; Aharon et al., 2014; Kim et al., 2012). Since CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> has ambipolar characteristics including both positive and negative charge carriers and is slightly more of a p-type material than of

an n-type one, it has been used to make p-n junction-like PSCs without hole-transporter materials, known as HTM-free photovoltaic cells (Aharon et al., 2014; Etgar et al., 2012; Laban and Etgar, 2013). A previous study has demonstrated that mesoporous TiO<sub>2</sub>:CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> heterojunction solar cells without any additional HTM layers show PCE of about 5.5% (Etgar et al., 2012). In this report, the CH<sub>3</sub>NH<sub>3</sub>PbI<sub>3</sub> acts simultaneously as both a light harvester and a hole conductor which simplify the solar cell architecture and potentially reduce its cost. By optimization of the deposited perovskite layer, the HTM-free PSCs efficiency has been further improved to around 8% (Laban and Etgar, 2013). Recently, it is also reported that HTM-free PSCs efficiency can be improved up to 11% by changing the perovskite film morphology via an anti-solvent treatment (Cohen et al., 2016). However, in spite of the remarkable increase in the efficiency of perovskite-based solar cells, there are still several optical and electrical phenomena, which must be investigated.

For further improvement of the efficiency, it is necessary to extend light absorption spectrum to harvest more energy of the incident sunlight in thin film solar cells, without increasing the thickness and architecture complexity of the devices. Recently,

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two approaches have been employed to increase light harvesting in PSCs. In one of them, by using alloyed perovskite, based on the band gap changing of  $\text{CH}_3\text{NH}_3\text{PbI}_3$  absorber material, broadened light harvesting has been achieved up to a wavelength of 1050 nm (Hao et al., 2014; Ogomi et al., 2014). But in this approach, the extension of the light absorption into the near-infrared as compared with that in  $\text{CH}_3\text{NH}_3\text{PbI}_3$  PSCs has decreased both the fill factor (FF) and the open-circuit voltage ( $V_{\text{OC}}$ ) considerably (Hao et al., 2014; Ogomi et al., 2014).

Another promising approach is to apply noble metal nanoparticles (NPs) to improve the solar cells' light harvesting ability and also their efficiency where localized surface plasmon resonance (LSPR) can be excited on the metal surface under the light illumination. These NPs serve as scattering centers and sub-wavelength antennas in which the confined electromagnetic energy based on LSPR may greatly improve the absorption factor of the active medium surrounding the NPs (Lu et al., 2015; Chen et al., 2013; Huang et al., 2009; Nourolahi et al., 2015). Using plasmonic nanostructures, the light harvesting enhancement and the efficiency improvement of different kinds of solar cells, including thin-film Si solar cells, dye-sensitized solar cells (DSSCs) (Jang et al., 2014; Atwater and Polman, 2010; Baba et al., 2011; Smeets et al., 2014), and organic photovoltaics (OPVs) (Notarianni et al., 2014; Kalfagiannis et al., 2012; Wu et al., 2011), have been reported recently. Previously, our team also using silver NPs developed a metal/polymer nanocomposite interconnection layer for organic tandem solar cells (Torabi et al., 2015).

In the case of perovskite solar cells, proficiency of the plasmonic strategy has been taken into account for enhancement of device performance incorporating Au NPs in the  $\text{Al}_2\text{O}_3$  mesoporous layer (Zhang et al., 2013) as well as popcorn shape Au-Ag NPs embedding into the  $\text{TiO}_2$  mesoporous framework of PSCs (Lu et al., 2015; Mali et al., 2016). The interlayers between the electrodes and the perovskite layer (i.e. hole or electron transport layer) have been optimized in order to increase the charge carrier mobility in the device or to reduce the energy barrier at the interface (Zhou et al., 2014). In another approach, plasmonic gold (Au) and silver (Ag) NPs are employed in hole transport layers such as P3HT and Spiro-OMeTAD to enhance the optical and electrical responses of PSCs (Wang et al., 2015; Hsu et al., 2015; Lee et al., 2015). Furthermore, a numerical simulation has been reported where embedding plasmonic nanostructures in the perovskite absorbing medium leads to an enhancement of light absorption (Carretero-Palacios et al., 2015). This is in contrast to another study that showed plasmonic NPs in organic absorbing layers can serve as carrier recombination centers, often leading to a reduction in device open-circuit voltage as well as current density (Mandoc et al., 2007).

In the construction of PSCs, compact  $\text{TiO}_2$  hole-blocking layers are essential and play important roles in deterring the carrier recombination at the interface of fluorine doped tin oxide (FTO) and perovskite layer and, consequently, in preventing short-circuits (Peng et al., 2004). Therefore, modifying  $\text{TiO}_2$ -blocking layers can contribute significantly to the reduction of carrier recombination and, thus, PSCs enhancement (Gao et al., 2015).

This study aims to maximize the positive effects of Ag NPs in compact  $\text{TiO}_2$  as the interfacial layer of HTM-free perovskite solar cells while minimizing their negative effects such as charge carrier recombination generally observed in plasmonic NPs in the photovoltaic perovskite layer. Here, the configuration of the device is Glass/FTO/compact  $\text{TiO}_2$  (with or without Ag NPs)/mesoporous  $\text{TiO}_2$ : $\text{CH}_3\text{NH}_3\text{PbI}_3$ /Au electrode. The present study demonstrates that the photocurrent and efficiency enhancement in HTM-free mesostructured organometal halide perovskite/ $\text{TiO}_2$  heterojunction solar cells incorporated with Ag NPs delivers a device efficiency of up to 5.85% with a short-circuit photocurrent density of 12.42 mA/cm<sup>2</sup> and open-circuit voltage of 0.78 V. This is in

comparison to the control PSC with 4.39% efficiency; short-circuit photocurrent density of 10.44 mA/cm<sup>2</sup> and open-circuit voltage of 0.72 V.

## 2. Experimental section

### 2.1. Synthesis of Ag nanoparticles

To fabricate the silver NPs, a modified two-step reduction synthesis procedure was implemented, which was developed based on the conventional reduction method (Agnihotri et al., 2014). First, 90 mL of an aqueous solution containing sodium borohydride ( $\text{NaBH}_4$ ) and tri-sodium citrate (TSC) at the ratio of 2:7 ( $1 \times 10^{-3}$  mol dm<sup>-3</sup>: $3.5 \times 10^{-3}$  mol dm<sup>-3</sup>) was heated to 60 °C for 30 min under vigorous stirring at 300 rpm to ensure a homogenous solution. After 30 min, 4 ml of an aqueous solution of  $\text{AgNO}_3$  ( $4 \times 10^{-3}$  mol dm<sup>-3</sup>) was added drop-wise to the mixture, and the temperature was further raised to 95 °C to make the solution boil quickly. The reaction was allowed to continue for another 30 min. Finally, the solution was cooled down to room temperature with stirring, and the NPs were collected by centrifugation at 5000 rpm and redispersed in ethanol via sonicating for 15 min.

### 2.2. Device fabrication

The perovskite solar cell devices were prepared according to earlier reports (Aharon et al., 2014). After etching,  $\text{SnO}_2$ :F conducting glass substrates (with the sheet resistance of 14  $\Omega$ /sq) were cleaned by successively ultrasonically in acetone, ethanol and deionized water for 20 min in each step and then drying them in air flow. To fabricate plasmonic sensitized photoanodes, a solution of titanium isopropoxide in ethanol was mixed with a silver NP ethanol solution and stirred for 20 min. The ratio of plasmonic NPs to the compact  $\text{TiO}_2$  layer could be easily adjusted by varying the concentration of Ag NPs in the solution. The plasmonic compact  $\text{TiO}_2$  solution was spin-coated on the FTO glass substrate at 4000 rpm for 30 s and dried at 120 °C for 15 min in an oven then 500 °C for 30 min in air. For comparison, a compact  $\text{TiO}_2$  solution without an Ag NPs hole block layer was also prepared and spin coated on an FTO substrate. A mesoporous  $\text{TiO}_2$  layer composed of 20-nm particles was also deposited by spin coating at 4000 rpm for 15 s on compact  $\text{TiO}_2$  /FTO substrates (Aharon et al., 2014; Kim et al., 2012). Then, the photoanodes were sequentially sintered for five minutes at 125 °C, five minutes at 325 °C, five minutes at 375 °C, fifteen minutes at 450 °C and fifteen minutes at 500 °C. For the light absorber layer,  $\text{CH}_3\text{NH}_3\text{I}$  (MAI) was synthesized by a reaction of 27.86 ml methylamine (40% in methanol) with 30 ml hydroiodic acid (57 wt.% in water, Merck) in a 250 ml solution at 0 °C for 2 h under stirring. The precipitate was recovered via evaporation at 60 °C for 120 min. The methylammonium iodide ( $\text{CH}_3\text{NH}_3\text{I}$ ) was dissolved in ethanol, recrystallized from diethyl ether, and dried at 65 °C in an oven for 24 h.

The deposition of the lead halide iodide perovskite on the mesoporous  $\text{TiO}_2$  was carried out based on the two-step solution deposition method (i.e. spin and dip coating) explained earlier (Aharon et al., 2014). The sequential solution deposition method was used with lead iodide ( $\text{PbI}_2$ ) (~1.0 M) kept in N,N-dimethylformamide (DMF) at 70 °C, deposited via spin-coating, dried at 90 °C for 15 min, and then allowed to cool down. The  $\text{PbI}_2$ -deposited substrate was then submerged into an MAI solution in 2-propanol (10 mg/ml). Perovskite formation occurred when the color changed from yellow to dark brown-black. After the formation of the perovskite layer, the samples were rinsed with 2-propanol, dried at room temperature, and annealed thermally on a hot plate for about 10 min. Finally, for the counter electrode, 60-nm-thick Au was

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