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COMMUNICATION

# Plasmonic-Enhanced Perovskite Solar Cells Using Alloy Popcorn Nanoparticles

Cite this: DOI: 10.1039/x0xx00000x

## *Supporting Information*

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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## 1. Energy Dispersive Spectroscopy Spectra

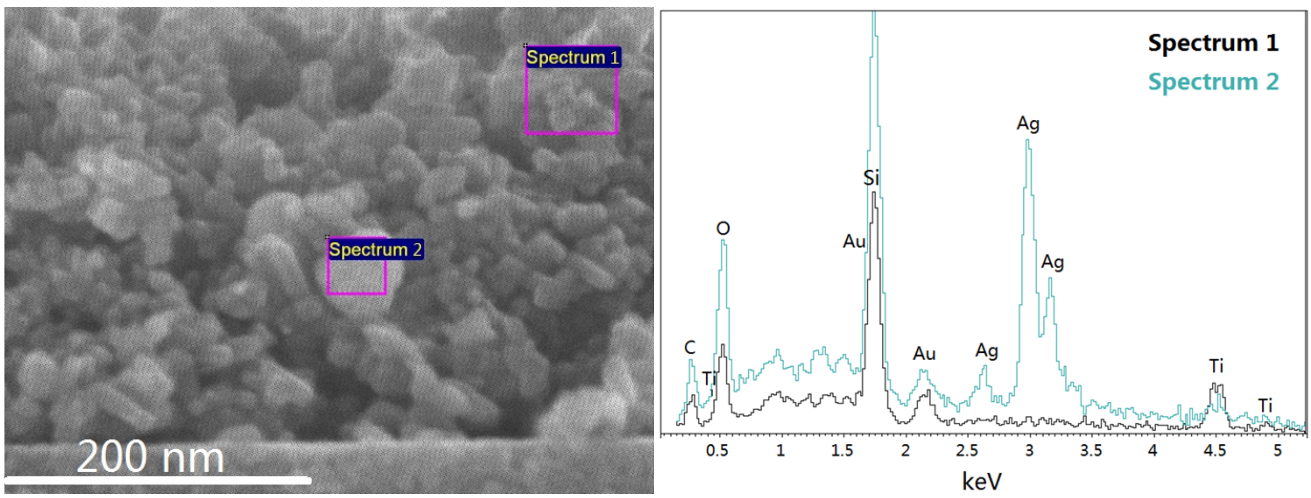


**Fig. S1** Energy dispersive spectroscopy (EDS) spectra of popcorn nanoparticle (NP) and mesoporous $TiO_2$. Spectrum 1 and 2 represents the EDS spectra of mesoporous $TiO_2$ and popcorn NP, respectively. The C peak in both spectra is due to the carrier and clamp used in scanning electron microscope (SEM) measurements, while the Si peak comes from the silicon substrate on which the samples are prepared just for SEM measurement.

## 2. Methods

### Synthesis of NPs

To fabricate the popcorn NPs, a modified two-step co-reduction synthesis procedure was implemented, which was developed based on the conventional co-reduction method. First, a 100 mL aqueous solution containing 0.038 g $HAuCl_4$ and 0.068 g $AgNO_3$ (both purchased from Sigma-Aldrich) was heated to 97 $^oC$ (close to its boiling point) under vigorous stirring at 4,000 r.p.m. in an oil bath system; then, 2 ml of a 1 wt% sodium citrate (Sigma-Aldrich) solution was injected quickly into the solution to react for 8 minutes. The solution turned to dark red and then dark yellow. The temperature of the heating system was then adjusted to 150 $^oC$ to make the solution boil rapidly, and 2 ml of a 5 wt% sodium citrate solution was added; the reaction was allowed to continue for another 30 minutes. Then the solution turned to dark grey. Finally, the solution was cooled down to room temperature with stirring, and the NPs were collected by centrifugation at 5,500 r.p.m. and redispersed in ethanol by sonication for 5 minutes.

In order to prepare plasmonic $TiO_2$ paste, a 20-nm-sized $TiO_2$ paste (Heptachroma, DHS-TPP3) was diluted in the above popcorn NPs incorporating ethanol solution and stirred sufficiently. The ratio of $TiO_2$ to ethanol was 2:7, and the ratio of plasmonic NPs to $TiO_2$ was 0.7 wt%. A $TiO_2$-only paste was also prepared by mixing the $TiO_2$ paste with ethanol in the same proportion for comparison. The plasmonic $TiO_2$ paste and $TiO_2$-only paste were used for sample preparation in the following SEM, optical absorption and photoluminescence measurements and for perovskite devices fabrication.

## General Measurements

Transmission electron microscopy (TEM) images of the popcorn NPs were taken on a JEOL 2011 system. Silicon wafers sputtered with ITO were chosen as the substrate to prepare samples for SEM measurements, and then a compact $TiO_2$ layer and a mesoporous $TiO_2$ film incorporated with or without popcorn NPs were successively fabricated, using the exact condition in the device fabrication process below. SEM (HITACHI S-5500, 30kV) images and EDS（Horiba EX-250) spectra of the popcorn NPs and $TiO_2$ layers were then obtained. The optical absorption spectroscopy measurements were performed using an UV-visible spectrophotometer (Agilent 8453). In the time-resolved photoluminescence measurement, the samples were excited by a pulsed laser (Coherent Legend system with a Coherent OperA Solo optical parametric amplifier (OPA)) with a wavelength and frequency of 632 nm and 1 KHz, respectively. The PL photons were counted by a HAMAMATSU C10910 streak camera with a time window of 50 ns. The integral of time-resolved photoluminescence data in the entire time window gave the steady-state photoluminescence value at each wavelength. And these values were normalized for further analysis.

## Device Fabrication and Measurements

FTO glasses were first cleaned by ultrasonic bath in deionized water, acetone and ethanol for 20 min, respectively, and then treated in plasma cleaner for 15min. After that, the cleaned FTO glasses were spin-coated with 0.15 M titanium diisopropoxide bis (acetylacetonate) (75%, Sigma-Aldrich) in 1-butanol (Sigma-Aldrich) solution at 4, 000 r.p.m. for 30s, then heated at 125 $^oC$ for 5 min to make a compact $TiO_2$ blocking layer. After the film had cooled down to the room temperature, the same process was repeated twice with the concentration of titanium diisopropoxide bis (acetylacetonate) solution changing to 0.3 M. Then the film was heated at 500 $^oC$ for 15 min. Thereafter, the FTO glasses were immersed into a 40 mM $TiCl_4$ aqueous solution at 70 $^oC$ for 30 min and washed with deionized water and ethanol and then heated at 500 $^oC$ for another 15 min. After that, plasmonic $TiO_2$ paste and $TiO_2$-only paste were spin-coated, respectively, at the same condition of 5, 000 r.p.m. for 30s. After drying at 125 $^oC$ for 5 min, the film was heated again at 500 $^oC$ for 15 min. To prepare the perovskite layers, we followed the procedure of two-step sequential solution process.[1,2] $PbI_2$ was initially introduced into the mesoporous $TiO_2$ by spin-coating. After drying at 70 $^oC$ for 30 min, the film was pre-wetted by 2-propanol for 2 s and dipped in the solution of $CH_3NH_3I_3$ in 2-propanol and kept the reaction for tens of seconds to let the small $PbI_2$ crystals completely transform into perovskite until the color changed from yellow to dark brown. Then, the film was rinsed with 2-propanol and dried on a hot plate at 70 °C for 30 min. After finishing all these procedures, a solution of 2,2′,7,7′-tetrakis(*N*,*N*-di-*p*-methoxyphenylamine)-9,9′-spirobifluorene (spiro-MeOTAD), 4-*tert*-butylpyridine (96%, Aldrich), and lithium bis(trifluoromethylsulphonyl)imide (98%, Alfa Aesar) in chlorobenzene (99.9%, Alfa Aesar) was spin-coated at 2, 000 r.p.m. for 45 s, as the hole transporting material. Finally, 100 nm Ag was thermally evaporated under vacuum as the anode.

*J-V* characteristics of photovoltaic cells were taken using Keithley 2611 source meter under simulated sunlight from Oriel 300 solar simulator. The IPCE was recorded using a monochromatic light from a system consisting of a xenon lamp, a monochromator, and appropriate filters (Crowntech Qtest station 2000AD). Both two systems were calibrated against a certificated reference Si solar cell.

## 3. Optical absorbance of thinner perovskite layers

To investigate whether popcorn nanoparticles could improve the light absorption in broadband range, thinner perovskite layers incorporated with/without NPs were fabricated. Thinner perovskite layers can be obtained by reducing the concentration of $PbI_2$ in N,N-dimethylformamide (DMF) solvent from 1M to 0.8M while keeping all the other experiment conditions unchanged. Light absorption property of thinner perovskite layers is shown in Fig. S2.

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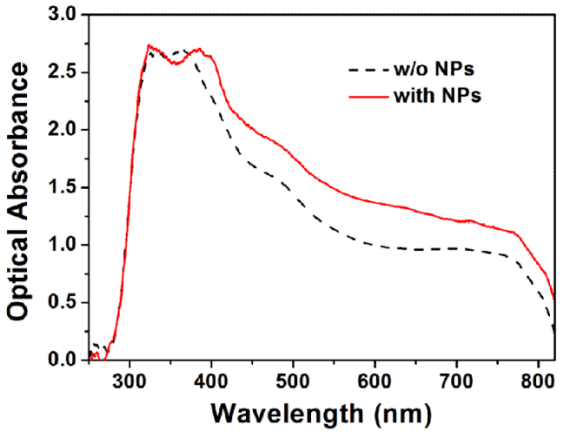


**Fig. S2** Optical absorption of thinner perovskite films on mesoporous $TiO_2$ framework with and without popcorn NPs, respectively.

## Notes and references

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1 Y. Ma, L. Zheng, Y. H. Chung, S. Chu, L. Xiao, Z. Chen, S. Wang, B. Qu, Q. Gong, Z. Wu and X. Hou, *Chem. Commun.*, 2014, 50, 12458-12461.
2 L. Zheng, Y. Ma, S. Chu, S. Wang, B. Qu, L. Xiao, Z. Chen, Q. Gong, Z. Wu and X. Hou, *Nanoscale*, 2014, **6**, 8171-8176.